

Multiresonant Plasmonics with Spatial Mode Overlap

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ABSTRACT

Plasmonic nanostructures can enhance light-matter interactions in the subwavelength domain, which is useful for photodetection, light emission, optical biosensing, and spectroscopy. However, conventional plasmonic devices are optimized to operate in a single wavelength band, which is not efficient for wavelength-multiplexed operations and quantum optical applications involving multi-photon nonlinear processes at multiple wavelength bands. Overcoming the limitations of single-resonant plasmonics requires development of plasmonic devices that can enhance the optical interactions at the same locations but at different resonance wavelengths. This dissertation comprehensively studies the theory, design, and applications of such devices, called “multiresonant plasmonic systems with spatial mode overlap”. We start by a literature review to elucidate the importance of this topic as well as its current and potential applications. Then, we briefly discuss the fundamentals of plasmonic resonances and mode hybridization to thoroughly explore, classify, and compare the different architectures of the multiresonant plasmonic systems with spatial mode overlap. Also, we establish the black-box coupled mode theory to quantify the coupling of optical modes and analyze the complicated dynamics of optical interactions in multiresonant plasmonic systems. Next, we introduce the nanolaminate plasmonic crystals (NPCs), wafer-scale metamaterials structures that support many (>10) highly-excitabile plasmonic modes with spatial overlap across the visible and near-infrared optical bands. The enabling factors behind the NPC’s superior performance as multiresonant systems are also theoretically and experimentally investigated. After that, we experimentally demonstrate the NPCs application in simultaneous second harmonic generation and anti-Stokes photoluminescence (ASPL) with controllable nonlinear emission properties. By designing specific non-linear optical experiments and developing advanced ASPL models, this work addresses some important but previously unresolved questions on the ASPL mechanism as well. Finally, we conclude the dissertation by discussing the potential applications of out-of-plane plasmonic systems with spatial mode overlap in wavelength-multiplexed devices and presenting some preliminary results.

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GENERAL AUDIENCE ABSTRACT

Emergence of electronic devices such as cellphones and computers has revolutionized our lifestyles over the past century. By manipulating the flow/storage of electrons at the nanometer scale, electronic components can be very compact, but their speed and energy performance is ultimately limited due to ohmic losses and finite velocity of the electrons. In parallel, photonic devices and circuits have been proposed that by molding the flow of light can overcome the mentioned limitations but are not as integrable as their electronic counterparts. Plasmonics is an emerging research field that combines electronics and photonics using nanostructures that can couple the light waves to the free electrons in metals. By confining the light at deep subwavelength scales, plasmonic devices can highly enhance the light-matter interactions, with applications in ultrafast optical communications, energy-harvesting, optical sensing, and biodetection. Conventionally, plasmonic devices are optimized to operate with a single light color, which limits their performance in wavelength-multiplexed operations and ultrafast non-linear optics. For such applications, it is far more efficient to use the more advanced “multiresonant plasmonic systems with spatial mode overlap” that can enhance the optical interactions at the same locations but for multiple light colors. This dissertation comprehensively studies these systems in terms of the fundamental concepts, design ideas, and applications. Our work advances the plasmonic field from both science and technology perspectives. In particular, we explore and classify the strategies of building multiresonant plasmonic systems with spatial mode overlap for the first time. Also, we establish the black-box coupled mode theory, a novel framework for analysis and design of complicated plasmonic structures with optimized performance. Furthermore, we introduce the “nanolaminate plasmonic crystals” (NPCs), large area and cost-effective devices that can enhance the optical processes for both visible and near-infrared lights. Finally, we demonstrate NPCs ability in simultaneous frequency-doubling and broadband emission of light and come up with advanced theoretical models that can explain the light generation and color conversion in plasmonic devices.

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Table of Contents

List of Figures.....	viii
List of Tables	xxiii
Chapter 1: Introduction	1
1.1. Applications of multiresonant plasmonics with spatial mode overlap.....	2
1.1.1. Multiresonant Plasmonic Enhancement of both Pumping and Emission Processes	2
1.1.2. Wavelength-Multiplexed Nanoplasmonic Multimodality	8
1.2. Dissertation structure and contributions	10
Acknowledgements.....	12
Chapter 2: Fundamental Concepts and Design Strategies.....	13
Abstract.....	13
2.1. Introduction.....	13
2.2. Fundamental concepts.....	14
2.2.1 Propagating SPP modes at continuous metal-dielectric interface	15
2.2.2. LSP modes in individual metal nanostructures	16
2.2.3. Delocalized Bloch plasmonic modes in periodic metal-dielectric nanostructures.....	17
2.2.4. Mode hybridization.....	19
2.2.5. Effects of geometrical symmetry	21
2.3. How to build multiresonant plasmonic systems with spatial mode overlap?	22
2.3.1. Coupling between two or more localized plasmonic modes.....	23
2.3.2. Coupling between localized and delocalized modes.....	34
2.3.3. Coupling between delocalized modes.....	38
2.4. Conclusions and outlook.....	39
Acknowledgements.....	41
Appendix A.....	42
A.1. Multi-resonant optical nanocavities by out-of-plane magnetic plasmon hybridization	42
Chapter 3: Black-Box Coupled-Mode Theory: An Eigenmode Expansion Framework to Analyze Electromagnetic Interactions of Open, Lossy, and Dispersive Resonators	49
Abstract.....	49
3.1. Introduction.....	50
3.2. BBCMT formulations for a single resonator	53
3.2.1. Coupled-mode equation, mode normalization, and energy.....	53
3.2.2. Scattering and absorption.....	58
3.2.3. Background perturbation.....	59

3.2.4.	Resonator ports	61
3.2.5.	Resonator perturbation and basis set generalization	64
3.2.6.	Signal flow graph, characteristic equation, and scattering matrix	65
3.2.7.	Parameter retrieval by reverse engineering.....	66
3.3.	BBCMT formulations for coupled resonators.....	68
3.3.1.	Loading effects on coupled resonators.....	69
3.3.2.	Energy, scattering, and absorption of the coupled resonators.....	75
3.3.3.	Non-resonant background approximation.....	77
3.4.	Applications and numerical validation	80
3.4.1.	Background perturbation example	81
3.4.2.	BBCMT-aided resonator design	83
3.5.	Summary and Outlook	94
	Acknowledgments.....	95
Appendix B	96	
B.1.	Conjugated form of Lorentz's reciprocity theorem	96
B.2.	Single resonator BBCMT formulations	97
B.2.1.	Mode amplitudes and energy	97
B.2.2.	Scattering and absorption.....	101
B.2.3.	Background perturbation.....	103
B.2.4.	Resonator perturbation and basis set generalization	107
B.2.5.	Parameter retrieval by reverse engineering.....	108
B.3.	Relationships between the resonators' coupling parameters.....	112
B.4.	Simulation settings and materials	112
B.5.	Calculations of section 3.4 examples in the main text.....	113
B.5.1.	MIM nanodisk array embedded in a SiO ₂ slab	113
B.5.2.	Nanolaminate plasmonic crystal	115
Chapter 4: Two-tier Nanolaminate Plasmonic Crystals for Broadband Multiresonant Light Concentration with Spatial Mode Overlap.....	121	
Abstract.....	121	
4.1.	Introduction.....	122
4.2.	Results and Discussion	125
4.3.	Conclusion	134
Acknowledgements.....	135	
Appendix C	136	
C.1.	Methods.....	136

C.2.	Temporal coupled mode theory analysis of the two-tier nanolaminate plasmonic crystals.....	137
C.2.1.	CMT model for the subsystem of nanolaminate nanodome array	137
C.2.2.	CMT model for the subsystem of nanolaminate nanohole array	138
C.2.3.	CMT model for the two-tier nanolaminate plasmonic crystal	140
Chapter 5: Anti-Stokes Emission from Plasmonic Structures: Mechanisms and Correlation with Second Harmonic Generation.....		153
	Abstract.....	153
5.1.	Introduction.....	154
5.2.	Results and discussion	156
5.3.	Summary and Outlook	173
	Acknowledgements.....	174
Appendix D.....		175
D.1.	Experimental methods.....	175
D.2.	Energy distribution of the hot carriers	175
D.3.	Photoluminescence model.....	177
D.3.1.	Intraband recombination (IBR) process	178
D.3.2.	Electronic Raman Scattering (ERS) process.....	181
D.3.3.	Photoluminescence rate.....	182
D.4.	Emission analysis.....	183
D.4.1.	Purcell effect and radiative decay enhancement	183
D.4.2.	The emission enhancement factor L_{eff}	185
D.4.3.	Emission polarization.....	186
D.4.4.	Effects of the excitation conditions	186
D.5.	Second Harmonic Generation analysis	187
Chapter 6: Summary and outlook.....		197
6.1.	Summary.....	197
6.2.	Outlook	199
6.2.1.	Non-linear optical sensing	199
6.2.2.	Active and Multimode optical devices.....	200
Appendix E		202
E.1.	Conductive Gap-Plasmon Nanocavity	202
E.2.	Fixed-Size Double-resonant Nanolaminate Plasmonic Nanoantennas with Wide Spectral Tunability and High Optical Cross-sections	207
References.....		212

List of Figures

Figure 1.1. A block-diagram illustration of the strategy to create multiresonant plasmonic systems by plasmonic mode hybridization and the potential applications enabled by multiresonant plasmonics with spatial mode overlap. By the optical coupling between elementary modes (e.g., LSP modes, SPP modes, and Bloch modes) in different types of plasmonic building blocks, it is possible to design and create “multiresonant plasmonic systems with spatial mode overlap” that can support multiple plasmonic modes with strong local field enhancements at same locations in multiple different wavelength ranges. Potential applications regarding multiresonant plasmonics include: (1) multiphoton nonlinear optical nanodevices that can enhance both excitation and emission rates in multi-photon nonlinear processes or in multi-photon upconversion luminescence processes; and (2) wavelength-multiplexed optical nanodevices that can achieve multimodal optical operations at nanoscale using multiple spectral bands..... 2

Figure 1.2. Energy diagram illustration of multiresonant plasmonic enhancement of nanoscale parametric nonlinear optical processes by integrating the non-linear optical material with a multiresonant plasmonic system with spatial mode overlap. (a) The three-photon sum-frequency process. (b) The three-photon optical parametric amplification process. 6

Figure 1.3. Energy diagram illustration of (a) Excited state absorption (ESA) UC process, (b) energy transfer up-conversion (ETU) UC process, and (c) plasmon enhanced ETU process by optically coupling an UC activator ion to a multiresonant plasmonic system with spatial mode overlap..... 7

Figure 1.4. Schematic illustration of the wavelength-multiplexed nanoplasmonic system concept, i.e., merging several different types of plasmonics enabled/enhanced modalities into the same nanoscale device by using different wavelength channels. 9

Figure 2.1. Schematic illustrations of plasmonic modes in different types of plasmonic building blocks. (a) Surface plasmon polariton (SPP) modes at the continuous metal-dielectric interfaces. (b) Localized surface plasmon (LSP) modes in individual metal nanostructures¹⁰⁰. (c) Delocalized Bloch-SPP modes in the metal thin film perforated with periodic nanohole arrays¹⁰¹. (d) Delocalized out-of-plane lattice plasmon modes in Au nanoparticle arrays¹⁰². 16

Figure 2.2. (a) Schematic illustration of two coupled oscillators with the coupling strength g and individual damping coefficients γ_1 and γ_2 ¹²¹. (b) Phase diagram showing the separation between

the strong coupling regime ($g \gg \gamma_1, \gamma_2$) and the weak coupling regimes ($g \ll \gamma_1, \gamma_2$)¹²¹. (c) Energy diagram showing the Rabi splitting for two strongly coupled electric dipolar LSP modes in σ and π configurations¹³¹. (d) Schematic illustration of the analogy between the plasmonic mode hybridization and molecular orbital hybridization¹⁴⁶. (e) Dispersion curves for the symmetric and anti-symmetric modes of a MIM slot waveguide based on silver and SiO₂ (100 nm thickness)¹⁴⁸; The inset shows the E_x profiles at $\lambda = 410$ nm. (f) Plasmon energy vs aspect ratio for the solid prolate spheroid and the prolate cavity systems. The solid and dashed lines represent longitudinal and transverse polarizations, respectively¹⁴⁹. (g) The energy diagrams regarding LSP hybridization in concentric (left) and nonconcentric (right) nanoshells¹³². 21

Figure 2.3. Two examples of multiresonant plasmonic systems based on the optical coupling between localized plasmonic modes in in-plane dimer nanostructures. (a) A plasmonic dimer structure and its far-field scattering spectra²⁸; (b-d) The near-field distribution maps of electric field intensity enhancement at its three different resonant wavelengths²⁸. (e, g, i) Charge plots and extinction cross sections for cavities formed by different combinations of a disk with $D_{\text{disk}}=150$ nm and a ring with $D_{\text{out}}=350$ nm and $D_{\text{in}}=350$ nm. Legends: ring (solid dark gray), disk (black), symmetric ring/disk (red), symmetry-broken ring/disk (green) at normal incidence, and ring (dotted light gray) at grazing incidence¹⁶⁴; (f, h, j) Logarithmic electric field enhancement colormaps at the indicated resonances in parts e, g and i¹⁶⁴. The range for each figure is from 1 up to the maximum enhancement (white number). 25

Figure 2.4. Two examples of multiresonant plasmonic systems based on the optical coupling between localized plasmonic modes in in-plane trimer nanostructures. (a) Schematic illustration and the spectra of near-field electric field intensity enhancement at two nanogaps in an asymmetric trimer with a linear arrangement¹⁸⁷; (b-c) The near-field distribution maps of electric field intensity enhancement at (b) $\lambda = 400$ nm and (c) $\lambda = 800$ nm¹⁸⁷. (d) Schematic illustration and (e) the spectra of electric field at two nanogaps in a trimer system with a circular arrangement under two different polarization conditions of incident light¹⁵⁹. 28

Figure 2.5. Multiresonant plasmonic systems based on the optical coupling between localized plasmonic modes in out-of-plane composite nanostructures^{207, 209}. (a) The energy diagram, (b) the far-field scattering and absorption spectra, and (c) the near-field distribution maps of electric and magnetic field intensities for a MIM structure with a single dielectric gap. (d) The energy diagram,

(e) the far-field scattering and absorption spectra, and (f) the near-field distribution maps of electric and magnetic field intensities for a MIMIM structure with two dielectric gaps. 33

Figure 2.6. Two examples of multiresonant plasmonic systems based on the optical coupling between localized plasmonic modes and delocalized plasmonic modes. (a) Schematic illustration of the 1D periodic arrays of MIM nanocavities consisting of 1D periodic array of gold nanowires on an Ag film separated with a SiO₂ dielectric layer ²¹⁰; (b) Calculated transmission (solid lines) and absorption spectra (shaded area) for $L_{sp}=20$ nm, $d_x=500$ nm with TM polarized normal light incidence that shows two resonant features associated with two hybridized modes ²¹⁰; (c) Electric and magnetic field distribution maps for the two hybridized modes at 1.35 eV and 1.61 eV ²¹⁰. (d) Schematic illustration and SEM image of the 2D periodic arrays of MIM nanocavities consisting of a 2D periodic array of gold nanoparticles on an Au film separated with a dielectric layer ²¹¹; (e) Dispersion diagram showing the anti-crossing behavior when the LSP mode is strongly coupled with the Bloch plasmonic Mode ²¹¹; (f) Electric field distribution maps for the two branches of modes in the region with no coupling (i) and (iii) and with the strong coupling (ii) and (iv)²¹¹. 36

Figure 2.7. A multiresonant plasmonic system based on the optical coupling between LSP modes and grating diffraction modes ²¹⁷. (a) A single bow-tie nanoantenna (two sections of a disk with radius of $2.2\ \mu m$, opening angle of 45° and central gap of $100\ nm$), surrounded by three periodic arrays (with periodicities of $3.6\ \mu m$, $5.7\ \mu m$ and $7.2\ \mu m$) of metallic disks (with diameters of $1.8\ \mu m$, $2.85\ \mu m$ and $3.6\ \mu m$, respectively). All elements have a thickness of $70\ nm$ and are deposited over a BaF₂ substrate which is transparent in the mid-infrared regime. The bow-tie antenna can couple with the metal particle arrays grating diffraction modes; (b) Simulated electric field intensity enhancement at the center of the bow-tie antenna for the system (red curve) as well as in an isolated state (blue curve). 38

Figure 2.8. A multiresonant plasmonic system based on the optical coupling between delocalized plasmonic modes ²²². (a) The SEM image of a width-graded rainbow trapping 1D plasmonic nanograting consisting of 29 in-plane MIM rectangular grooves separated from each other by $100\ nm$ thick mesas. All grooves have the same depth of $100\ nm$. However, their widths increase from $40\ nm$ at the center to $180\ nm$ in both ends in increments of $10\ nm$; (b) The system schematic diagram; The darker green areas inside the central grooves represents the trapped fields as a result of SPP coupling. Also, the two orange arrows indicate the light guiding in the direction of increasing refractive index toward the center; (c-e) Electric field enhancement factor ($|E/E_0|^4$)

patterns in the system for TM-polarized laser excitations at three different wavelengths: (c) 785 nm, (d) 638 nm, and (e) 532 nm. 39

Figure A1. (a) Hybridization between the two electric dipolar modes of two in-plane adjacent Ag nanodisks. (b) Hybridization between the two electric dipolar modes of two vertically-stacked (out-of-plane) Ag nanodisks. Together, the two nanodisks form a one-cavity MIM system. (c) Hybridization between the two magnetic dipolar modes of two vertically-stacked MIM nanocavities with a shared Ag nanodisk. This system forms a two-cavity MIM system. 44

Figure A2. (a, d) Schematics of a one-cavity (a) and a two-cavity MIM structures in a background with $n=1.5$. (b, e) Scattering and absorption spectra of the one-cavity (b) and two-cavity (e) MIM structures. (c, f, g) Near-field profiles of the modes marked in b and e. $\lambda_{Fund} = 876 \text{ nm}$ and $\lambda_{A - Bond} = 828 \text{ nm}$ modes represent magnetic dipolar natures. However, $\lambda_{Bond} = 904 \text{ nm}$ represents a magnetic-quadrupolar nature. $\lambda_{A - Bond}$ and λ_{Bond} modes form due to the magnetic hybridization between two vertically-stacked λ_{Fund} modes. For both one-cavity and two-cavity systems, the broad spectral feature belongs to the electric dipole mode which is dominated by the top and bottom interfaces of the structure. Furthermore, the low-wavelength resonances on the shoulder of the electric dipole mode correspond to the high-order modes with features inside the gap or on the sidewalls. 45

Figure A3. Anti-crossing behavior and spatial overlap condition. (a) To understand how detuning the top and bottom gap modes affect their hybridization, we sweep the thickness of the top nanocavity while keeping the bottom nanocavity thickness constant. (b) Extinction spectra of the system as a function of the top gap thickness (t_2). When two similar modes couple, their common resonance energy splits into two new lower and higher resonance energies. In this regard, the resonance energy loci of the two hybrid modes cannot cross each other. This phenomenon, called the anti-crossing or avoided crossing, evidences the mode coupling event. (c, d) Near-field profiles of the bonding and anti-bonding resonances for $t_2 = 20 \text{ nm}$. We see that when the two nanocavities are detuned, their modes have a weak hybridization. This scenario results in a weak spatial overlap between the bonding and antibonding modes. These simulations point out to the following general rule: “To have a good spatial mode overlap between the hybrid modes, their parent modes should both spectrally and spatially overlap” 46

Figure A4. Tuning the optical response by changing the middle metal thickness. (a) Resonance energy of the fundamental mode (one-cavity system), bonding mode (two-cavity system), and the

anti-bonding mode (two-cavity system) as a function of h_2 , which represents the bottom metal thickness in the one-cavity system and the middle metal thickness in the two-cavity system. The fundamental mode blueshifts with increasing h_2 which stems from the bonding nature of this mode and weakening of the coupling between the two interfaces of the bottom nanodisk. Changing h_2 affects the modes of the two-cavity system in two manners: 1- shifting the fundamental mode; 2- Modulating the coupling strength between the top and bottom cavities. These factors shift the bonding mode in the same direction while shift the antibonding mode in the opposite directions. In this regard, resonance energy of the bonding mode is much more sensitive to h_2 . (b) scattering and absorption cross sections of the three modes as a function of h_2 . Consistent with part a, the antibonding mode appears less sensitive to h_2 compared to the other two modes. For the fundamental mode, increasing of the scattering cross section as a function of h_2 is due to larger area of the MD mode, which increase its magnetic dipole moment. However, for the bonding mode, this increase is due to the augmented phase retardation between the two nanocavities. Both the fundamental and bonding mode are underdamped²²⁷, which causes their absorption cross-sections to also increase. (c) Maximum intensity enhancement of the three modes (at the edges of the nanocavities) as a function of h_2 . Bonding and anti-bonding modes are evaluated in both the top and bottom nanocavities of the two-cavity system. We see that E_2 curves generally follow the absorption spectra for each mode. The mismatch between the E_2 curves of the top and bottom nanocavities are due to interference effects. 47

Figure A5. Tuning the modes by changing the diameter (D) for systems with $h_2 = 40 \text{ nm}$ (a) and $h_2 = 12 \text{ nm}$ (b). Increasing the diameter redshifts all the three modes (fundamental, bonding, and anti-bonding) with almost the same slop. This result can be justified if we view the nanocavities as Fabry-Perot resonator with an effective length proportional to the system diameter. In contrast, changing the diameter almost does not affect the energy splitting between the bonding and antibonding modes. This result reveals that the two nanocavities' coupling strength is almost independent of the system diameter. 48

Figure 3.1. BBCMT model for a single resonator. (a, b) Resonator A is getting excited by the current source Jr, ω inside (a)/outside (b) of it. (c) Resonator A is getting excited by the incident field E^{inc} . Each waveguide mode in the medium that delivers power to the resonator corresponds to a port. (d) Decomposing a resonator into a background structure (Ab) and a residual structure (Ar). (e) Resonator A' is defined as a combination of resonator A and the dielectric function

perturbation $\delta\epsilon$ inside it or in its proximity. (f) The signal flow graph of resonator A showing how its modes are coupled to the input and output power wave vectors. (g, h) Fundamental ideas of Kappa-estimation (g) and F-estimation (h) lemmas to reverse engineer the resonator pole matrix, non-radiative decay rate, and coupling coefficients from the data obtained of numerical simulations or experimental measurements. 55

Figure 3.2. BBCMT model for the system of coupled resonators. (a) System of the coupled resonators A and B in the medium. (b) Diagram of energy circulation for the system of coupled resonators reveals the mutual loading effect between them. (c) The SFG for the system of the coupled resonators. Output-coupling of the system modes is not shown in the SFG for simplicity. (d, e) The equivalent scenarios of the coupled background-loaded resonators (d) and the decoupled-loaded resonators (e). 70

Figure 3.3. An example to clarify the concept of a proper background structure and numerically validate the background perturbation method. (a) The resonator geometry: An MIM nanodisk array embedded in an SiO₂ slab. (b) Reflectance, (c) transmittance, and (d) absorbance spectra over the designated frequency. The dashed lines represent the spectra calculated from the FDTD simulation. The solid lines represent the spectra calculated by BBCMT models with (e) background 1: a metal nanodisk array embedded in the SiO₂ slab, (f) background 2: the embedding SiO₂ slab, (g) background 3: a PEC ground plane slab, and (h) background 4: a free space slab. Backgrounds 3 and 4 correspond to the directly-coupled and the side-coupled TCMT versions, respectively. 81

Figure 3.4. The nanolaminate plasmonic crystal and its constituent nanodome and nanohole arrays. (a) The geometry of the nanolaminate plasmonic crystal. d represents the distance between the nanodome and nanohole arrays. The system is illuminated with an x-polarized plane wave incident from the top side. (b, c) The FDTD-simulated reflectance, transmittance, and absorbance spectra of the uncoupled nanodome array (b) and the uncoupled nanohole array (c). The figures also show the near-field distributions of the dominant mode for each subsystem (at resonance) in the designated frequency range of interest ($\omega = 1.6 \times 10^{15}$ rad/s to $\omega = 2.2 \times 10^{15}$ rad/s) shaded in purple. 83

Figure 3.5. (a) BBCMT model for the nanolaminate plasmonic crystal. (b) The SFG of the system when we assume a free space background structure for the nanodome array and a background

structure of the PEC ground plane for the nanohole array. (c) The SFG resulted from the simplification of the SFG in part (b) by the SFG decomposition rules. 87

Figure 3.6. Reverse-engineering the parameters in the BBCMT model of the nanolaminate plasmonic crystal from the FDTD-simulated absorbance spectra. (a-d) finding the parameters of the uncoupled resonators by the Kappa-estimation lemma. We used the FDTD-simulated absorbance spectra of the nanodome array (a) and nanohole array (c) for top-side and bottom-side illuminations as the data for the Kappa-estimation lemma. The parameters obtained from the lemma are such that the BBCMT-calculated absorbance spectra for top-side and bottom-side illuminations can fit the background-subtracted absorbance spectra from the FDTD simulations, as illustrated for the nanodome array (b) and the nanohole array (d). (e) We found the parameters of coupling between the resonators by fitting the absorbance spectra of the nanolaminate plasmonic crystal for $d=80$ nm and $d=120$ nm. Nevertheless, the BBCMT-calculated spectra for several other values of d also show a decent match to the FDTD-simulated spectra. 91

Figure 3.7. Side-by-side comparison between the BBCMT calculations and FDTD simulations for the absorbance spectra of the nanolaminate plasmonic crystal and its sub-arrays for $d=0$ up to $d=2000$ nm. The resulting spectra are shown as colormaps in the $d - \omega$ plane. (a, d) Absorbance colormap of the nanolaminate plasmonic crystal from BBCMT (a) and FDTD (d). (b, e) Absorbance colormap of the coupled nanodome array from BBCMT (b) and FDTD (e). (c, f) Absorbance colormap of the coupled nanohole array from BBCMT (c) and FDTD (f). 92

Figure B1. (a) Dielectric function, (b) dispersion factor, and (c) loss tangent of the Palik silver model..... 113

Figure B2. Near field distributions of the resonator at the resonance frequency of $\Omega_A=2.19 \times 10^{15}$ rad/s reveals that the dominant mode belongs to the gap between the nanodisks. 114

Figure B3. (a-c) Normalized FOM_{abs} from BBCMT calculations and FDTD simulations for the nanolaminate plasmonic crystal (a), the coupled nanodome array (b), and the coupled nanohole array (c). For each value of d , we have defined the figure of merit (FOM) as the area under the absorbance curve. Also, we have normalized the FOM for all values of d to that of $d=0$. (d-f) BBCMT-calculated and FDTD-simulated absorbance of the nanolaminate plasmonic crystal (d), the coupled nanodome array (b), and the coupled nanohole array (f) at the frequency of $\omega = 1.9 \times 10^{15}$ rad/s. All the data in this figure are acquired from the colormaps in Figure 7 of the main text..... 117

Figure B4. (a, d) Absorption enhancement of the nanodome (a) and nanohole (d) arrays in the coupled state with respect to those for the uncoupled state. (b, e) Enhancement ratio of the input-coupling coefficients for the nanodome (b) and nanohole (e) arrays in the coupled state with respect to those for the uncoupled state. (c, f) Enhancement ratio of the resonance factors for the nanodome (b) and nanohole (e) arrays in the coupled state with respect to those for the uncoupled state. All the colormaps are obtained from the BBCMT analysis for the excitation from the top side and are plotted in the $d - \omega$ plane. 118

Figure B5. Comparison of the reflectance and transmittance spectra of the nanolaminate plasmonic crystal calculated by BBCMT versus those simulated by FDTD for $d=0$ up to $d=2000$ nm. The resulting spectra are shown as colormaps in the in the $d - \omega$ plane. The colormaps calculated from BBCMT and FDTD share several features, such as: 1) When d gets large, reflectance and transmittance asymptotically become periodic functions of d ; 2) The maximum transmittance is attained for $d \sim 0$; 3) The transmittance is pretty small for both cases such that the reflectance colormaps of the nanolaminate plasmonic crystal look almost like its absorbance colormaps in Figure 7(a, d) of the main text. 119

Figure B6. CMT calculations of reflectance, transmittance, and absorbance spectra for $d=0$ up to $d=2000$ nm when the non-resonant loading effect is not considered. The resulting spectra are shown as colormaps in the in the $d - \omega$ plane. As observed, the quality of fitting considerably degrades when we do not consider the non-resonant loading effect. 120

Figure 4.1. Nanolaminate plasmonic crystals in the two-tier configuration for broadband multiresonant nanolocalized light concentration. (a) Scheme of nanolaminate plasmonic crystals consisting of nanolaminate nanodomains and nanohole arrays as the two multiresonant subsystems. (b) Nanolaminate nanodomains support multiple localized plasmonic modes M_n^L by hybridization. (c) Nanolaminate nanohole arrays support multiple delocalized plasmonic modes M_n^D by hybridization. However, the high-order modes from hybridization in multiresonant subsystems tend to have a dark multipolar nature. (d) Coupled-mode theory (CMT) modeling and analysis of optical interactions between the representative Mode A and Mode B in the two subsystems, showing that the coupled system can have a higher light absorption than the summation of those from the two uncoupled subsystems. (e) Schematic energy diagram and absorption spectra for the two-tier multiresonant systems that can support multiple hybrid plasmonic modes M_n^{L-D} with spatial overlaps and with stronger interactions with free-space light. 124

Figure 4.2. Multiresonant optical responses of fabricated nanolaminate plasmonic crystals with different numbers of metal-dielectric layers. (a) Top-view and (b) tilted-view optical camera images of a wafer-scale sample of the four-metal-layer nanolaminate plasmonic crystal. (c) Top-view, and (d) cross-sectional scanning electron microscope (SEM) images of the 4MLs nanolaminate plasmonic crystal. (e) Scheme of four different types of fabricated nanolaminate plasmonic crystals with 1 metal layer (1ML), 2 metal layers (2MLs), 3 metal layers (3MLs), and 4 metal layers (4MLs). The thicknesses of dielectric nanogap layers for nanolaminate plasmonic crystals increase from 8 nm in the bottom to 10 nm in the middle and 15 nm in the top, respectively. (f) Measured, and (g) FDTD-calculated reflection and transmission spectra for the different samples of nanolaminate plasmonic crystals in (e)..... 126

Figure 4.3. The strong dependence of multiresonant optical responses on the dielectric nanogap thickness (t). (a) Measured and (b) FDTD-calculated reflection spectra for 2MLs nanolaminate plasmonic crystals with different t from 5 to 40 nm. (c-d) FDTD-calculated absorption spectra for the 2MLs nanolaminate nanodome (c) and the 2MLs nanolaminate nanohole (d) arrays as the two multiresonant plasmonic subsystems ($t = 15$ nm). (e-f) FDTD-calculated spectra of (e) absorption and (f) near-field $|E|^2/|H|^2$ intensities for 2MLs nanolaminate plasmonic crystals with $t = 15$ nm. (g-k) The FDTD-calculated x - z distribution maps of $|E|^2$ and $|H|^2$ for the modes λ_1 - λ_5 marked in Figure 4.3(e). l, Geometrically-averaged x - z distribution maps of $|E|^2$ and $|H|^2$ among λ_1 - λ_5 modes. 128

Figure 4.4. Broadband multiresonant light concentration in dense arrays of nanogap hotspots. FDTD-calculated absorption spectra for (a) 4MLs nanolaminate nanodome and (b) 4MLs nanolaminate nanohole arrays as the two multiresonant plasmonic subsystems. (c-d) FDTD-calculated spectra of (c) absorption and (d) near-field $|E|^2/|H|^2$ intensities for the 4MLs nanolaminate plasmonic crystal. (e-m) FDTD-calculated x - z distribution maps of $|E|^2$ and $|H|^2$ for the modes λ_1 - λ_9 marked in part (c). (n) Geometrically averaged x - z distribution maps of $|E|^2$ and $|H|^2$ among λ_1 - λ_9 modes..... 131

Figure 4.5. The strong dependence of multiresonant optical responses on the separation distance (d) between the two multiresonant subsystems. (a) FDTD-calculated absorption spectra for the 4MLs nanolaminate plasmonic crystal with different d between 0 and 160 nm. (b) Peak absorption values for λ^A and λ^B modes (also labeled in part (a)) by FDTD calculations (solid curves & dots) and CMT modeling (dashed lines) as a function of d . Horizontal lines represent the absorption

values for the corresponding modes in the uncoupled multiresonant subsystems. (c-d) FDTD-calculated near-field intensities of (c) $|E|^2$ and (d) $|H|^2$ at resonant wavelengths for λ^A and λ^B modes as a function of d 133

Figure C1. (a) Measured and (b) FDTD-calculated transmission spectra for the 2MLs nanolaminate plasmonic crystals with different t from 5 to 40 nm. 144

Figure C2. (a) The 2MLs nanolaminate nanodome array with $t = 15$ nm illuminated from the top and bottom ports. (b-d) FDTD-calculated far-field spectra for top-port (downward) and bottom-port (upward) illuminations. (e-f) The FDTD-calculated x - z distribution maps of $|E|^2$, $|H|^2$, E_z , and H_y for the modes λ_{1L} and λ_{2L} marked in b-d..... 145

Figure C3. (a) The 2MLs nanolaminate nanohole array with $t = 15$ nm illuminated from the top and bottom ports. (b-d) FDTD-calculated far-field spectra for top-port and bottom-port illuminations. (e-j) The FDTD-calculated x - z distribution maps of E^2 , H^2 , E_z , and H_y for the modes $\lambda_{1D} - \lambda_{6D}$ marked in b-d..... 146

Figure C4. (a) The 2MLs nanolaminate plasmonic crystal with $t = 15$ nm illuminated from the top port. (b-d) FDTD-calculated far-field spectra for the top-port illumination. (e-i) The FDTD-calculated x - z distribution maps of E^2 , H^2 , E_z , and H_y for the modes $\lambda_1 - \lambda_5$ marked in b-d. 147

Figure C5. (a) The 4MLs nanolaminate nanodome array illuminated from the top and bottom ports. (b-d) FDTD-calculated far-field spectra for top-port and bottom-port illuminations. (e-j) The FDTD-calculated x - z distribution maps of E^2 , H^2 , E_z , and H_y for the modes $\lambda_{1L} - \lambda_{6L}$ marked in b-d. 148

Figure C6. (a) The 4MLs nanolaminate nanohole array illuminated from the top and bottom ports. (b-d) FDTD-calculated far-field spectra for top-port and bottom-port illuminations. (e-j) The FDTD-calculated x - z distribution maps of E^2 , H^2 , E_z , and H_y for the modes $\lambda_{1D} - \lambda_{6D}$ marked in b-d. 149

Figure C7. (a) The 4MLs nanolaminate plasmonic crystal illuminated from the top port. (b-d) FDTD-calculated far-field spectra for the top-port illumination. (e-m) The FDTD-calculated x - z distribution maps of E^2 , H^2 , E_z , and H_y for the modes $\lambda_1 - \lambda_9$ marked in b-d. 150

Figure C8. (a-b) CMT fitting of the background-subtracted FDTD-calculated absorption spectra of the 4MLs nanolaminate nanodome (a) and nanohole (b) arrays for top-port and bottom-port illuminations in the wavelength range 800-1200 nm. (c) The parameters in the CMT equations are

set to fit the FDTD-calculated absorption spectra of the nanolaminate plasmonic crystal for $d=80$ nm and $d=120$ nm cases. Then, the CMT predicts the absorption spectra for the rest of d values. Side-by-side comparison between the CMT-calculated and the FDTD-calculated spectra reveals a decent match between the two in terms of resonance wavelengths and resonant absorption values for λA and λB modes. 151

Figure 5.1. (a) Simultaneous second harmonic and up-conversion photoluminescence emissions from nanolaminate plasmonic crystals upon excitation by a near infrared (NIR) ultrafast laser pulse. (b) Cross-sectional view SEM pictures of H1, H2, and H3 samples. The samples are only different in terms their TiO₂ thickness. (c-d) Anti-Stokes Photoluminescence (ASPL) process based on the intraband recombination (IBR) and electronic Raman scattering (ERS) pictures, respectively. (e) The second harmonic generation (SHG) process. 155

Figure 5.2. (a-c) Absorption spectra of the samples under normal white light excitation. (d-f) Nonlinear emission spectra of the samples under P-polarized, 1020 nm, and 128 mW excitation. The H and G samples in each graph have the same TiO₂ cladding thickness. 158

Figure 5.3. (a) H3 nonlinear emission spectra for fixed incident wavelength (1020 nm) and polarization (P) but different incident powers ranging from 48 mW up to 128 mW. (b) SHG (experimental), ASPL (experimental), IBR (model), and ERS (model) power-laws as a function of the incident power (P_{inc}). (c) Experimental and modeled spectral power-laws at two different power levels. (d) Comparison of the emission lineshapes for $64, 80, 112$, and 128 mW incident powers. 159

Figure 5.4. PL model for a system with $M = 0.26$ and $\beta = 1$ (IBR-dominant picture) excited by a laser pulse ($\lambda_{inc} = 1020$ nm) peaking at $t = 260$ fs. (a) Electron energy distributions at different times before, during, and after the excitation for $P_{inc} = 128$ mW. (b) Comparison of the emission lineshapes for $64, 80, 112$, and 128 mW incident powers. (c) Incident and ASPL (530-890 nm) power and energy versus time for $P_{inc} = 128$ mW. Energy curves are acquired by integration of the power curves. The total ASPL power and energy can be divided into two components contributed by the non-thermal (ρ_{nt}) and thermal (ρ_t) hot carriers, respectively. $\tau_{10} - 90\%$, r_{nt} , and r_t represent the ASPL emission time, and non-thermalized and thermalized contribution levels to ASPL, respectively. (d) Dependency of r_{nt} , $\tau_{10} - 90\%$ (normalized to $\tau_e - p_h = 850$ fs), and power-law on the incident power. The ASPL process could fall into weak (blue), moderate (green), or strong (red) excitation regimes. 161

Figure 5.5. (a) H3 nonlinear emission spectra ($S\lambda_{inc}, \lambda$) for fixed incident power (128 mW) and polarization (P) but different incident wavelengths ranging from 960 nm up to 1040 nm. (b) M (in Eq. (1)), $ISHG$ (505 – 515 nm), and $IASPL$ (530 – 890 nm) as a function of the incident wavelength. (c) ASPL spectral intensity ratios ($R\lambda_{inc}, \lambda = S\lambda_{inc}, \lambda S1040\text{ nm}, \lambda$) acquired from the spectra in part (a). (d) laser-induced perturbation of the electron distribution when the electron-electron and electron-phonon scattering effects are neglected. (e, f) $R\psi\lambda_{inc}, \lambda$ and $RL\lambda_{inc}, \lambda$ represent the $R\lambda_{inc}, \lambda$ components due to modification of the available hot electron-hole pairs ($\psi(v)$) and the effective emission enhancement factor ($Leff$), respectively. 166

Figure 5.6. (a) H3 nonlinear emission spectra ($S(polinc, \lambda)$) for fixed incident power (128 mW) and wavelength (1020 nm) but different incident polarizations (P and S). (b) $D\lambda = S(polinc = S, \lambda)/S(polinc = P, \lambda)$ is the spectral intensity ratio between the S and P incident polarizations acquired from part (a) spectra. $D\psi\lambda$ and $DL\lambda$ represent the $D\lambda$ components due to modification of the available electron-hole pairs energy ($\psi(v)$) and the effective emission enhancement factor ($Leff$), respectively. (c) $IASPL$ (530 – 890 nm) dependency on the emission polarization ($polem$) for each of P and S incident polarizations. (d) FDTD-simulated $Re(Ez)$ distributions in the H3 dome part for two cases of normal excitation with perpendicular polarizations (at 761 nm). NPCs possess degenerate plasmonic modes with perpendicular polarizations. (e) FDTD-simulated $E2$ distributions in the H3 dome part for 30°-angled excitation with P and S polarizations (at 1020 nm). $E2$ profiles at the excitation wavelength (denoted by $Eex2$ in the text) estimate the hot carriers' spatial distributions right after the generation. (f) $ISHG$ (505 – 515 nm) dependency on $polem$ for P and S incident polarizations. 169

Figure D1. (a) Top-view and cross-sectional view SEM pictures of H1, H2, and H3 samples. The samples are only different in terms their TiO₂ thickness. (b) The experimental setup for the nonlinear optical measurements. L1, L2, and L3 are convex lenses for laser condensation, emission collection, and coupling to the spectrometer, respectively. The optical filter has a ~490-890 nm pass band. The polarizer on the output path only exists when measuring the emission polarization. 189

Figure D2. (a) 2D schematics of the nanolaminate plasmonic crystals (NPCs) used in this work. H1-H3 consist of a corrugated Ag-SiO₂-Ag nanolaminate array coated by 25 nm, 60 nm, and 130 nm TiO₂ cladding layers, respectively (Figure 5.1(c)). G1-G3 are similar except not possessing the top SiO₂ and Ag layers. (b, c) Measured (b) and FDTD-simulated (c) reflectance spectra of the

samples. Due to having the ground plane layer, transmission is negligible. Hence, $R=1-A$, where R and A denote the reflectance and absorbance, respectively. (d) FDTD-simulated near-field E_2 profiles corresponding to the resonances marked in part (c). 190

Figure D3. (a) H3 nonlinear emission spectra for fixed incident wavelength (1020 nm) and polarization (P) but different incident powers ranging from 48 mW up to 128 mW. (b) SHG (experimental), ASPL (experimental), IBR (model), and ERS (model) integrated intensities as a function of the incident power. The axes are in logarithmic scale. The power-laws (n) are acquired by exponential fitting ($R^2 > 0.99$). (c) The SHG, ASPL, IBR, and ERS power-laws as a function of the incident power (P_{inc}). ASPL and SHG power-laws generally go up as P_{inc} increases. The anomaly at 80 mW is possibly due to non-linear resonance effect, though further investigation is needed. IBR power-law also goes up with P_{inc} . However, ERS power-law is a decreasing function of P_{inc} . (d-f) ASPL (d), IBR (e), and ERS (f) spectral power laws at different P_{inc} levels. Again, ASPL and IBR power-laws generally go up with P_{inc} . However, ERS power-law below ~ 1.9 eV is a decreasing function of P_{inc} . Also, ERS power-law below ~ 1.9 eV cannot go above 2, unlike ASPL and IBR power-laws..... 191

Figure D4. (a) H3 nonlinear emission spectra for fixed incident wavelength (1020 nm) and polarization (P) but different incident powers ranging from 48 mW up to 128 mW. (b) Spectral lineshapes for different incident powers. (c) Magnified lineshapes from part (b). (d-e) Spectral lineshapes extracted from the spectra calculated based on the ERS (d) and IBR (e) models. (f) Magnified lineshapes from part (e). 192

Figure D5. Time evolution of the electron distribution for a system with $M = 0.26$ excited by a laser pulse ($\Delta t_{inc} = 140$ fs, $\lambda_{inc} = 1020$ nm, and $P_{inc} = 128$ mW) that peaks at $t = 260$ fs. (a-c) Total (a), non-thermalized (b), and thermalized (c) electron energy distributions at different times before, during, and after the excitation. (d) Energy stored in the non-thermalized (blue curve) and thermalized (red curve) hot electrons over time. The dashed black curve shows the temperature of the thermalized hot electrons over time. $T_0=300$ K and $E_0 = 2\pi^2\hbar^3mq^32EF\infty 1\exp\epsilon - EFKB T_0 + 1\epsilon 32d\epsilon$ represent the temperature and energy of the native (pre-excitation) electron distribution, respectively..... 193

Figure D6. FDTD simulations show that $Flr, \lambda = \gamma r \gamma_0$ highly depends on the wavelength λ as well as the dipole's position r and direction l . P1z curve decently mimics the resonances in the experimental lineshapes of Figure 5.3(d) in the main text..... 194

Figure D7. (a) H3 nonlinear emission spectra for fixed incident power (128 mW) and polarization (P) but different incident wavelengths ranging from 960 nm up to 1040 nm. (b) Spectral lineshapes corresponding to part (a).	194
Figure D8. (a) FDTD-simulated absorption spectra for the H3 sample under S-polarized and P-polarized 30°-angled plane wave excitations. (b) Experimental $1-R_{\text{specular}}$ of the sample, where R_{specular} is the specular reflectance measured using an ellipsometry setup. The two figures indicate that S and P incident polarizations cause comparable absorption levels at $\lambda_{\text{inc}} = 1020 \text{ nm}$...	195
Figure D9. Emission spectra for different excitation and emission polarizations.	195
Figure D10. (a-b) $E_{\text{ex}}.n_2$ distributions at the dome level for S and P polarized excitations (at $\lambda_{\text{inc}} = 1020 \text{ nm}$). (c-d) $E_{\text{p}}.n$ distributions at the dome level for normal excitation (at $\lambda_{\text{inc}} = 768 \text{ nm}$) with two perpendicular polarizations.	196
Figure E1. (a) Normalized scattering and absorption spectra of the MIM nanocavity system with SiO ₂ , ITO, Al, Ti, and Au as the gap materials. (b) Electric and magnetic intensity profiles of SiO ₂ (same index as the background) and Au in the x-z and x-y gap cross sections. SiO ₂ has the same index ($n=1.5$) as the background and hence, its optical response serves as the reference.	205
Figure E2. Resonance wavelength (a), scattering and absorption spectra (b), and intensity enhancement (c) of the magnetic dipole mode for different gap materials.	205
Figure E3. Optical (a) and electrical (b) performances of ITO and Au as a function of the gap nanodisk diameter.	206
Figure E4. Conductive gap MIM systems can be used as electrochemical electrodes with and optical sensing capability.	206
Figure E5. Fixed-size double-resonant NLPNAs. (A) Cross-sectional schematic of a fixed-size nanolaminate plasmonic nanoantenna with a fixed-diameter (D) and a fixed-height (H) in water ($n = 1.33$) under x-polarized normal incident light. The nanolaminate plasmonic nanoantenna consists of alternating layers of Au thickness (t) and SiO ₂ thickness (h) nanodisks. (B) Schematic illustration of the evolution of resonant wavelengths for hybridized electric dipole (ED) and magnetic dipole (MD) modes in a fixed-size nanolaminate plasmonic nanoantenna at different Au-SiO ₂ thickness ratios (t/h). (C) Scheme of the mode hybridization strategy for engineering the double-resonant optical properties of fixed-size NLPNAs. NLPNAs consist of two types of plasmonic building blocks in the vertical stack, which are the insulator-metal-insulator (IMI)	

nanostructures, supporting the electric dipole (ED) modes, and the metal-insulator-metal (MIM) nanostructures, supporting the magnetic dipole (MD) modes. 209

Figure E6. Spectral tunability of fixed-size double-resonant NLPNAs with different numbers of vertically stacked MIM building blocks by controlling the metal-to-insulator thickness ratio (t/h). (A-C) The dependence of the resonant wavelength and the peak absorption/scattering cross-sections of the ED mode and the MD mode on the Au layer thickness (t) for fixed-size NLPNAs with (A) one insulator layer, (B) two insulator layers, and (C) three insulator layers, in water ($n=1.33$). The diameter and the total height of NLPNAs with different numbers of Au-SiO₂-Au building blocks are fixed as ~ 100 nm. In the top panel of (A-C), the vertical shaded blue bands depict the range of Au layer thickness (t) for the ED mode with high peak scattering ($\sigma_{sca}/\sigma_0 \geq 8$), and horizontal shaded grey bands represent the tunable resonant wavelength range for a high scattering regime. In the bottom panel of (A-C), the vertical shaded red bands depict the range of Au layer thickness (t) for the MD mode with high peak absorption ($\sigma_{abs}/\sigma_0 \geq 8$), and horizontal shaded grey bands represent the tunable resonant wavelength range for the MD mode with the peak absorption $\sigma_{abs}/\sigma_0 \geq 8$ 210

Figure E7. Far-field and near-field optical properties of fixed-size MIMIM NLPNAs with different metal-to-insulator thickness ratios (t/h). (A) FDTD-calculated spectra of normalized absorption and scattering cross-sections for fixed-size Au-SiO₂-Au-SiO₂-Au nanoantennas in water ($n=1.33$) with different thicknesses for Au (t) and SiO₂ (h) layers, which have the fixed diameter (D) and the height (H) of ~ 100 nm. (B-C) FDTD-calculated distribution maps of E^2 , $\phi(E_x)$, $\phi(E_z)$, H^2 , and $\phi(H_y)$ for the MD related modes of fixed-size Au-SiO₂-Au-SiO₂-Au nanoantennas with different thicknesses of Au and SiO₂ layers in water ($n=1.33$), including (B) $t = 28$ nm and $h = 8$ nm, (C) $t = 16$ nm and $h = 26$ nm, and (D) $t = 4$ nm and $h = 44$ nm. 211

List of Tables

Table B1. Big picture overview of TCMT, common QNM theories, and BBCMT (this work)	120
Table C1. Quality factors (Q-factors) and dominant natures of the resonances in the 4ML nanolaminate plasmonic crystal structure. For each resonance, the quality factor is estimated from the corresponding resonance in the dominant array. We estimate the Q-factors of the fabricated 4ML system to be about half of their corresponding simulated results. Compared to other multiresonant plasmonic systems ^{297, 302} , the plasmonic crystal modes' Q-factors are in the medium range.....	152
Table 5.1. Description of the samples used in this work (PPA: polymer pillar array). H3 is the main sample and the other samples are used to analyze the effects of the system geometry on the non-linear emission. Our sample designs offer independent control over the plasmonic modes at the excitation ($> 950\text{ nm}$) and emission wavelengths ($490 - 890\text{ nm}$).....	157
Table D1. Comparison of the second harmonic generation (SHG) and anti-stokes photoluminescence (ASPL) general behaviors in this work.....	196

Chapter 1: Introduction

(This chapter is adopted from the review paper “Multiresonant plasmonics with spatial mode overlap: overview and outlook” by Seied Ali Safiabadi Tali, and Wei Zhou, published in journal of Nanophotonics 8.7 (2019): 1199-1225 and has been reproduced here with the permission of the copyright holder.)

Plasmonic devices and systems based on bottom-up synthesized or top-down fabricated metal nanostructures can be used to enhance light-matter interactions at nanoscale in physical, chemical, and biological systems¹⁻¹⁹. For example, plasmonic nanocavities and nanoantennas have shown unique capabilities for ultra-sensitive detection and analysis of chemical and biological species⁸⁻¹⁰, collection and concentration of light in nanoscale optoelectronics and nonlinear optics devices²⁻⁷, localized photothermal intervention of cells or cellular networks¹¹⁻¹⁵, and optical generation of hot carriers in photocatalytic processes¹⁶⁻¹⁹. For some of the directions being pursued with plasmonic nanostructures, such as surface-enhanced Raman spectroscopy and refractive-index sensing at nanoscale, single-resonant enhancement of light-matter interactions in one wavelength range is sufficient. Nevertheless, solar cells²⁰, broadband absorbers²¹, wavelength-multiplexed multimodal nanodevices²²⁻²⁴, and applications involving multi-photon parametric and non-parametric nonlinear processes²⁵⁻³⁹ prefer “multi-resonant plasmonic systems” to enhance the light-matter interaction across a wide wavelength range or in multiple wavelength bands. Some multiresonant plasmonic applications such as those including multi-photon non-linear optical processes and wavelength-multiplexed operations further require the resonant optical phenomena to take place at the same areas, requiring the spatial overlap of the plasmonic modes. We refer to this type of systems as “multiresonant plasmonic systems with spatial mode overlap” (Figure 1.1).

This dissertation comprehensively studies the “multiresonant plasmonic systems with spatial mode overlap” in terms of the fundamental concepts, design ideas, and applications in non-linear optics. The rest of this chapter is organized as follows; Section 1.1 discusses some current and potential applications that can benefit from multiresonant enhancement of local optical fields at the same locations. Section 1.2 explains the dissertation structure and briefly mentions the different contributions we have made to the field.

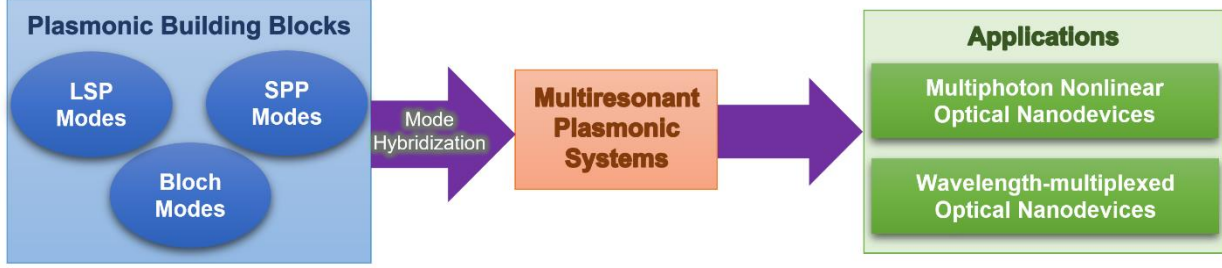


Figure 1.1. A block-diagram illustration of the strategy to create multiresonant plasmonic systems by plasmonic mode hybridization and the potential applications enabled by multiresonant plasmonics with spatial mode overlap. By the optical coupling between elementary modes (e.g., LSP modes, SPP modes, and Bloch modes) in different types of plasmonic building blocks, it is possible to design and create “multiresonant plasmonic systems with spatial mode overlap” that can support multiple plasmonic modes with strong local field enhancements at same locations in multiple different wavelength ranges. Potential applications regarding multiresonant plasmonics include: (1) multiphoton nonlinear optical nanodevices that can enhance both excitation and emission rates in multi-photon nonlinear processes or in multi-photon upconversion luminescence processes; and (2) wavelength-multiplexed optical nanodevices that can achieve multimodal optical operations at nanoscale using multiple spectral bands.

1.1. Applications of multiresonant plasmonics with spatial mode overlap

Multiresonant plasmonic systems with spatial mode overlap can be useful in two categories: (1) Simultaneous enhancement of optical excitation and emission processes at nanoscale, in applications that include multi-photon non-linear optical processes; (2) Enabling multiple optical multimodalities at different wavelengths but in the same location, to achieve wavelength-multiplexed multifunctional devices with nanoscale footprint. In what follows, we elucidate each of these categories in more details.

1.1.1. Multiresonant Plasmonic Enhancement of both Pumping and Emission Processes

In optics, Frequency conversion has long attracted a great deal of attention spawning a variety of applications in information technology, sensing and optoelectronics⁴⁰⁻⁴⁹. Several frequency conversion optical devices have been demonstrated so far. These optical devices operate based on several nonlinear optical processes in all of which, some incident (pumped) photons at one or several frequencies are absorbed and one or several photons with frequencies different from the original ones are emitted.

Depending on their mechanisms, many of these nonlinear optical processes have inherently small efficiencies due to either or both of multiphoton absorption and emission probabilities being low, especially when the pumping rate is low^{5, 50-57}. Plasmonic systems have been demonstrated to be a considerable solution to alleviate these limitations and enhance the fast non-linear optical

processes. In general, plasmonic systems could cause two types of enhancements for a non-linear optical process; excitation enhancement and emission enhancement. Excitation enhancement is achieved through increasing the photon absorption rate via generating large field enhancements at the fundamental wavelengths. On the other hand, emission enhancement is obtained by increasing the emission decay rate (Purcell effect) as well as altering the emission quantum yield^{52, 57, 58} via increasing the local density of optical states. In the existing literature, most of the plasmonic systems that have been utilized to enhance non-linear optical processes are single resonant⁵⁷. Such devices have been proven to be very efficient for enhancement of single-photon nonlinear optical processes in which the frequency difference between the input and output photons is small (like Raman and down-conversion fluorescence)⁵⁹⁻⁶³. The reason is that plasmonic modes are wide and thus, both of excitation and emission processes can usually be enhanced by a single mode. However, single-resonant plasmonic devices are usually far less efficient to enhance multi-photon nonlinear optical processes such as sum and difference frequency generation, and (multiphoton) up-conversion luminescence. The reason is that in such processes, the frequency difference between the input and output photons is often large due to which, one mode is not sufficient to enhance both of them simultaneously. The solution to resolve this issue is to use multiresonant plasmonic systems with spatial mode overlap which are capable to enhance every single photon absorption or emission step in a multi-photon non-linear optical process. In the following subsections, we give short descriptions about parametric non-linear optical processes and up-conversion luminescence. Also, we discuss the mechanisms through which they can be enhanced using multiresonant plasmonic systems with spatial mode overlap.

Parametric nonlinear optical processes

Electromagnetic waves interact with materials via displacing of their electrons through the electric and magnetic fields. In classic electromagnetics, such interactions are quantified using electric and magnetic susceptibilities, which, express the induced electric and magnetic dipole moment (or polarization) densities, respectively^{54, 56, 64}. Normally, for a certain material, the electric susceptibility is a constant and does not depend on the field intensity. Yet, when the electric field is large, as can be the case for the lasers, electric susceptibility (or refractive index, equivalently speaking) gets modified according to the field strength i.e. it becomes nonlinear. Such nonlinearity, which is called a parametric nonlinearity if the susceptibility is a real-value⁵⁴, can be described by a Taylor series expansion of the polarization density in terms of the electric field. In this regard,

linear effects are described by $\chi^{(1)}$ which is a unitless parameter, quadratic field dependence corresponds to $\chi^{(2)}$ which has the units of m/V and so on. In addition to the classical picture based on high order electric susceptibilities, quantum mechanical picture, centered on energy and charge conservation, can also be used to describe the parametric nonlinear optical phenomena. In this view, by absorption or emission of photons, electrons gain or lose energy via transitioning through a ladder of virtual states, which are very short-lived and unobservable quantum states. While the classical description based on the electric susceptibility concept very well serves mathematical analysis purposes, quantum mechanical picture gives a more intuitive view and thus is usually utilized to qualitatively describe the non-linear optical phenomena^{54, 56}.

Two major classes of parametric non-linear optical processes which are highly discussed in the literature are second order processes consisting of three-photon sum-frequency generation and three-photon optical parametric amplification (difference frequency generation), and third order effects including four-photon sum-frequency process and the four-photon parametric amplification^{5, 54, 56, 57}. All of these processes rely on simultaneous absorption of multiple photons which makes their efficiencies very low unless the pumping sources have very high intensities^{5, 54-56}. In addition, second order non-linear processes are not allowed in the systems that exhibit inversion symmetry, called centrosymmetric systems^{5, 54-57}. At macro scale, high non-linear optical conversion efficiencies are commonly achieved by phase matching in birefringent materials^{25, 30, 56}. Yet, typical large dimensions of this materials as well as their dependence upon the incident light polarization prohibits their use to fabricate chip scale tunable nonlinear optical devices²⁵.

During the past years, plasmonic systems have been considered a promising solution to address these issues^{5, 25-36, 55, 57, 65-75}. There are two major reasons for this consideration; First, as mentioned, plasmonic systems can efficiently enhance excitation or emission processes. Second, the choice of material becomes much more versatile since, although second-order nonlinear optical processes are prohibited in bulk centrosymmetric materials, they are allowed at interfaces due to the broken symmetry. This allows the optical nanoantennas with non-centrosymmetric design to excite second order optical response from a large range of materials even the centrosymmetric ones.

Commonly, enhancement of parametric nonlinear optical processes is achieved through augmenting of only the excitation rate at the fundamental frequency by single-resonant plasmonic systems⁶⁶⁻⁷⁵. Yet, it has been shown that the enhancement factor can be much higher if we also

simultaneously augment the emission process⁶⁵. A task which can be accomplished only by multiresonant plasmonic systems with spatial mode overlap. Please note that if we have multiple pump wavelengths, the electronic transitions corresponding to each of these wavelengths can be separately enhanced through matching them with the system resonances. These concepts are schematically illustrated in Figure 1.2(a-b) which represent the energy diagrams regarding the coupling of a multiresonant plasmonic system with a non-linear material to enhance a three-photon sum-frequency process and a three-photon optical parametric amplification process, respectively. In part A, electronic transitions from the $|0\rangle$ state to the $|1\rangle$ state and from the $|1\rangle$ state to the $|2\rangle$ state are first induced by absorption of pump photons with respective energies of $\hbar\omega_1$ and $\hbar\omega_2$ in the non-linear optical material. These transitions are augmented through the field enhancements provided by the M'_1 and M'_2 modes of the multiresonant plasmonic system. After being excited to the $|2\rangle$ state, excited electrons fall down to the ground state ($|0\rangle$) via radiative decay with the photon energy of $\hbar\omega_3$. The radiative decay rate can be modified through the coupling with M'_3 mode of the plasmonic system. In part B, by absorbing the pump photons with the energy $\hbar\omega_3$, the system can be excited from the $|0\rangle$ state to the $|2\rangle$ state. This transition is enhanced through the electric field enhancement created by the M'_3 plasmonic mode. Then, through stimulated emission of photons with the energy of $\hbar\omega_2$ amplified by the M'_2 plasmonic mode, these excited electrons fall down to the $|1\rangle$ electronic state. Finally, via radiative decay of photons with $\hbar\omega_1$ energy, amplified by M'_1 plasmonic mode, the system goes back to the ground state. Although the two examples discussed here were about second order (three photon) nonlinear optical processes, similar enhancements by the multiresonant plasmonic systems can be realized for the case of third order (four photon) processes. During the past recent years, scientists have utilized the idea exhibited in Figure 1.2(a) to enhance both second harmonic generation^{25-31, 33, 34, 55, 57, 65} and third harmonic generation^{35, 36, 57} processes. Feasibility of the idea presented in Figure 1.2(b), i.e. enhancement of optical parametric amplification by multiresonant plasmonic systems, has also recently been demonstrated^{32, 57}.

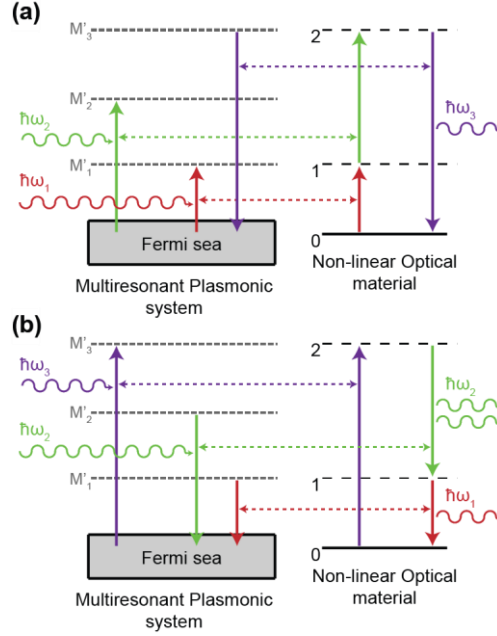


Figure 1.2. Energy diagram illustration of multiresonant plasmonic enhancement of nanoscale parametric nonlinear optical processes by integrating the non-linear optical material with a multiresonant plasmonic system with spatial mode overlap. (a) The three-photon sum-frequency process. (b) The three-photon optical parametric amplification process.

Non-parametric up-conversion Photoluminescence

Up-conversion (UC) luminescence is an anti-stokes type photoluminescence process in which low-energy photons in the infrared (IR) or near IR range can be converted into high-energy photons in visible or NIR range^{51-53, 76-78}. Unlike parametric non-linear multiphoton processes mediated by the transition into and from ultrashort-lived virtual states, up-conversion luminescence relies on the excitation and emission transitions between metastable real states. In other words, a parametric nonlinear optical process requires a strict spatiotemporal overlap of multiple photons at different wavelengths for both absorption and radiation, and thus is usually induced under pulsed laser excitation with a high optical density. On the other hand, the up-conversion luminescence can be generated by a sequential absorption and emission of multiple photons at the same location, which makes it possible to achieve UC luminescence using continuous wave (CW) laser excitation with a low optical density^{50, 51, 76, 78}.

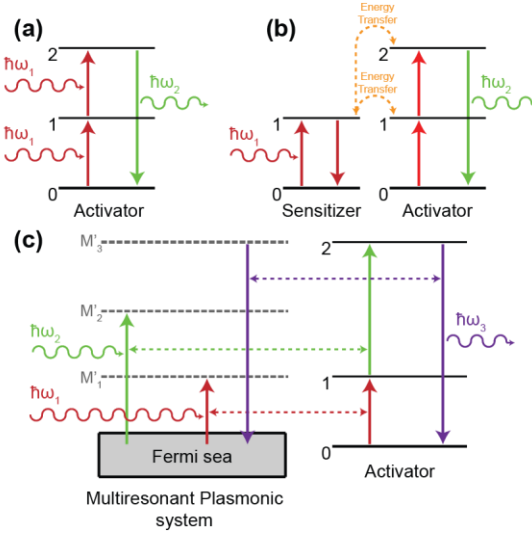


Figure 1.3. Energy diagram illustration of (a) Excited state absorption (ESA) UC process, (b) energy transfer up-conversion (ETU) UC process, and (c) plasmon enhanced ETU process by optically coupling an UC activator ion to a multiresonant plasmonic system with spatial mode overlap.

Several mechanisms have so far been identified for multiphoton UC processes^{50, 52, 53, 78}. The most elementary of these processes is excited state absorption (ESA). This process, which is illustrated by the energy diagram in Figure 1.3(a), works based on successive absorption of two or more photons by a single ion, called the activator. First, if the resonance conditions are met, the electron gets excited from the ground state to the first metastable excited state (denoted by $|1\rangle$) by absorption of a pump photon. Then, since this state has a rather long lifetime, the electron remains in it long enough to absorb the second pump photon leading to its further promotion to a higher excited state (denoted by $|2\rangle$). Finally, a photon with a higher energy is emitted upon radiative relaxation. Please note that if the energies for the ground and excited states are not equally spaced, more than one pump wavelength is required for the described process. Yet being simple, ESA is a very low efficiency UC mechanism due to low concentration of UC ions dopants as well as their small absorption cross section. In addition, this process has a very low luminescence quantum yield ($< \%2$)^{50, 79}. The most common way to enhance the UC efficiency, is to use one or more ions, called sensitizers, which have higher absorption cross sections in the neighborhood of the activator ion. The most efficient type of sensitized UC processes is energy transfer up-conversion (ETU)^{50, 52, 53, 78}. In this scenario, which is depicted in Figure 1.3(b), the activator ion excitation rate is enhanced through non-radiative resonance energy transfer from the sensitizer ion. The maximum efficiency happens when the sensitizer electronic transition matches both electronic transitions in the activator as is the case in Figure 1.3(b). Despite their improved efficiencies, sensitized UC

processes still suffer from the very low quantum yield⁵⁰. In addition, the efficiency of all UC processes, including ETU, is highly dependent upon the excitation intensity such that they show much higher efficiencies when the incident power is large⁵¹⁻⁵³.

During the past years, scientists have demonstrated that plasmonic systems can be used to enhance UC luminescence processes^{37-39, 50-52, 76, 77, 80-88}. In general, these systems can improve the efficiency of sensitized UC processes in three ways; excitation rate enhancement, emission rate enhancement, and energy transfer rate enhancement^{51, 52}. Most of previous study on plasmonic enhancement of UC luminescence is focused on single-resonant enhancement of either the emission process^{77, 80-82, 87} or the excitation process^{76, 83-86}. Yet, the highest enhancement factors can be achieved when both of excitation and emission rates are simultaneously enhanced, which can be achieved by exploiting multiresonant plasmonic systems with spatial mode overlap^{37, 39}. If the local field enhancement factors are large for multiple plasmonic modes, it is possible to achieve high UC yields even under the low optical excitation powers. Furthermore, through large enhancement of both emission and excitation rates in activation ions emitters using plasmonic system with spatial mode overlap, it is possible to directly make the ESA process efficient, without the need for any sensitizer³⁸. This idea is illustrated in Figure 1.3(c), which shows when an UC activator ion is resonantly coupled to a multiresonant plasmonic system with three spatially overlapped modes (M'_1 , M'_2 , M'_3 resonant at ω_1 , ω_2 , and ω_3 , respectively), the UC luminescence efficiency can be significantly increased through a simultaneous enhancement of both absorption processes at two fundamental frequencies (ω_1 , and ω_2) and the emission process at the emission frequency (ω_3). By avoiding the use of sensitizers for efficient UC luminescence, we will be able to relax the selection of UC activator ions without considering the match of transition energy with limited choices of sensitizer ions. Indeed, it is possible since, by the proper geometric design, one can continuously tune the resonant energies of different modes in multiresonant plasmonic systems to match them with the transitions of the desired activator ion. In this regard, it is notable that while, theoretically speaking, UC can be achieved from most transition metals, lanthanides and actinides, only a few of them have so far been practically reported to give large UC luminescence efficiencies⁵⁰.

1.1.2. Wavelength-Multiplexed Nanoplasmonic Multimodality

Besides multiresonant enhancement of multiphoton nonlinear optical processes and UC luminescence, multiresonant plasmonic systems with spatial mode overlap will open interesting

opportunities by enabling wavelength-multiplexed nanoplasmonic multimodality. Excitation of plasmonic modes can strongly enhance light-matter interactions at nanoscale which can lead to different types of optical processes or effects (Figure 1.4), including enhanced optical scattering in the far-field, enhanced optical fields in the near-field⁸⁹, nanolocalized photothermal heating⁹⁰, or transient generation of hot carriers in metal nanostructures⁹¹.

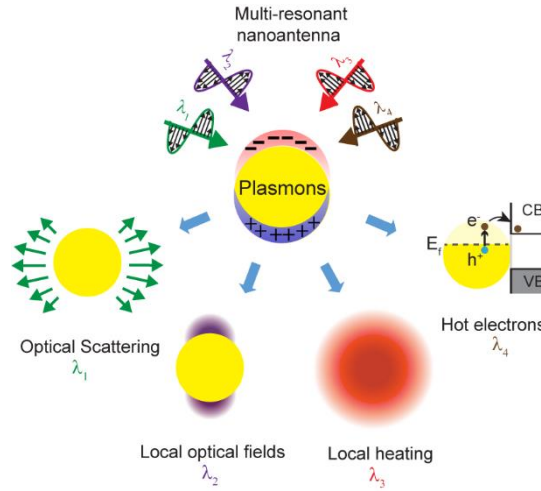


Figure 1.4. Schematic illustration of the wavelength-multiplexed nanoplasmonic system concept, i.e., merging several different types of plasmonics enabled/enhanced modalities into the same nanoscale device by using different wavelength channels.

Up to now, most works on plasmon-enhanced or plasmon-enabled applications focus on utilizing plasmonic effects at a single resonant wavelength range. By exploiting different resonant wavelength bands in multiresonant plasmonic systems with spatial mode overlap, we will be able to combine and merge several different types of plasmonics enabled/enhanced modalities into the same nanoscale devices. Such wavelength-multiplexed multimodal optical nanodevices may find significant applications in fields ranging from biotechnology, to renewable solar energy, and to optical information technology. Potential examples include (1) multimodal biophotonics nanotransducers for combined optical sensing and optical modulation of biochemical and biophysical processes with a subcellular resolution in in-vitro or in-vivo biological systems; (2) multimodal broadband light-harvesting substrates that can optically enhance photocatalysis processes in the hot spots and simultaneously achieve in-situ optical spectroscopy monitoring of photocatalysis processes using another wavelength channel; and (3) wavelength-multiplexed nanoscale all-optical switches or modulators that can use light signals in a group of multiple wavelength bands to control light signals in another group of multiple wavelength bands.

1.2. Dissertation structure and contributions

Chapter 1 (the current chapter) introduces the “multiresonant plasmonic systems with spatial mode overlap” and then clarifies their importance and applications through a comprehensive literature review. Chapter 2 first briefly reviews the fundamentals of plasmonic modes and their types. Then, with an emphasis on the mode hybridization as the key enabling factor, the chapter explores and compares the different architectures of the multiresonant plasmonic systems with spatial mode overlap. The architectures are also classified according to the localization characteristics of their elementary modes before hybridization. Chapters 1 and 2 are based on the following publications:

- Safiabadi Tali SA, Zhou W. Multiresonant plasmonics with spatial mode overlap: overview and outlook. *Nanophotonics*. 2019 Jul 1;8(7):1199-225.
- Safiabadi Tali SA, Zhou W. Magnetic plasmon hybridization in vertically stacked double-gap nanocavities. In 2018 Conference on Lasers and Electro-Optics (CLEO) 2018 May 13 (pp. 1-2). IEEE.
- Safiabadi Tali SA, Zhou W. Multi-resonant optical nanocavities by out-of-plane magnetic plasmon hybridization. In *Frontiers in Optics* 2018 Sep 16 (pp. JTU3A-53). Optical Society of America.

Chapter 3 develops the Black-box Coupled-Mode Theory (BBCMT), an ab initio modal analysis framework based on Maxwell’s equations to analyze the electromagnetic interactions of open, lossy, and dispersive resonators. The chapter first establishes the formulations for single resonators and then discusses the resonator coupling. BBCMT is a versatile theoretical framework for modeling the coupling of optical modes and analyzing the complicated dynamics of optical interactions in multiresonant plasmonic systems. Chapter 3 is based on the following publications:

- Safiabadi Tali SA, Zhou W. Black Box Coupled Mode Theory: Analysis of Loading Effects in Optical interactions between Nanoresonators. In *Frontiers in Optics* 2020 Sep 14 (pp. FW1B-3). Optical Society of America.
- Safiabadi Tali SA, Yuan L, Zhou W. Black-Box Coupled-Mode Theory: An Ab Initio Framework to Model Electromagnetic Interactions of Open, Lossy, and Dispersive Resonators. arXiv preprint arXiv:2011.10035. 2020 Nov 19.

- Safiabadi Tali SA, Yuan L, Zhou W. Black-Box Coupled-Mode Theory: An Eigenmode Expansion Framework to Analyze Electromagnetic Interactions of Open, Lossy, and Dispersive Resonators. 2021 Dec 10 [submitted].

Chapter 4 introduces the nanolaminate plasmonic crystals (NPCs), wafer-scale metamaterials in a two-tier configuration can support many (~ 10) spatially overlapped and highly-excitable hybrid plasmonic modes under free-space light illumination between 400 – 1400 nm. The chapter further studies the parameters affecting the NPCs performance analytically, using BBCMT, and experimentally, via fabrication of NPCs with different architectures and passive optical measurements. Chapter 4 is based on the following publications:

- Safiabadi Tali SA, Song J, Nam W, Zhou W. Two-Tier Nanolaminate Plasmonic Crystals for Broadband Multiresonant Light Concentration with Spatial Mode Overlap. *Advanced Optical Materials*. 2021 May;9(10):2001908.
- Safiabadi Tali SA, Song J, Nam W, Zhou W. Multiresonant Nanolaminate Plasmonic Metamaterials with Spatial Mode Overlap. In 2020 Conference on Lasers and Electro-Optics (CLEO) 2020 May 10 (pp. 1-2). IEEE.

Chapter 5 demonstrates the NPCs application in uncovering the mechanisms of the second harmonic generation and broadband anti-Stokes photoluminescence (ASPL) from plasmonic structures excited by ultrafast pulsed lasers. This chapter achieves its goal by taking advantage of the following factors: 1- Taking the NPC designs to the next level, such that the plasmonic modes at the excitation and emission wavelengths become independently controllable; 2- Non-linear optical measurements specifically designed to identify the various aspects of the non-linear emission mechanisms. 3- Using BBCMT, quantum optics, and statistical mechanics to develop advanced SHG and ASPL models that can explain the experimental results. Chapter 5 is based on the following publications:

- Safiabadi Tali SA, Mudiyanse Rathsara R. H. H (co-first), Qian Y, Smith N, Zhao Y, Morral A, Song J, Nie M, Magill B. A., Khodaparast G. A., Zhou W. Mechanisms of plasmonic anti-Stokes photoluminescence and its correlations with second harmonic generation. 2022 Conference on Lasers and Electro-Optics (CLEO).
- Safiabadi Tali SA, Mudiyanse Rathsara R. H. H (co-first), Qian Y, Smith N, Zhao Y, Morral A, Song J, Nie M, Magill B. A., Khodaparast G. A., Zhou W. Anti-Stokes Emission

from Plasmonic Structures: Mechanisms and Correlation with Second Harmonic Generation. 2021 Dec 10 [submitted].

Finally, chapter 6 concludes the dissertation with summarizing the materials in previous chapters and discussing the future works on non-linear optical sensors and wavelength-multiplexed multifunctional optical devices. Some preliminary data are also presented in this chapter. Chapter 6 uses some materials from the following publications:

- Safiabadi Tali SA, Zhou W. Conductive Gap-Plasmon Nanocavity. In Laser Science 2018 Sep 16 (pp. JTu2A-58). Optical Society of America.
- Qian Y, Safiabadi Tali SA (co-first author), Mejia E, Zhou W. Fixed-size double-resonant nanolaminate plasmonic nanoantennas with wide spectral tunability and high optical cross-sections. *Optik*. 2021 Mar 1;230:166332.

Acknowledgements

This chapter uses some materials from the review paper “Multiresonant plasmonics with spatial mode overlap: overview and outlook” by Seied Ali Safiabadi Tali, and Wei Zhou, published in journal of Nanophotonics 8.7 (2019): 1199-1225 and has been reproduced here with the permission of the copyright holder. The work was supported by AFOSR Young Investigator Award FA9550-18-1-0328 and NIST grant 70NANB18H20. Also, the authors thank Yuming Zhao and Yizhou Qian for their help in preparing the figures and proofreading the material in the review paper.

Chapter 2: Fundamental Concepts and Design Strategies

(This chapter is adopted from “Multiresonant plasmonics with spatial mode overlap: overview and outlook” by Seied Ali Safiabadi Tali, and Wei Zhou, published in journal of Nanophotonics 8.7 (2019): 1199-1225 and has been reproduced here with the permission of the copyright holder.)

Abstract

Plasmonic nanostructures can enhance the optical processes at the nanoscale for various applications in energy harvesting, optical communications, and biological sensing. Conventional plasmonic devices are optimized for operation in a single wavelength band, which is sufficient for applications such as surface-enhanced Raman spectroscopy and refractive index sensing. Nevertheless, as discussed in the previous chapter, single-resonant systems are not suitable for active nanophotonics applications that either prefer multiresonant enhancement of non-linear processes in a quantum system or require wavelength-multiplexed operations at nanoscale. Such applications instead require multiresonant plasmonic systems with spatial mode overlap that can enhance the light-matter interactions at the same locations but in multiple wavelength bands. This chapter summarizes the recent advances in the study of the multiresonant plasmonic systems with spatial mode overlap and extensively explores their architecture and design strategies. The chapter first briefly reviews the fundamentals of plasmonics, including the different types of modes and the mode hybridization concept, which is the key design strategy in multiresonant plasmonics. The chapter then proceeds with categorizing the multiresonant plasmonic systems according to the localization characteristics of their elementary modes before hybridization. Furthermore, various architectures in each category are examined and compared in terms of fabrication and performance.

2.1. Introduction

Plasmonic devices can enhance the light-matter interactions at nanoscale for ultra-sensitive of chemical and biological sensing⁸⁻¹⁰, light generation and detection in nanoscale optoelectronics and nonlinear optics devices²⁻⁷, photothermal cell manipulation¹¹⁻¹⁵, and hot carrier generation for photocatalytic processes¹⁶⁻¹⁹. In some of these applications, such as plasmonic-enhanced fluorescence probes and surface-enhanced Raman spectroscopy, single-resonant enhancement of

light-matter interactions in one wavelength range is sufficient. However, effective trapping and nano-localization of different colored photons simultaneously at the same position is far more efficient in applications based on nonlinear multiphoton processes^{5, 92-94} or wavelength-multiplexed operations²²⁻²⁴. Realizing this capability requires the system plasmonic modes to have spatially overlapped electromagnetic fields while resonant at distinct wavelengths.

This chapter comprehensively examines the operation theory and design strategies of the “multiresonant plasmonic systems with spatial mode overlap”. The chapter first summarizes the basic concepts related to different types of localized and delocalized plasmonic modes, the mode hybridization theory^{95, 96}, and geometrical symmetry effects. It is then shown that achieving multiresonant plasmonics with spatial mode overlap requires composite plasmonic systems with closely-assembled building blocks⁹⁷, such that their elementary plasmonic modes can optically couple and generate new hybrid modes with distinct resonant wavelengths but spatially-overlapped fields. Based on the locality of the building blocks’ elementary modes, multiresonant plasmonic systems with spatial mode overlap are then classified into three categories that work by exploiting the optical coupling between (1) two or more localized modes, (2) localized and delocalized modes, and (3) two or more delocalized modes. Each category is further categorized according to the geometrical properties of its building blocks. Due to small footprints and volumetric compactness, multiresonant systems based on the coupled localized modes hold a great potential for high-resolution biosensing applications and hence, constitute the most studied category. Nevertheless, multiresonant plasmonic systems using the delocalized-localized mode hybridization are advantageous in offering a higher number of design parameters and degrees of freedom. Accordingly, these systems are preferred when 3D device miniaturization is not a requirement.

2.2. Fundamental concepts

In this section, we briefly review the physics governing elementary surface plasmon modes in different types of plasmonic building blocks and their optical interactions. We begin by a short explanation of elementary plasmonic modes in the several types of basic building blocks, including propagating surface plasmon polariton (SPP) modes at extended continuous metal-dielectric interfaces, localized surface plasmon (LSP) modes at confined nanoscale metal-dielectric interfaces, and delocalized Bloch plasmonic modes (or lattice plasmon modes) in periodic metal-

dielectric nanostructures. Then, we give a brief discussion of plasmonic mode hybridization. Finally, we explain the effects of the geometrical symmetry on optical properties of plasmonic systems.

2.2.1 Propagating SPP modes at continuous metal-dielectric interface

Surface plasmon polaritons (SPPs) are evanescent electromagnetic surface waves propagating at an extended continuous metal-dielectric interface where the real part of the dielectric function changes sign⁹⁸. The simplest structure that can sustain SPP waves is a single and flat interface between a lossless dielectric half-space and a metal half-space (Figure 2.1A). In such case, only transverse magnetic (TM) SPPs are allowed⁸⁹ and the SPP dispersion relation is as follows (Eq. 1):

$$\beta = k_0 \sqrt{\frac{\varepsilon_d \varepsilon_m}{\varepsilon_d + \varepsilon_m}}, \quad (1)$$

In which, β is the SPP wavenumber, k_0 is the free space wavenumber, ε_d is the dielectric relative permittivity, and ε_m is the metal dielectric function. As revealed by Equation 1, SPPs carry larger momentums than free-space photons and thus can achieve the subwavelength confinement of optical fields beyond the diffraction limit. However, for optical excitation of SPPs, we need to bridge this momentum mismatch using methods such as prism coupling, grating coupling, and near field coupling by nanostructured geometries^{89, 99}. Since there are both radiative and non-radiative losses for SPPs propagating at the metal-dielectric interface, the wavevector of SPP modes is a complex number. While the radiative losses of SPPs are mainly associated with the scattering by nanoscale surface roughness, their non-radiative losses mostly originate from the intraband and the interband damping of the SPP-excited conduction band electrons in the metal. In general, the dispersion properties of SPPs can be engineered either by choosing different metal and dielectric materials (and thus their optical constants), or by the optical hybridization with other plasmonic modes in the neighboring building blocks.

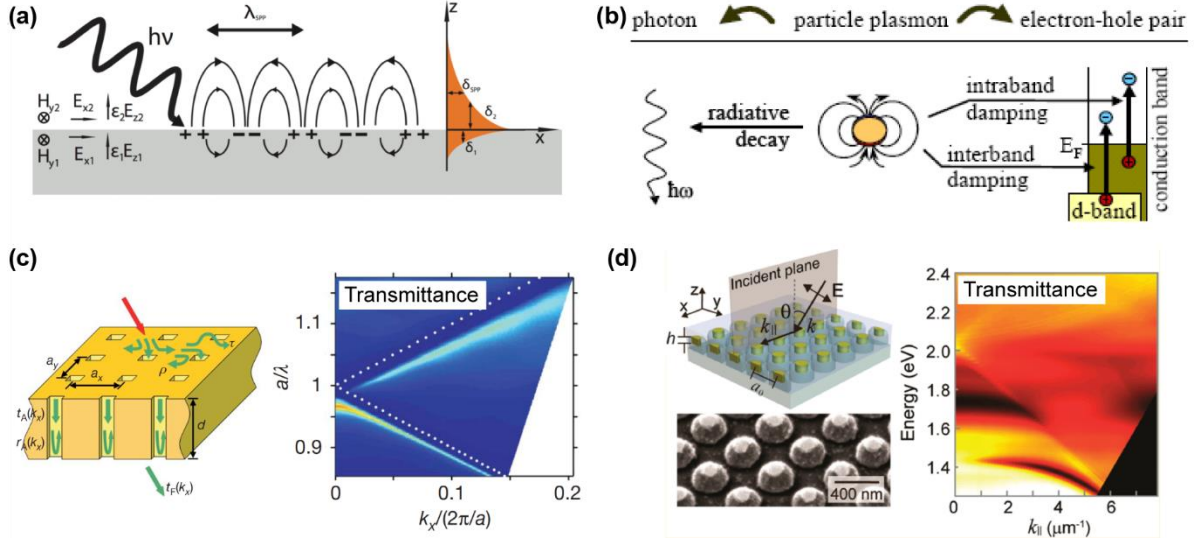


Figure 2.1. Schematic illustrations of plasmonic modes in different types of plasmonic building blocks. (a) Surface plasmon polariton (SSP) modes at the continuous metal-dielectric interfaces. (b) Localized surface plasmon (LSP) modes in individual metal nanostructures¹⁰⁰. (c) Delocalized Bloch-SPP modes in the metal thin film perforated with periodic nanohole arrays¹⁰¹. (d) Delocalized out-of-plane lattice plasmon modes in Au nanoparticle arrays¹⁰².

2.2.2. LSP modes in individual metal nanostructures

Localized surface plasmons (LSPs) are associated with the collective oscillations of conduction band electrons in coupling with surface EM fields in confined nanoscale metal-dielectric interfaces (Figure 2.1(b)).^{100, 103} This confinement, which can be three-dimensional as in nanoparticles or nanovoids, or could be two-dimensional in the case of nanowires or nanogrooves, causes charge accumulations of opposite signs on metallic surfaces. This leads to formation of amplified electric fields in the nanostructure near-field zone. Similarly, electric currents form inside the nanostructure which cause magnetic field enhancement. Due to more concentrated charge accumulations, electric and magnetic field enhancements are much larger for LSPs compared to SPPs. Intuitively, LSPs can be considered as standing wave SPP modes at metal-dielectric interfaces in confined nanostructures, and therefore it is possible for the same metal-dielectric nanostructures to support multiple LSP modes with different (standing wave) orders at different wavelengths in optical wavelength range. However, high-order LSP modes typically have a dark multipolar nature and thus cannot interact with free-space light effectively.^{104, 105} In contrast, the lowest-order LSP mode (in analogy with the ground state in a quantum system) has an electric dipolar nature and thus can effectively interact with the free-space light in both excitation and scattering processes. LSPs can decay through radiative channels (scattering) by conversion to

photons and non-radiative channels (absorption) due to the creation of electron-hole pairs (Figure 2.1(b)).¹⁰⁰ One of the simplest LSP cases, is that of a metallic subwavelength nanosphere⁸⁹ for which, scattering and absorption cross sections are as shown in Eqs. 2 and 3, respectively:

$$C_{sca} = \frac{8\pi}{3} k_0^4 a^6 \left| \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right|^2, \quad (2)$$

$$C_{abs} = 4\pi k_0 a^3 \text{Im} \left[\frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + 2\varepsilon_d} \right], \quad (3)$$

In which, k_0 is the free space wavenumber, a is the sphere radius, ε_d is the dielectric relative permittivity, and ε_m is the metal dielectric function. According to these equations it is seen that while radiative decay is the major loss mechanism for LSPs in larger nanoparticles, nonradiative decay dominates for smaller nanoparticles. By tailoring the geometries (e.g., size and shape), materials at nanoscale metal-dielectric interface, and optical interactions with other plasmonic modes, it is possible to control both far field and near field characteristics of LSPs.

2.2.3. Delocalized Bloch plasmonic modes in periodic metal-dielectric nanostructures

Periodic dielectric structures called photonic crystals can support Bloch photonic modes, which can be considered as the electromagnetic analogue of Bloch electron waves in the periodic atomic crystals¹⁰⁶. Similarly, periodic metal-dielectric nanostructures can support Bloch plasmonic modes delocalized over the whole lattice system under the Bloch boundary condition. Compared to Bloch photonic modes in a dielectric system, Bloch plasmonic modes can induce much higher local optical field enhancement factors as well as larger optical losses as a result of the collective coupling between surface EM waves in the dielectric medium and surface charge density waves in the metal nanostructures¹⁰⁷. Based on the Bloch theorem¹⁰⁶, the electric and Magnetic field of a Bloch plasmonic mode can be expressed in the form of $E/H_k(r) = e^{i\vec{k}\cdot\vec{r}} u_{\vec{k}}(r)$, where $\vec{k}$ is the Bloch wavevector and $u_{\vec{k}}(r)$ is the periodic envelope function with the periodicity of the lattice constant. Analogous to Bloch photonic modes in photonic crystals, Bloch plasmonic modes in periodic metal-dielectric nanostructures can exhibit dispersive band structures that determine the dependence of its mode resonant energy on its wavevector (momentum)¹⁰⁸ (Figure 2.1(c-d)). Therefore, the optical properties of periodic metal-dielectric nanostructures, which can support not only localized plasmonic modes but also delocalized Bloch plasmonic modes, can be very different from their individual unit cells, which only support localized plasmonic modes.

Periodic metal-dielectric nanostructures can be constructed in a large variety of designs with many degrees of freedom in choosing geometry and material parameters. However, depending on geometric continuity of the metal-dielectric interface across the boundary of unit cells, there are two basic types of periodic metal-dielectric nanostructures: (1) periodically modulated continuous metal surfaces, and (2) periodic arrays of discretized metal nanostructures.

Periodically modulated continuous metal surfaces, such as 1D/2D opaque metal gratings, and metal thin films perforated with periodic arrays of nanoholes (Figure 2.1(c)), can support so-called SPP-Bloch modes at the continuous metal-dielectric interface. By adding the grating momentum to bridge the momentum mismatch between photons and SPP-Bloch modes, the excitation condition of SPP-Bloch modes in a periodic structure can be described by the Bragg coupling equation: $\vec{k}_{||} + \vec{G} = \vec{k}$, where $\vec{G}$ is a reciprocal lattice vector, and $\vec{k}_{||}$ is the in-plane wave vector of the incident light¹⁰⁸. In the past two decades, numerous experimental and theoretical studies on the optical properties of the periodic nanohole arrays in the opaque metal film have revealed that the excitation of Bloch-SPP modes on both sides of the metal film has mediated the extraordinary optical transmission process observed in such system^{101, 108, 109}.

Unlike periodically modulated continuous metal surfaces, periodic arrays of discretized metal nanostructures with a large dielectric spacing, such as 1D arrays of metal nanowires, and 2D arrays of metal nanoparticles (Figure 2.1(d)), do not support SPP-Bloch modes due to the large deviation from the continuous metal-dielectric interface boundary conditions of the unit cell. Instead, they can support collective lattice plasmon modes mediated by the diffractive coupling between LSP modes in individual metal nanostructures¹¹⁰. In an intuitive picture, the lattice plasmon modes in periodic metal nanoparticle array can be induced when the grating order is changed from radiative to evanescent so that the optical energy scattered by one nanoparticle can be collected by neighboring nanoparticles as collective lattice plasmons instead of decaying as free-space light¹¹¹⁻¹¹³. Coupled dipole theory has predicted that strongly coupled nanoparticles in one-dimensional arrays can produce extremely narrow lattice plasmon resonances by suppressing radiative loss¹¹⁴. Experiments have reported that two polarization types of lattice plasmon resonances can exist in two-dimensional arrays of gold and silver nanoparticles: (1) the in-plane lattice plasmon modes mediated by in-plane dipolar interactions between unit cells¹¹⁵⁻¹¹⁸, and (2) the out-of-plane lattice plasmon modes mediated by out-of-plane dipolar interactions between unit cells^{102, 113}. From the

framework of Bloch theorem, lattice plasmon modes can be considered as a type of surface Bloch mode composed of many Bloch harmonics in periodic arrays of discretized metal nanostructures, and also can exist in transverse electric (TE) polarization mode mediated by in-plane dipolar interactions as well as transverse magnetic (TM) polarization mode mediated by out-of-plane dipolar interactions. A recent study has shown that out-of-plane lattice plasmon modes in 2D Au nanoparticle arrays exhibit dispersive quality factors associated with the highly dispersive nature of such TM Bloch mode ¹⁰². As the dispersion curve of the out-of-plane lattice plasmon modes evolves from a stationary state to a propagating state, the nonradiative loss decreases because of weak local field confinement, whereas the radiative loss increases because of strong coupling to the leaky zero-order Bloch harmonic component ¹⁰².

2.2.4. Mode hybridization

The previous sections have introduced SPPs, LSPs, and Bloch lattice plasmons as elementary plasmonic modes supported in different types of building blocks. By putting two plasmonic building blocks very close to each other, their elementary modes with similar resonant energies can exert EM forces and exchange EM energy with each other through very intense near-field EM interactions. In such situation, we call these two elementary plasmonic modes are “coupled” with each other and two new “hybridized” modes form at modified resonant wavelengths which have mutually mixed far-field and near-field optical characteristics. In order to achieve a strong coupling between modes, three conditions need to be satisfied for the participating elementary modes: (1) spectral overlap of mode resonant energies, (2) spatial overlap of mode profiles, and (3) the nonorthogonality between the modes.

If we model the interacting plasmonic modes as mechanical oscillators with attenuation coefficients γ_1 and γ_2 (Figure 2.2(a)), the coupling strength (g) between the two modes can be treated as the constant of spring connecting the two oscillators ¹¹⁹⁻¹²¹. Therefore, the coupling strength between the two plasmonic modes determines the energy exchange rate between them. As illustrated in the phase diagram in Figure 2.2(b), depending on the relative values of the decay constants of each mode (γ_1 and γ_2) with regard to the coupling strength (g), the interaction between the two plasmonic modes can be in the weak coupling regime (when $|g| \ll |\gamma_1|$, or $|\gamma_2|$), or in the strong coupling regime (when $|g| \gg |\gamma_1|$, and $|\gamma_2|$). Some important phenomena in the weak coupling regime include Fano resonance¹¹⁹⁻¹²³ (red region), electromagnetically induced

transparency (EIT)^{121, 124-126} (red region), and Kerker effect^{121, 127-129} (red and white regions). Fano resonance is an asymmetric resonance with a sharp change between a dip and a peak. Microscopically, it arises due to constructive and destructive interference of a discrete mode with a narrow linewidth (such as dark high order modes) with a broad-spectral-line mode (such as an electric dipole mode) or a continuum¹³⁰. In the two coupled oscillator model, Fano resonance happens when only one of the oscillators (the one with the larger damping) is driven¹²¹. EIT can be considered as a special case of Fano resonance in which, the two oscillators have the same resonance frequency¹²¹. Kerker effect is the directional scattering due to interference of the electric and magnetic dipole modes independent responses to the external field in the limit of vanishing direct coupling. In this case, both oscillators are driven and the damping rate ratios can be arbitrary¹²¹. In the strong coupling regime (blue region in Figure 2.2(b)), the energy exchange rate between the two coupled oscillators is much larger than the energy leaking rates, and thus two new hybridized eigenmodes can form with their resonance frequencies shifted away from those of the original uncoupled modes. The modification of eigen-energies, which are associated with the new hybridized eigenmodes of different charge distribution profiles, is called “Rabi splitting” or “Autler-Townes splitting” (Figure 2.2(c))^{121, 126, 131, 132}. As expected, the amount of energy splitting between new hybridized modes strongly depends on the amount of spatial mode overlap between interacting fundamental modes in the plasmonic building blocks¹³¹. So far, several types of numerical and analytical methods have been developed to analyze the plasmon coupling effect^{64, 133-145}. Introduced by Peter Nordlander group as an electromagnetic analog of the molecular orbital hybridization theory^{140, 145}, the method of “plasmon hybridization” can provide an intuitive microscopic picture to treat the plasmonic modes in a composite plasmonic nanostructures as the hybridized modes from the elementary modes in its plasmonic building blocks^{146, 147} (Figure 2.2(c-d)).

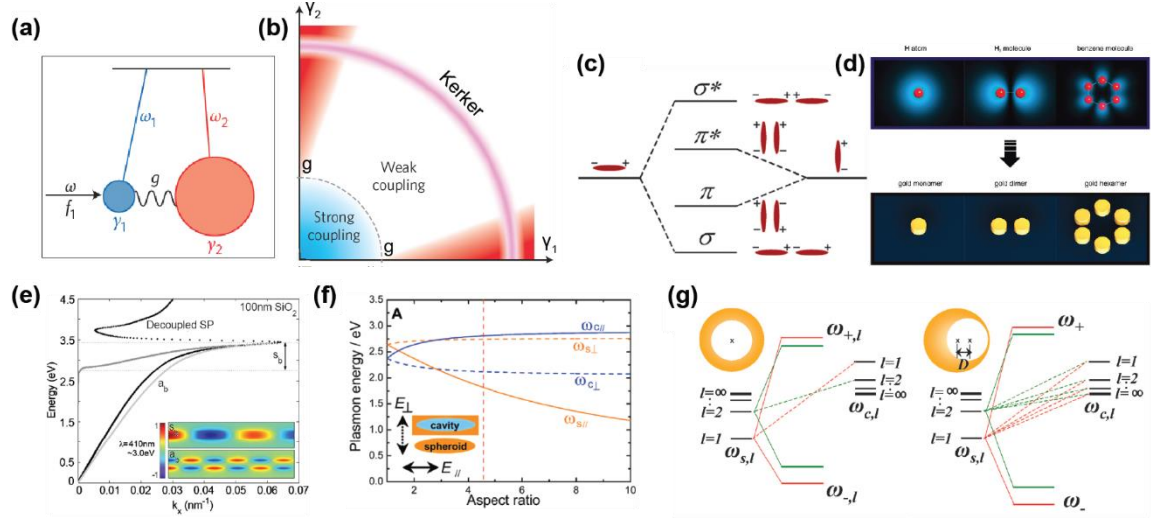


Figure 2.2. (a) Schematic illustration of two coupled oscillators with the coupling strength g and individual damping coefficients γ_1 and γ_2 ¹²¹. (b) Phase diagram showing the separation between the strong coupling regime ($g \gg \gamma_1, \gamma_2$) and the weak coupling regimes ($g \ll \gamma_1, \gamma_2$) ¹²¹. (c) Energy diagram showing the Rabi splitting for two strongly coupled electric dipolar LSP modes in σ and π configurations ¹³¹. (d) Schematic illustration of the analogy between the plasmonic mode hybridization and molecular orbital hybridization ¹⁴⁶. (e) Dispersion curves for the symmetric and anti-symmetric modes of a MIM slot waveguide based on silver and SiO_2 (100 nm thickness) ¹⁴⁸; The inset shows the E_x profiles at $\lambda = 410$ nm. (f) Plasmon energy vs aspect ratio for the solid prolate spheroid and the prolate cavity systems. The solid and dashed lines represent longitudinal and transverse polarizations, respectively ¹⁴⁹. (g) The energy diagrams regarding LSP hybridization in concentric (left) and nonconcentric (right) nanoshells ¹³².

Based on the localization nature of the elementary modes in the building blocks, there are three general scenarios to form new hybridized modes in a composite plasmonic system: (1) from the coupling between two or more localized plasmonic modes; (2) from the coupling between two or more delocalized plasmonic modes; and (3) from the coupling between localized and delocalized plasmonic modes. For example, the elementary SPP modes at the multiple interfaces in metal-insulator-metal (MIM) composite thin films can interact with each other to form multiple hybridized SPP modes, whose dispersion curves will shift away from those of their elementary modes (Figure 2.2(e))^{89, 148, 150-153}. The inset of Figure 2.2(e) depicts the mode profiles of two hybridized SPP modes respectively with symmetric and anti-symmetric distribution of their field components ¹⁴⁸.

2.2.5. Effects of geometrical symmetry

An object can have a symmetry when there is a geometrical transformation under which it is mapped to itself. Also, it is called to have an anti-symmetry if the object only change sign upon a transformation¹⁵⁴. In general, when the geometry of a plasmonic system is symmetric under a

specific geometrical transformation, its modes can be defined such that all of their components (electric field, magnetic field, and charge and current distribution) are either symmetric or antisymmetric with respect to the same transformation¹⁵⁵.

By reducing the geometrical symmetry of a composite plasmonic system that consists of multiple building blocks, it is possible to modify the optical characteristics of supported modes and then improve the multiresonant optical response of the system via following effects: (1) lifting-off the energy degeneracy of the supported modes^{149, 155} (Figure 2.2(f)), (2) increasing the nonorthogonality between the elementary modes for an effective mode hybridization¹³² (Figure 2.2(g)), and (3) increase the radiative decay rates of the supported dark modes for optical excitation under the free-space light illumination¹⁵⁵. The first scenario can happen when the high symmetry in the initial plasmonic system results in some degenerated modes at the same resonant energy with identical field profiles (as well as charge distributions) but with different polarization directions. The second scenario can happen when some elementary modes in the building blocks are initially orthogonal to each other and thus cannot interact with each other despite having spatial and spectral overlap. The last scenario can occur when the plasmonic mode initially have an opposite symmetry of fields with the incident free-space light.

2.3. How to build multiresonant plasmonic systems with spatial mode overlap?

Based on the above discussions, we can generate several guidelines for the design and creation of a composite plasmonic system that can support multiple hybridized plasmonic modes with spatial mode overlap. First, the composite system should be carefully designed using building blocks that support elementary modes with similar resonant energies to have the required spectral mode overlap for a further effective mode hybridization. Second, the building blocks of the composite plasmonic system should be closely packed to each other so that the elementary modes can spatially overlap and hybridize. For non-orthogonal modes, the higher this spatial mode overlap is, the higher the hybridization strength will be. Third, the symmetry of the composite plasmonic system can be reduced in order to lift-off the energy degeneracy of supported modes, and allow a higher nonorthogonality between elementary modes for their effective hybridization. Finally, the symmetry and the orientation arrangement between the composite plasmonic system and incident free-space light should be carefully considered so that the supported modes in the system are not so dark to prevent an effective interaction with the free-space light. This can be done either by

making their net electric or magnetic dipole moments non-zero (via non-symmetric geometry design for high order modes) to induce an electric/magnetic field component in the direction of their net electric/magnetic dipole, by a near-field coupling with a bright plasmonic mode, or by introducing the phase retardation. In this section, we review how to achieve multiresonant plasmonic systems through the optical coupling between elementary modes in their plasmonic building blocks. By considering the localization nature of the elementary modes before hybridization, we can broadly categorize into three basic types of multiresonant plasmonic systems based on the optical coupling between: (1) two or more localized modes, (2) localized and delocalized modes, and (3) two or more delocalized modes. More complex designs by combining two or all of these strategies is also possible.

2.3.1. Coupling between two or more localized plasmonic modes

In multiresonant plasmonic systems based on the optical coupling between two or more localized modes, the building blocks are closely located metal nanostructures that support LSPs as elementary modes for mode hybridization. According to the arrangement of the nanoparticle building blocks, the multiresonant systems using the localized-localized mode coupling strategy can be classified into three sub-groups: (1) in-plane composite nanostructures, (2) core-shell composite nanostructures, and (3) out-of-plane composite nanostructures.

In-plane composite nanostructures

In-plane composite nanostructures consist of metallic nanoparticles or nanovoids (continuous void pieces carved in metallic films) as the plasmonic building blocks in a planar arrangement close to each other. In-plane composite nanostructures can be classified in terms of the number of the nanoparticles or nanovoids that form them. A structure which is composed of “n” nanoparticles (or nanovoids) is called a n-mer (usually read in the Greek system) nanostructure. In this regard, these structures are also generally called “metallic oligomer clusters”. Several types of in-plane composite plasmonic nanostructures with various number, shape and arrangement of the nanoparticles have so far been reported in the literature. Monomers are the simplest type of in-plane nanostructures. They consist of only one metallic nanoparticle (or nanovoid) which can support several plasmonic modes depending on their geometric symmetry. In more complex oligomers (dimer and above), the LSP modes related to adjacent nanoparticles (or nanovoids) can hybridize with each other through near-field optical interactions. Properties of the hybridized modes depend on the nature of the individual building block modes, the number of nanoparticles

or nanovoids, and their arrangement with respect to each other. In-plane composite plasmonic systems typically can support multiple in-plane modes with a net in-plane polarization. Since the current distributions related to in-plane modes are also in-plane, their associated magnetic multipole moments are out-of-plane and typically cannot be excited by the in-plane magnetic field component of the normally incident light. Moreover, since there is no phase retardation between light and different in-plane building blocks under the normal light excitation condition, these in-plane modes can be excited by the electric field only if they have a non-zero net electric dipole moment. Without an optimized design to reduce the geometrical symmetry of the in-plane oligomer systems, in-plane multipolar high-order modes can be very dark and thus can hardly be observed from the far-field optical measurements¹⁵⁵⁻¹⁶⁹. Here, we first examine monomer, dimer, and trimer cases, and then, discuss higher order oligomer systems.

There exist several examples in the literature in which, monomer systems are reported to display multiresonant behaviors¹⁷⁰⁻¹⁷³. Yet, because of the following reasons, they are not generally considered to be appropriate for the tasks that require a multiresonant response under the free-space light excitation. First, symmetries in the system can make most high-order multipolar modes very dark under the normal incident light. Second, resonant wavelengths of individual modes cannot be tuned independently by geometric engineering due to their standing wave-like nature. Finally, without a tight optical field confinement in the metal-insulator-metal (MIM) nanogaps, the field enhancement of modes in plasmonic monomer nanostructures is usually much smaller compared to plasmon modes in MIM nanogaps.

When two plasmonic monomers get close to each other, they can form plasmonic dimer nanostructures. By introducing MIM nanogaps between two monomers, new hybridized bonding mode can be supported as a type of gap plasmon modes with very large enhancements of both electric fields (also sometimes magnetic fields) inside the MIM nanogap^{28, 145, 160-164, 174-186}. Upon proper design, dimer structures can achieve multiresonant response with spatial mode overlap^{28, 163, 164, 175-179, 181, 182, 184-186}. Figure 2.3(a) illustrates an example of such systems. This non-symmetric heterodimer consists of a V-shaped gold antenna with an arm length of 180 nm coupled to a 125 nm nanorod-shaped gold nanoantenna through a gap of ~17 nm. The width and thickness of the V-shaped nanoantenna and the nanorod are 30 nm and 40 nm, respectively²⁸.

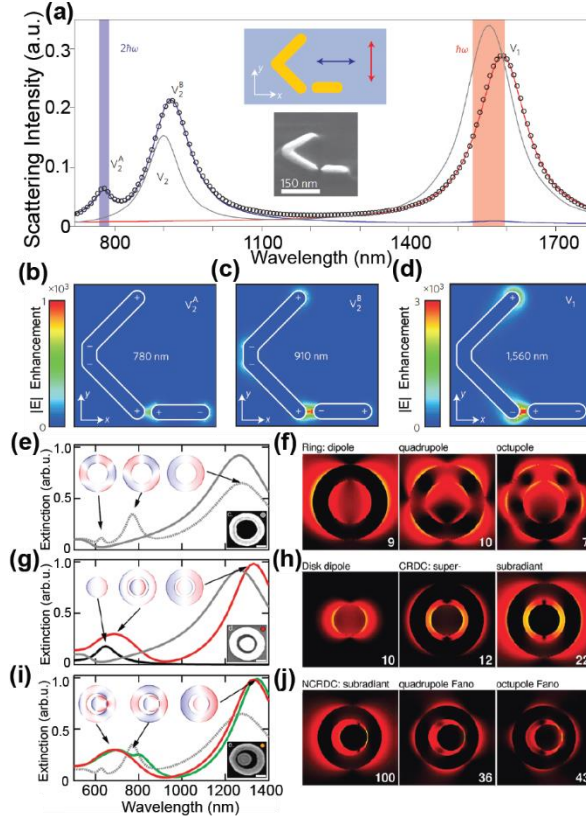


Figure 2.3. Two examples of multiresonant plasmonic systems based on the optical coupling between localized plasmonic modes in in-plane dimer nanostructures. (a) A plasmonic dimer structure and its far-field scattering spectra ²⁸; (b-d) The near-field distribution maps of electric field intensity enhancement at its three different resonant wavelengths ²⁸. (e, g, i) Charge plots and extinction cross sections for cavities formed by different combinations of a disk with $D_{\text{disk}}=150$ nm and a ring with $D_{\text{out}}=350$ nm and $D_{\text{in}}=350$ nm. Legends: ring (solid dark gray), disk (black), symmetric ring/disk (red), symmetry-broken ring/disk (green) at normal incidence, and ring (dotted light gray) at grazing incidence ¹⁶⁴; (f, h, j) Logarithmic electric field enhancement colormaps at the indicated resonances in parts e, g and i ¹⁶⁴. The range for each figure is from 1 up to the maximum enhancement (white number).

As can be seen from the scattering spectra, the composite dimmer plasmonic nanoantenna can support three major plasmonic modes at 780 nm (V_2^A), 910 nm (V_2^B) and 1560 nm (V_1); modes V_2^A and V_2^B are respectively the antibonding and the bonding modes resulted from the first-order longitudinal mode of the nanorod hybridized with the x-polarized electric dipole mode of the V-shaped nanoantenna. Also, V_1 resonance is almost the same as the fundamental y-polarized electric dipole mode of the V-shaped nanoantenna coupled weakly to the nanorod electric dipole mode. As shown in Figure 2.3(b-d), all these three modes correspond to an electric field enhancement in the gap ensuring their spatial overlap.

An important subtype of plasmonic dimer nanostructures is core-shell ring-disk nanostructure. Plasmonic modes of a cylindrical metallic ring (shell) can be regarded as a result of hybridization between the plasmonic modes of a metallic cylinder and those of a metallic cylindrical void¹⁷⁴. Yet, not every two modes can hybridize with each other. Due to the selection rule imposed by the system circular symmetry, only the modes which have the same multipolar order are nonorthogonal and can hybridize with each other^{164, 177}. Also, thickness of the shell is the main factor determining the strength of hybridization such that thinner shells lead to stronger hybridizations. Please note that unlike split-ring resonators, ring systems do not support any magnetic plasmonic mode. Figure 2.3(e) shows the extinction cross section spectra of a gold ring with $D_{\text{out}} = 350$ nm, $D_{\text{in}} = 200$ nm and thickness of 50 nm (SEM image is shown in the inset)¹⁶⁴. It can be seen that while the ring shows a series of multipolar (dipole, quadrupole and octupole) modes under the oblique incidence (dotted light gray curve), only the dipole mode has been excited for the case of the normal incidence illumination (solid dark gray curve). The reason is that due to symmetry effect, quadrupole and octupole modes are not allowed to be excited for this case. The corresponding charge distributions for the multipolar modes are shown in the inset. Electric field amplitude enhancements corresponding to each of these modes for the oblique incidence case is shown in Figure 2.3(f). It is seen that for all three modes, we get a small electric field enhancement near the outer and inner walls of the ring. This reveals that, with this illumination condition, the ring system acts as a multiresonant system with a partial spatial mode overlap. On the other hand, it does not show a multiresonant behavior under the normal incidence illumination.

Electric field enhancement factor of the ring system can be increased by putting a disk at its center (Figure 2.3(g)). Here, the disk diameter is chosen to be $D_{\text{disk}} = 150$ nm (SEM is shown in the inset). Also, the black, the grey and the red curves represent the disk, the ring and the ring/disk systems extinction spectra under normal illumination, respectively. In such case, the ring and the disk plasmonic modes hybridize with each other. Again, because of circular symmetry, only the modes with the same multipolar order can hybridize. Specifically, the electric dipole mode of the disk (shown in the inset) off-resonantly hybridizes with the bonding and antibonding electric dipolar modes of the ring giving rise to a superradiant (high-energy) hybrid mode and a subradiant (low-energy) one for which, the charge distributions are shown in Figure 2.3(g) inset. Figure 2.3(h) depicts the electric field amplitude enhancements for the disk electric dipole mode and the two concentric ring/disk system modes. It is seen that the maximum enhancement is 12 and 22 for the

ring/disk superradiant and subradiant modes, respectively. These values are higher compared to the maximum enhancements in both of the single ring and single disk systems electric dipole modes which have the enhancement factors of 9 and 10, respectively. Also, it is evident that both modes give the maximum enhancements inside the gap ensuring that the ring/disk system modes spatially overlap.

Performance of the ring/disk system can be further improved by breaking the structure symmetry. Such improvement is achieved through making possible the excitation of high order dark modes through Fano interference with superradiant modes. Due to having long decay lifetimes, these dark modes can store larger electromagnetic energy and thus, usually correspond to large field enhancements. A demonstrative example of this argument can be found in Figure 2.3(i). Here, the green curve represents the extinction cross section of a similar ring/disk system as Figure 2.3(g) but with its symmetry broken by offsetting the ring and disk centers (gap of 8 nm). In addition, the red and the dotted grey curves correspond to the concentric ring/disk under normal incidence and the ring under oblique incidence angle, respectively. Comparing these curves clearly reflects excitation of the ring high order modes for the non-concentric system. In this case, unlike the concentric system, the selection rules allow hybridization of the modes with a different multipolar order leading to each of the ring modes interacting with all of the disk modes. Modes in each of ring and disk systems can also indirectly interact with the modes in the same system. Accordingly, dark high order modes of the ring off-resonantly couple to the superradiant mode due to which, they can be excited in this geometry. Interference of these modes with the superradiant mode is the reason for the existence of the observed Fano resonances in the non-concentric ring/disk system extinction spectra in Figure 2.3(i). Charge distributions related to each of the non-symmetric system modes are shown in the Figure 2.3(i) inset. It is notable that at Fano interference wavelengths, the charge distribution in the disk is not purely dipolar anymore and instead, it resembles a quadrupolar charge distribution. Such deviation is due to interference of high order disk modes which get excited through coupling to the superradiant mode. Figure 2.3(k) depicts the electric field enhancement colormaps related to each of the non-concentric ring/disk system modes. It is obvious that while the spatial mode overlap is maintained, the enhancements are significantly larger with the maximum of 100, 36 and 43 for subradiant, quadrupole Fano and octupole Fano resonances, respectively. Thus, the system performance as a multiresonant system with spatial mode overlap has significantly improved.

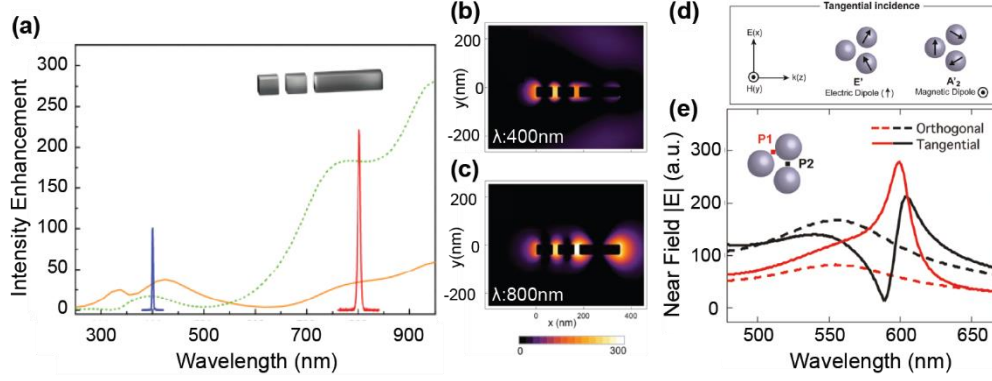


Figure 2.4. Two examples of multiresonant plasmonic systems based on the optical coupling between localized plasmonic modes in in-plane trimer nanostructures. (a) Schematic illustration and the spectra of near-field electric field intensity enhancement at two nanogaps in an asymmetric trimer with a linear arrangement¹⁸⁷; (b-c) The near-field distribution maps of electric field intensity enhancement at (b) $\lambda = 400$ nm and (c) $\lambda = 800$ nm¹⁸⁷. (d) Schematic illustration and (e) the spectra of electric field at two nanogaps in a trimer system with a circular arrangement under two different polarization conditions of incident light¹⁵⁹.

Trimers form when three nanoparticles are arranged in the proximity of each other. In this case, the three nanoparticles can be arranged in a linear style or a circular style. Figure 2.4(a) shows a linear heterotrimer system composed of three interacting nanorod-shaped Aluminum nanoantennas with the respective arm lengths of 50, 50 and 170 nm, and the same gap separations of 20 nm¹⁸⁷. The width and height of the nanoantennas are both 40 nm. In Figure 2.4(a), the dashed green curve represents the enhancement factors of electric field intensity at the center of the right gap and solid orange line shows that of the left gap. From these curves, it is clear that we have multiple resonances in the field enhancement inside each of the gaps indicating that the system has spatially overlapped modes. This is also evident in the electric field intensity colormaps of Figure 2.4(b-c) which correspond to $\lambda = 400$ nm and $\lambda = 800$ nm, respectively. The main reasons for the system having multiple resonances are equal size of the two gaps and their proximity (due to rather small arm length of the middle nanoantenna) which allow their corresponding modes to interact and hybridize with each other. Equal size causes the two gap modes to have a high overlap in the spectral domain. Also, spatial proximity causes them to have a high overlap in the spatial domain. Please note that in this example, if the left nanorod has the same length as the right one, the structure will become centrosymmetric. In such centrosymmetric condition, high order modes can become very dark and the system will lose its multiresonant behavior. This is the case that happens for the linear trimer structure reported by Wang et al¹⁸⁸. In this system, the antibonding magnetic mode does not get excited because it has a zero net electric dipole moment.

In circular trimers, when the electric dipole modes in individual nanoparticles interact in a bonding manner, they can collectively support an oscillating loop current. This causes their fundamental plasmonic mode to have a non-zero magnetic dipole moment. If the nanoparticles (or nanovoids) have similar geometries and also, the system is equilateral, the system will become centrosymmetric as a result of which, net electric dipole moment of this mode reduces to zero and it becomes purely magnetic. Thus, it cannot be excited by the normal incident light^{155, 159}. However, if the light illumination is off-normal it can be excited by coupling to the out-of-plane magnetic field of the incident light. Also, if the centrosymmetry is broken by violating either of the stated conditions, the mode net electric dipole moment will become non-zero and it can also be excited by normal excitation. Figure 2.4(d) shows a plasmonic trimer system composed of three adjacent nanoparticles in an equilateral arrangement¹⁵⁹. The near field electric field enhancement factor of the system at the designated gap points P_1 and P_2 is shown in Figure 2.4(e). Here, dashed curves are related to the x-polarized normal incidence condition and solid curves are related to the x-polarized tangential light illumination (as in Figure 2.4(d)). Under normal illumination, only the electric dipole mode with E' symmetry character (left schematic in Figure 2.4(d)) gets excited. Accordingly, the field enhancement at both P_1 and P_2 points only shows a single-resonance with a Lorentzian line shape. The enhancement factor is much stronger at P_2 which is inside the electric dipole gap, though. Under tangential illumination, in addition to the electric dipole mode, the magnetic dipole mode with A_2' symmetry character (right schematic in Figure 2.4(d)) can also get excited through coupling to the incident light magnetic field¹⁵⁵. In this case, as shown in Figure 2.4(e), the electric field at the point P_1 gets prevailed by the dominantly large response of the magnetic dipole mode although it still shows a rather large enhancement factor at the electric dipole mode resonance wavelength. However, at the point P_2 , both of the modes have a comparable field strength. Accordingly, the relatively narrow magnetic dipole optical response interferes with the electric dipole broad response to create a Fano-like resonance behavior with two peaks and a transparency window between them. In the tangential illumination case, the plasmonic trimer system is effectively acting as a multiresonant system with spatial mode overlap which can induce resonant nearfield enhancement of electric field over two broad spectra regions at its nanogap positions. It has been demonstrated that through breaking the trimer system symmetry (for example by making it isosceles instead of equilateral), it is possible to make the magnetic dipole mode net

electric dipole moment non-zero and thus, having a multiresonant system with spatial mode overlap even for the normal illumination condition¹⁵⁹.

As the number of nanoparticle or nanovoid building blocks further increase (beyond three) in the plasmonic oligomer system, the number of elementary modes in the building blocks as well as their hybridized modes in the composite oligomer system rapidly grows. Despite a more complicated optical response for these high order oligomers, the physics behind the mode hybridization in them is the same as the simpler dimer or trimer systems. Although these higher order oligomer systems can support more hybridized modes, many of these modes are not optically active under free space light illumination because their high order multipolar nature makes them very dark^{31, 155, 165, 166, 189-191}.

Core-shell composite nanostructures

Core-shell composite plasmonic nanostructures consist of multiple metal-dielectric core and shell layers. Intuitively, they can be considered as the 3D version of the 2D planar ring/disk plasmonic nanostructures. Similar to a planar plasmonic nanoring, plasmonic modes in a spherical metallic nanoshell originate from the hybridization between elementary plasmonic modes in a metallic sphere and a metallic spherical void. Thickness of the shell determines the strength of hybridization such that thinner shell results in stronger hybridization^{140, 145, 192}. As schematically shown in Figure 2.2(g), these hybridizations are governed by a selection rule imposed by the spherical system with a rotational symmetry; only modes with the same multipolar order (l) can hybridize with each other^{132, 140, 192}. While the bonding mode has a large net electric dipole moment and is a bright mode, the antibonding mode has an electric quadrupolar nature. With a sufficiently large shell thickness, the antibonding mode will also have a net electric dipole moment¹³², but this dipole moment will vanish as the shell thickness gets infinitely small¹⁹³. By offsetting the inner shell from the center of the outer shell, we can break the rotational symmetry of the core-shell system and relax the selection rule to allow effective hybridization between the elementary modes in the nanosphere and nanoshells (Figure 2.2(g)). Such a lower-symmetry core-shell system is called a “nanoegg”, which can support a larger number of hybridized modes than its concentric counterpart. In such “nanoeggs”, dark and narrow-linewidth hybrid high order modes can couple to the wideband dipolar modes and thus become bright. Such interaction between dark and bright modes adds several Fano-like resonances to the spectra^{132, 192}. Since many of these hybrid modes cause a field enhancement in the dielectric core, such core-shell plasmonic nanostructures show a

multiresonant optical response with spatially overlapped modes. Another way to reduce the rotational symmetry of core-shell systems is to increase its aspect ratio^{149, 192}. In this case, as illustrated in Figure 2.2(f), the degeneracy between the longitudinal and transverse modes gets lifted and consequently, the number of modes in the system get doubled under transverse and longitudinal polarization directions. Yet, despite apparent increasing of the system resonances, this method of symmetry breaking is not very effective to achieve spatial mode overlap between modes with different polarization directions.

By placing a metallic nanosphere close to a plasmonic nanoshell, we are able to create a heterodimer composite system, where the nanosphere plasmonic modes hybridize with those of the nanoshell. Just like a single nanoshell, rotational symmetry in the system causes the hybridization to be only possible between the modes with the same multipolar order¹⁹⁴. Since we have three interacting surfaces in this case, we get three hybrid modes for each multipolar order. Two of these three modes are the bonding and antibonding modes resulted from the hybridization between the nanosphere mode and the nanoshell bonding mode. Also, the third hybrid mode is the same as the original nanoshell antibonding mode as, due to symmetry effects, it does not hybridize with the nanosphere mode. Accordingly, the number of modes in a sphere-shell system is 3/2 that of a single shell structure. Usually, only the lowest order hybrid modes ($l=1$) are bright and thus, we only get up to three resonances in practice. By breaking the system rotational symmetry, the selection rule for mode hybridization can be relaxed and many dark high order modes can become bright through coupling to the bright and wide dipolar modes. Thus, like the nanoegg case, several Fano-like resonances get added to the system spectra. Since many of these modes can induce a large optical field enhancement in the gap, the heterodimer composite nanostructure can serve as a multiresonant plasmonic system with spatial mode overlap. The second case of two nanoparticle core-shell systems is the concentric nanoshell nanostructure^{140, 145, 192}. Such system can support four hybridized modes per each of the multipolar orders, which come from the interactions between two elementary modes in the inner nanoshell and the other two in outer one. In general, the number of modes in a core-shell system can be increased with the total number of metal-dielectric interfaces in the system. Many of these modes can provide large optical field enhancements in the dielectric gap layers.

Out-of-plane composite nanostructures

So far, we have talked about as the localized-localized coupling strategy based on core-shell and in-plane composite nanostructures to achieve a multiresonant plasmonic response with spatial mode overlap. In this subsection, we will discuss about out-of-plane composite nanostructures as a multiresonant plasmonic system. A common type of out-of-plane composite plasmonic system is based on multilayered metal-insulator-metal (MIM) nanostructures consisting of alternative stacks of metal and dielectric (insulator) layers¹⁹⁵⁻²⁰⁶. Figure 2.5(a) shows the energy diagram for a MIM nanocavity composed of two closely-spaced metallic slabs under the normal incidence light illumination with polarization along the x-axis²⁰⁷⁻²⁰⁹. The hybridization of the elementary electric dipole modes in the individual metallic slabs results in a high-energy antibonding mode with an electric dipole nature, and a low-energy bonding mode with a magnetic dipole (or electric quadrupolar) nature. Figure 2.5(b) shows the simulated scattering and absorption spectra for a single-gap MIM nanocavity. Two major resonances are clear in the far field spectra; the first one is the antibonding electric dipole mode resonance showing a broad peak in the scattering spectra and a very small peak in the absorption spectra around 615 nm, which gets excited by the electric field of the incident light. The second one is the magnetic dipole mode resonance showing narrow peaks in both of the scattering and absorption spectra at the wavelength of $\lambda_{\text{Fund}} = 876$ nm. It is seen that these two modes show a weak Fano-like interference behavior in the scattering spectra. This Fano-like behavior is much stronger if we consider the forward and backward scattering behavior rather than the total one (figure not shown here). The near field colormaps of the electric and magnetic dipole modes in Figure 2.5(c) reveal a significant near-field enhancement of electric fields at the gap edge and magnetic fields at the gap center.

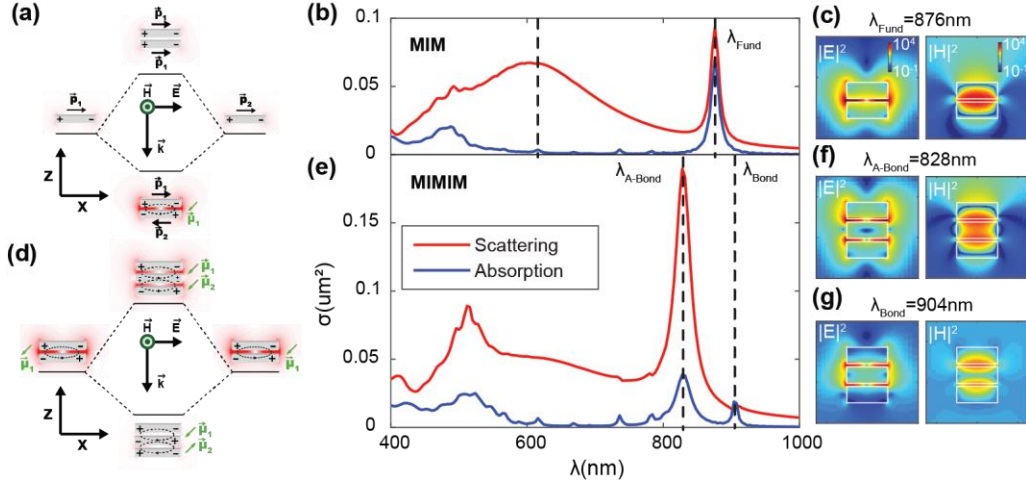


Figure 2.5. Multiresonant plasmonic systems based on the optical coupling between localized plasmonic modes in out-of-plane composite nanostructures^{207, 209}. (a) The energy diagram, (b) the far-field scattering and absorption spectra, and (c) the near-field distribution maps of electric and magnetic field intensities for a MIM structure with a single dielectric gap. (d) The energy diagram, (e) the far-field scattering and absorption spectra, and (f) the near-field distribution maps of electric and magnetic field intensities for a MIMIM structure with two dielectric gaps.

Despite providing large electric and magnetic field enhancements by the magnetic dipole mode, such MIM system cannot serve as a multiresonant system with spatial mode overlap. The reason is that the field enhancements are very weak inside the gap at the electric dipole mode resonance wavelength (Figure 2.5(a)). The solution to this problem is to create another nanocavity above the first one by switching to a three-metal-layer system as shown in Figure 2.5(d). In this way, the elementary magnetic dipole modes in each of the MIM cavities can hybridize with each other to form new bonding and anti-bonding modes. For the bonding mode, the two elementary magnetic dipoles are aligned in the opposite directions, which gives this mode a magnetic quadrupolar nature and makes it very dark as revealed in Figure 2.5(e). For the antibonding mode, the elementary magnetic dipoles are aligned in the same direction, which gives this mode a magnetic dipolar nature and makes it brighter as shown in Figure 2.5(e). Weak Fano-like interference between the electric dipole mode, magnetic dipole mode and magnetic quadrupole mode is also evident in the scattering spectra for this case. Please note that the amount of splitting depends on the strength of magnetic dipoles interaction which can be easily controlled by the middle metal thickness. The two other important parameters which can be used to control the resonances wavelengths are the gaps thicknesses and the metals diameter. Figure 2.5(f-g) show a significant near-field enhancement of both bonding and antibonding modes in nanogaps. These observations prove that

the two gap MIM system has spatially overlapped large field enhancements at two tunable wavelengths.

Since we can control the multiresonant optical response of the out-of-plane composite nanostructures by simply engineering out-of-plane geometric parameters of individual building blocks, such designs provide some unique opportunities compared to conventional in-plane plasmonic engineering approaches²⁰⁴. First, the vertical arrangement of MIM building blocks results in a nanoscale footprint and a nanoscale volume of such multiresonant devices. Second, by sharing the metal layer between neighboring MIM building blocks in the vertical stack, the out-of-plane arrangement can enable efficient transport of heat or charges between neighboring building blocks triggered by light excitation at multiple different wavelengths. Third, it is much easier to control the out-of-plane geometric parameters at nanoscale (i.e., thin-film thicknesses) than to define in-plane geometric features by lithography-based processes. Finally, we can incorporate layers of different functional materials (e.g. phase change materials, luminescent materials, and nonlinear optical materials) in different MIM building blocks in the vertical stack, which opens the opportunities to create multiband multifunctional photonics nanodevices. Appendix A analyzes the out-of-plane plasmonic systems in more detail.

2.3.2. Coupling between localized and delocalized modes

In this section, we will review multiresonant plasmonic systems that support hybridized modes formed by the optical coupling between elementary localized modes and delocalized modes in their building blocks. In general, the localized modes can be LSPs associated with metal nanoparticles, while the delocalized modes can be plasmonic Bloch modes in periodic metal-dielectric nanostructures, surface diffraction modes of the grating structure, or SPP modes at the continuous metal-dielectric interface.

Coupling between LSP modes and plasmonic Bloch modes

Large arrays of periodic metal-dielectric nanostructures can support both LSP modes and delocalized plasmonic Bloch modes²¹⁰⁻²¹⁶. Compared with a periodically nanotextured continuous metal-insulator interface (e.g. metal nanohole arrays, and 1D and 2D metal gratings), arrays of metal-insulator-metal (MIM) multilayered nanostructures can support a richer set of optical properties because of the interplay between LSP modes and plasmonic Bloch modes at different metal-dielectrics interfaces.

Extensive studies have been carried out to understand the optical response of 1D periodic arrays of MIM nanocavities^{210, 212, 214}. Figure 2.6(a) illustrates a 1D array of MIM nanocavities that consist of gold nanowire arrays (periodicity of $d_x = 500 \text{ nm}$) on top of a 20 nm thick silver film with a SiO₂ spacing layer (thickness $L_{sp} = 20 \text{ nm}$) illuminated by a TM plane wave at the normal angle²¹⁰. Absorption spectra (shaded gray area) of the system in part B reveal that the system has two resonances in the wavelength range of interest each of which correspond to a resonance in the transmission spectra (black solid line) with a Fano lineshape. The reason for emergence of these Fano resonances in the transmittance spectra is interference of the plasmonic modes scattering in the backward direction, which correspond to discrete resonances with finite linewidth in the spectral domain, with the normal transmittance through the silver film (dashed curve in Figure 2.6(b)) which can be considered as a continuum. From numerical analysis, it gets revealed that the two plasmonic resonances come from the hybridization between elementary localized modes associated with individual nanowires and delocalized plasmonic Bloch modes at periodically modulated metal-dielectric interface. In particular, the localized mode itself is an electric quadrupole (magnetic dipole) mode because of out-of-phase coupling between the electric dipole modes in the isolated nanowires and their image dipoles in the silver film. As shown in near field enhancement colormaps of the electric and the magnetic fields (Figure 2.6(c)), both modes carry localized and delocalized features of nearfield profiles, indicating their microscopic nature as the hybrid modes from the coupling between localized and delocalized modes. In particular, the localized features of both modes resemble that of the electric quadrupole mode in a MIM nanocavity, for which, maximum electric field enhancements happen at the gap edges and maximum magnetic field enhancement occurs at the gap center. On the other hand, for both modes, the spatial period of field amplitude at metal-dielectric interface is half of the grating period, which reveals their delocalized nature associated with plasmonic Bloch mode with a grating order of ± 1 at the Brillouin zone edges. Since both modes show field enhancements in nanogap regions, such periodic 1D MIM nanostructures can serve as multiresonant plasmonic systems with spatial mode overlap. By altering the nanostructure geometries and the structural periodicity of the system, it is possible to tune and match the resonance wavelengths of elementary localized and delocalized modes to achieve the required spectral mode overlap. By tailoring the SiO₂ spacer layer thicknesses, we can control the coupling strength between elementary localized and delocalized modes, and thus modulate the energy splitting between the two hybridized modes.

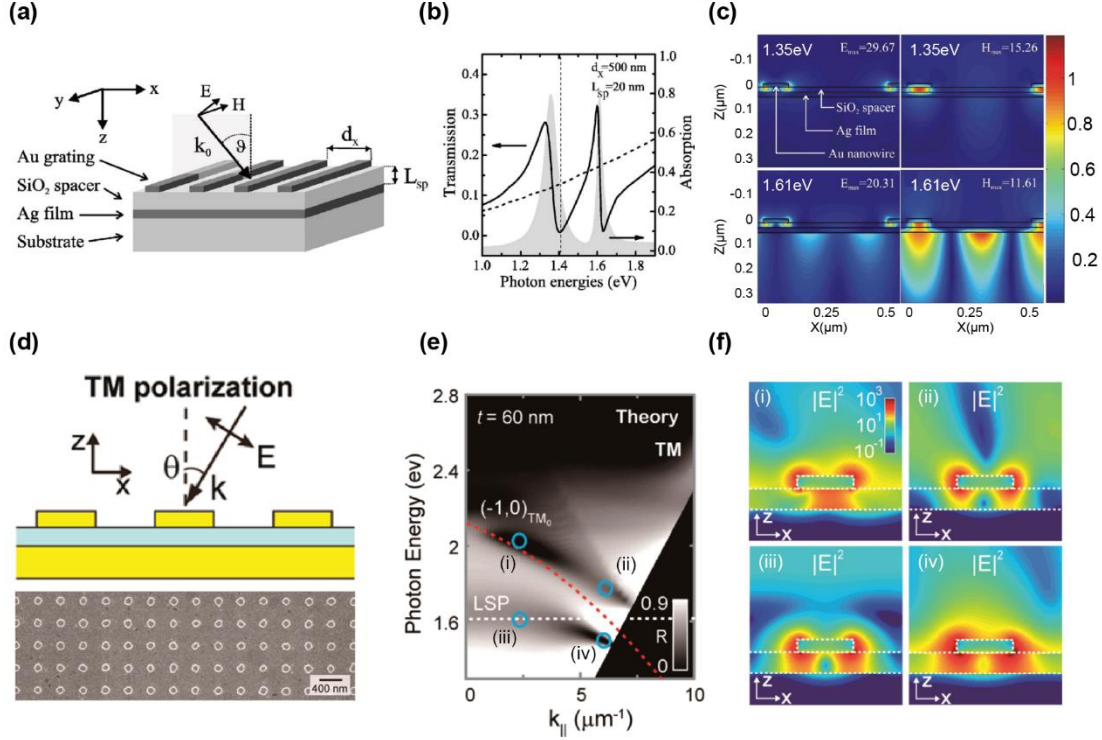


Figure 2.6. Two examples of multiresonant plasmonic systems based on the optical coupling between localized plasmonic modes and delocalized plasmonic modes. (a) Schematic illustration of the 1D periodic arrays of MIM nanocavities consisting of 1D periodic array of gold nanowires on an Ag film separated with a SiO₂ dielectric layer²¹⁰; (b) Calculated transmission (solid lines) and absorption spectra (shaded area) for L_{sp}=20 nm, d_x=500 nm with TM polarized normal light incidence that shows two resonant features associated with two hybridized modes²¹⁰; (c) Electric and magnetic field distribution maps for the two hybridized modes at 1.35 eV and 1.61 eV²¹⁰. (d) Schematic illustration and SEM image of the 2D periodic arrays of MIM nanocavities consisting of a 2D periodic array of gold nanoparticles on an Au film separated with a dielectric layer²¹¹; (e) Dispersion diagram showing the anti-crossing behavior when the LSP mode is strongly coupled with the Bloch plasmonic Mode²¹¹; (f) Electric field distribution maps for the two branches of modes in the region with no coupling (i) and (iii) and with the strong coupling (ii) and (iv)²¹¹.

Despite easy design of 1D periodic MIM nanocavity arrays, their 1D translational symmetry imposes restrictions on the allowed excitation polarizations and directions to achieve multiresonant response. The solution is to use 2D arrays of MIM plasmonic nanocavities that not only avoid such constraints but also provide additional tuning parameters (e.g., lattice symmetry and nanostructure shape) to engineer their optical properties^{211, 213, 215, 216}. Figure 2.6(d) illustrates an example of such systems²¹¹. Here, the substrate is a 100 nm gold film and the spacer layer is a poly methyl methacrylate (PMMA) thin film which has a thickness of $t = 60$ nm and refractive index of 2.16. Also, the top grating layer has the periodicity of $a_0 = 400$ nm, and is made of gold nanodisks with the diameter of $d = 150$ nm and thickness of $h = 40$ nm. By angle-resolved reflectance measurements, the band structure of supported optical modes in the 2D MIM plasmonic

nanocavity array has been experimentally determined, which also shows a good agreement with the calculation results (Figure 2.6(e))²¹¹. It is seen that at each $k_{\parallel}$ value, there is a sharp switch between dark and bright regions which is indicative of Fano-type resonance. The reason for this type of behavior is the interference between the light scattered from the plasmonic modes (which correspond to discrete resonances with finite linewidth) and part of the light reflected from the metal film which can be considered as a continuum in the spectral domain. In addition, the calculated E-k dispersion diagram reveals that the localized plasmon mode and the delocalized Bloch SPP mode can induce an anti-crossing behavior when they are strongly coupled with each other. By comparing the near-field optical properties of the guided and LSP modes from when there was no coupling to when there was relatively strong hybridization in the anti-crossing region (four different points in Figure 2.6(f)), we can see that the hybridization between localized mode and delocalized Bloch mode will result in mixed near-field characters with a very large local field concentration in the gap as well as a 10-fold higher field enhancement surrounding the insulator layer across the entire unit cell²¹¹.

Coupling between LSP modes and diffraction modes

In a plasmonic nanoparticle array system, LSP modes can interact with Diffraction surface waves to increase the local field enhancement. Figure 2.7(a) depicts a system composed of a single bow-tie nanoantenna surrounded by periodic arrays of metallic disks²¹⁷. The bow-tie antenna aims to provide plasmonic enhancement of optical fields in its gap, while the periodic arrays can further diffractively collect light over a large area and funnel it into the bow-tie antenna at specific wavelengths. To this end, the system is designed such that the broad gap plasmon mode (electric dipole mode) in the bow-tie nanoantenna spectrally overlaps with diffraction modes in the periodic nanodisk arrays (compare blue and red curves in Figure 2.7(b)). Furthermore, the nanodisk arrays can be posited in a radial arrangement around the bow-tie antenna to increase the polarization-independent response. Figure 2.7(b) reveals that the local optical field intensity in the gap can be highly resonantly enhanced at different wavelengths. Under the free-space illumination, the central bow-tie antenna broad gap mode can be excited through two pathways: (1) direct excitation by the incident wave (continuum) and (2) indirect excitation by the diffraction wave from the periodic disk arrays (discrete resonances). Depending on whether two excitation pathways constructively or destructively interfere, we can see subsequent peaks and dips (Fano-lineshape) in both far-field absorption spectra of the system and near-field enhancement spectra at the gap region of the bow-

tie antenna (Figure 2.7(b)). By controlling the periodicity of the disk arrays and geometry structure of the bow-tie antenna, we can easily tune the multiresonant response of such system.

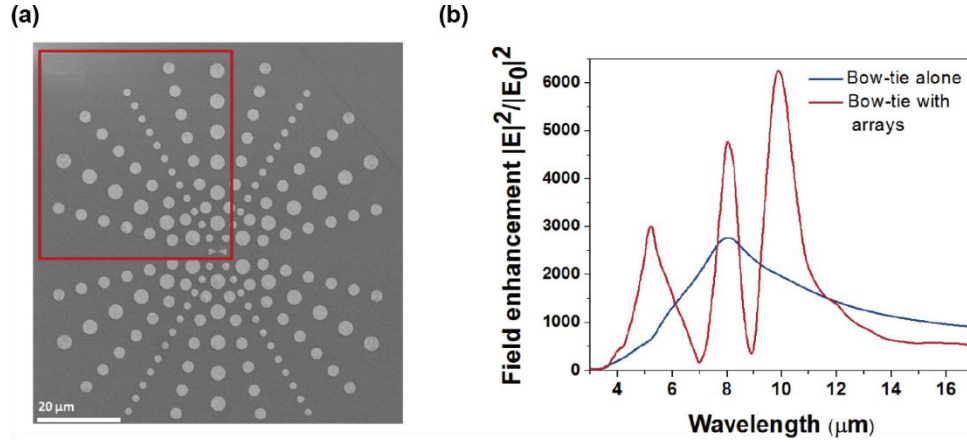


Figure 2.7. A multiresonant plasmonic system based on the optical coupling between LSP modes and grating diffraction modes ²¹⁷. (a) A single bow-tie nanoantenna (two sections of a disk with radius of $2.2 \mu\text{m}$, opening angle of 45° and central gap of 100 nm), surrounded by three periodic arrays (with periodicities of $3.6 \mu\text{m}$, $5.7 \mu\text{m}$ and $7.2 \mu\text{m}$) of metallic disks (with diameters of $1.8 \mu\text{m}$, $2.85 \mu\text{m}$ and $3.6 \mu\text{m}$, respectively). All elements have a thickness of 70 nm and are deposited over a BaF_2 substrate which is transparent in the mid-infrared regime. The bow-tie antenna can couple with the metal particle arrays grating diffraction modes; (b) Simulated electric field intensity enhancement at the center of the bow-tie antenna for the system (red curve) as well as in an isolated state (blue curve).

2.3.3. Coupling between delocalized modes

In this section, we briefly discuss the strategy to build multiresonant plasmonic systems through the optical coupling between delocalized plasmonic modes based on rainbow trapping effect in graded grating structures ²¹⁸⁻²²². Figure 2.8(a-b) represent a width-graded rainbow trapping 1D plasmonic nanograting structure ²²². We can consider each groove unit as a lossy Fabry-Perot-like resonator supporting SPP standing-waves bouncing back and forth between the two silver side walls. Depending on the groove width, the free-space light only at certain wavelengths can satisfy the phase matching condition and effectively excite SPP standing-wave modes in an individual groove resonator.

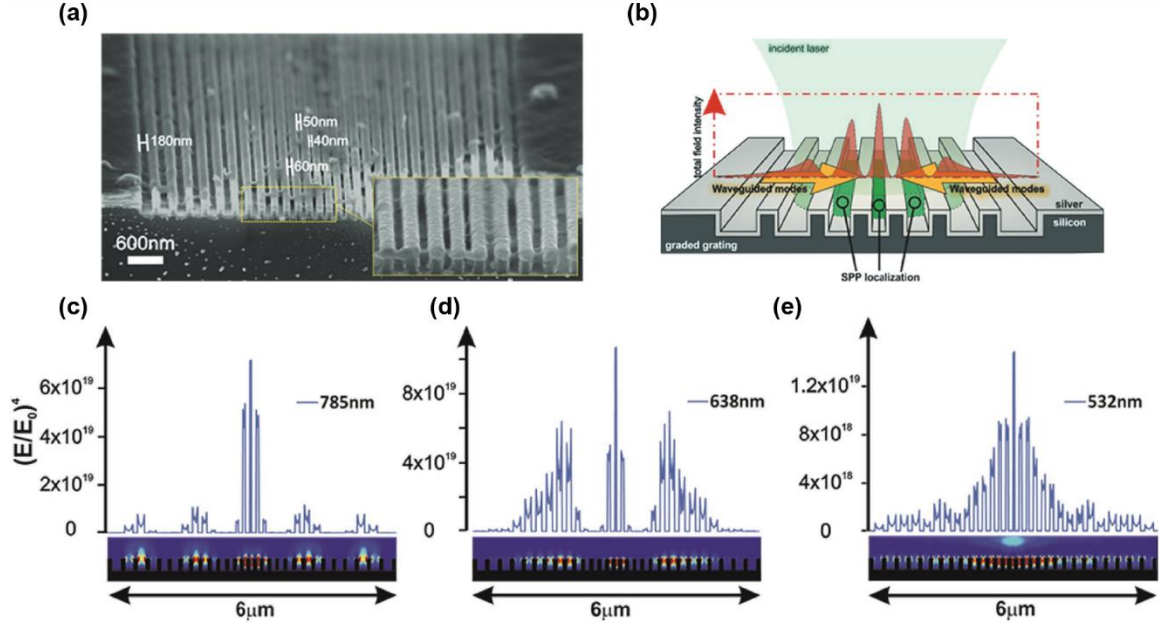


Figure 2.8. A multiresonant plasmonic system based on the optical coupling between delocalized plasmonic modes ²²². (a) The SEM image of a width-graded rainbow trapping 1D plasmonic nanograting consisting of 29 in-plane MIM rectangular grooves separated from each other by 100 nm thick mesas. All grooves have the same depth of 100 nm. However, their widths increase from 40 nm at the center to 180 nm in both ends in increments of 10 nm; (b) The system schematic diagram; The darker green areas inside the central grooves represent the trapped fields as a result of SPP coupling. Also, the two orange arrows indicate the light guiding in the direction of increasing refractive index toward the center; (c-e) Electric field enhancement factor ($|E/E_0|^4$) patterns in the system for TM-polarized laser excitations at three different wavelengths: (c) 785 nm, (d) 638 nm, and (e) 532 nm.

By putting together large arrays of grooves with different widths side by side, the heterogeneous groove resonator array system can support multiple coupled SPP modes and get excited by the free space light under multiple wavelengths. Moreover, the graded design of the groove widths can result in width-dependent gradient of refractive index for coupled SPP modes in the lateral direction across individual grooves in the system, and then cause a build-up of optical fields and energy in the center region with increased refractive index (Figure 2.8(b)). Thus, the graded grating system can act as a multiresonant plasmonic system to induce strong local field enhancement at multiple different wavelengths, as shown in Figure 2.8(c-e).

2.4. Conclusions and outlook

This chapter summarized the important advances in multiresonant plasmonics with spatial mode overlap. First, we reviewed the basics of different types of plasmonic modes, the mode hybridization concept, and the geometrical symmetry effects on the optical properties of plasmonic

systems. Then, we discussed how one can build the multiresonant plasmonic systems with spatial mode overlap. The key strategy to design these systems is to closely assemble the plasmonic building blocks (metallic nanostructures) into a composite system, such that the elementary modes in the constitutive building blocks can strongly couple and form new hybrid modes that spatially overlap but are resonant at different wavelengths. In addition, deep understanding of geometrical symmetry effects on the near-field and far-field optical properties of composite plasmonic structures is required to design them in a way that their modes can effectively interact with the free-space light.

Next, we discussed three categories of multiresonant plasmonic systems based on the optical coupling between: (1) two or more localized modes, (2) localized and delocalized modes, and (3) two or more delocalized modes, with the first and third categories being the most and least common, respectively. According to their geometric arrangement, multiresonant systems based on the coupled localized modes, can be further classified into the three sub-types of in-plane, core-shell, and out-of-plane composite nanostructures. A big advantage of these systems is compactness in footprint and overall volume, making them suitable for high-resolution biosensing applications.

For multiresonant plasmonic systems using the delocalized-localized mode hybridization, localized modes are typically LSPs associated with metal nanoparticles, while the delocalized modes can be the Bloch SPP modes in periodic metal-dielectric nanostructures, or surface diffraction modes of the grating structures. By coming in a large variety of in-plane and out-of-plane designs and offering many degrees of freedom across each unit cell and the lattice, these systems are the optimum candidate in applications not requiring 3D device miniaturization.

Further development in multiresonant plasmonic systems may require more advanced theoretical analysis methods that properly model the interplay between the different channels of optical coupling among the elementary modes, especially when high-order multipolar LSP modes are involved. Compared to the electric dipolar LSP modes, multipolar LSP modes tend to be more sensitive to the effects such as phase retardation, geometric symmetry, and near-field coupling. In addition, a deeper understanding is needed on how polarization and dispersion properties of the delocalized modes affect their coupling to the LSP modes.

Acknowledgements

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Appendix A

A.1. Multi-resonant optical nanocavities by out-of-plane magnetic plasmon hybridization

(This appendix is based on the following publications:

- Safiabadi Tali SA, Zhou W. Magnetic plasmon hybridization in vertically stacked double-gap nanocavities. In 2018 Conference on Lasers and Electro-Optics (CLEO) 2018 May 13 (pp. 1-2). IEEE.
- Safiabadi Tali SA, Zhou W. Multi-resonant optical nanocavities by out-of-plane magnetic plasmon hybridization. In Frontiers in Optics 2018 Sep 16 (pp. JTU3A-53). Optical Society of America.

)

Optical properties of metallic nanostructures are determined by the collective oscillations of their conduction band electrons with respect to the positive ion background, known as surface plasmons²²³. In complex metallic nanostructures, plasmonic modes of the neighboring nanostructures or surfaces interact to form hybrid plasmonic modes, just like the atomic wave functions hybridize to form molecular orbitals. Accordingly, plasmonic properties of such complex systems can be predicted through deconstructing the complex system into more elementary ones and then analyzing the hybridization of these basic plasmon modes⁹⁵. While optical interaction between plasmon modes can be of electrical or magnetic nature, previous works mainly focus on plasmon hybridization through electrical capacitive interactions in the quasi-static limit where phase retardation effects are negligible^{96, 224}. In addition, most of the reported experimental works on plasmon hybridization are in-plane or in core-shell structures while less attention has been given to out-of-plane plasmon hybridization^{95, 96, 225}. In this appendix, we aim to investigate the out-of-plane hybridization of magnetic plasmon modes in vertically stacked Metal-insulator-metal (MIM) nanocavities.

Figure A1(a) and Figure A1(b) compare the main plasmonic modes of the simple in-plane and out-of-plane structures that can form by closely assembling two similar silver (Ag) nanodisks. In the in-plane structure (Figure A1(a)), plasmonic hybridization between the electric dipolar modes of the elementary nanodisks (p_1 and p_2) leads to the formation of bonding and antibonding modes, resonating at lower and higher energies compared to the fundamental ED mode, respectively. The

bonding mode has again an electric dipolar nature since p_1 and p_2 are in-phase in this case. However, the antibonding mode has a dark electric quadrupolar nature since p_1 and p_2 are out-of-phase in this scenario. Accordingly, only the bonding mode is excitable by the normally incident plane waves for an in-plane configuration. Out-of-plane hybridization of the elementary p_1 and p_2 modes again results in the formation of two bonding and anti-bonding modes (Figure A1(b)). However, now p_1 and p_2 are in-phase in the anti-bonding mode and they are out-of-phase for the bonding mode. As Figure A1(b) illustrates, this arrangement gives the anti-bonding mode an electric dipolar nature which is easily excitable by the incident plane waves. The arrangement also makes the bonding mode simultaneously an electric quadrupole and a magnetic dipole. Although the quadrupolar component of the bonding mode is still dark, this mode can still interact with the normally incident plane waves through its magnetic component. Thus, the out-of-plane configuration outperforms its in-plane counterpart in terms of the mode excitability. Out-of-plane structures are also easier to fabricate; In-plane structures are usually created using the expensive electron-beam-lithography (EBL) method while the out-of-plane systems can be created using low-cost lithography techniques combined with electron beam deposition. In an out-of-plane system, the modes can easily be tuned by changing the materials or controlling the thicknesses of different layers. By stacking multiple out-of-plane MIM systems, the magnetic modes in adjacent nanocavities further hybridize, and thus, one can achieve more number of plasmonic modes with spatial overlap (Figure A1(c)).

Figures A2-A6 further analyze the properties of the vertically-stacked two-cavity MIM systems. Briefly, these systems offer a magnetic dipole (MD) mode and a magnetic quadrupole (MQ) mode with spatial overlap and large electric and magnetic field enhancements inside the two dielectric nanocavities. MD mode results from the anti-bonding (in-phase) hybridization of the fundamental MD modes in each nanocavity while the MQ mode is a result of bonding (out-of-phase) hybridization between the fundamental MD modes. The MD and MQ modes of the two-cavity MIM system are resonant at two different wavelengths and can be individually tuned by manipulating the fundamental MD modes or their coupling strength. For example, one can shift the resonance wavelength of the fundamental MD modes by controlling the system diameter and change their coupling strength by controlling the middle metal thickness.

As tunable and easy-to-fabricate multiresonant plasmonic systems with spatial mode overlap, two-cavity MIM systems (as well as multiple-cavity systems) are suitable devices for multiresonant

enhancement of multiphoton non-linear optical processes and wavelength-multiplexed operations at nanoscale.

Methods. The simulations for this work were done using Ansys-Lumerical FDTD software with Perfectly Matched Layer (PML) boundary conditions. The background refractive index was set to 1.5. Also, Johnston and Christy silver model²²⁶ was used for the metallic cylinders. The structures were illuminated with a Total Field Scattered Field (TFSF) source in the $-z$ direction to get the far-field spectra and the near-field profiles.

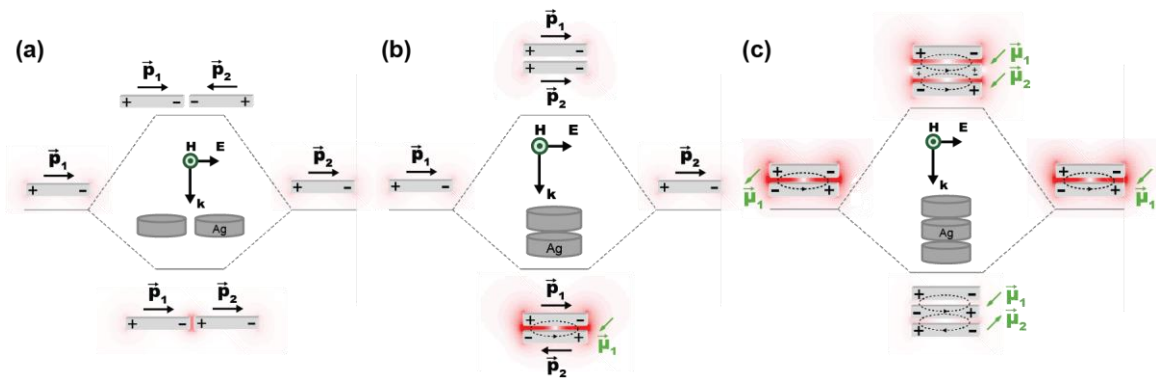


Figure A1. (a) Hybridization between the two electric dipolar modes of two in-plane adjacent Ag nanodisks. (b) Hybridization between the two electric dipolar modes of two vertically-stacked (out-of-plane) Ag nanodisks. Together, the two nanodisks form a one-cavity MIM system. (c) Hybridization between the two magnetic dipolar modes of two vertically-stacked MIM nanocavities with a shared Ag nanodisk. This system forms a two-cavity MIM system.

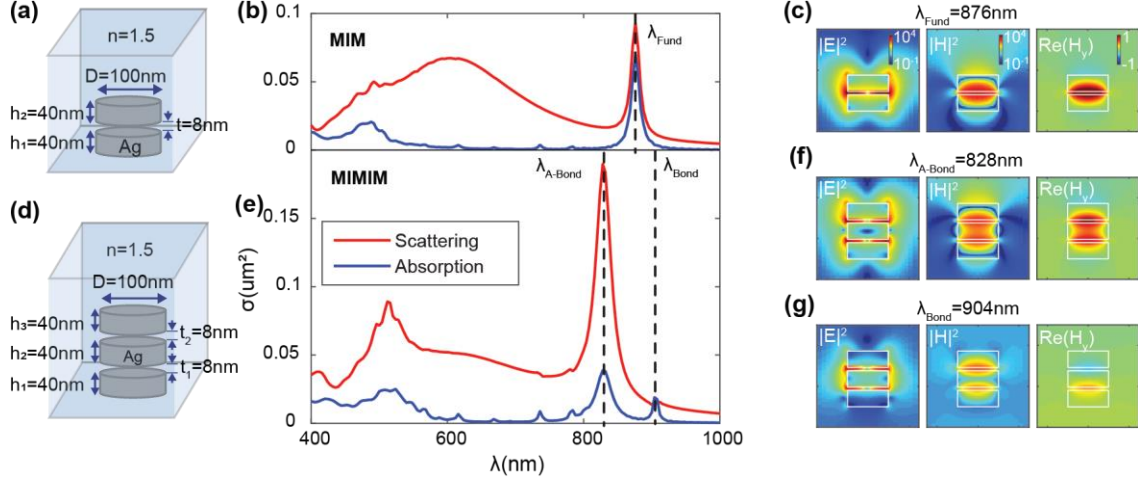


Figure A2. (a, d) Schematics of a one-cavity (a) and a two-cavity MIM structures in a background with $n=1.5$. (b, e) Scattering and absorption spectra of the one-cavity (b) and two-cavity (e) MIM structures. (c, f, g) Near-field profiles of the modes marked in b and e. $\lambda_{Fund} = 876\text{ nm}$ and $\lambda_{A-Bond} = 828\text{ nm}$ modes represent magnetic dipolar natures. However, $\lambda_{Bond} = 904\text{ nm}$ represents a magnetic-quadrupolar nature. λ_{A-Bond} and λ_{Bond} modes form due to the magnetic hybridization between two vertically-stacked λ_{Fund} modes. For both one-cavity and two-cavity systems, the broad spectral feature belongs to the electric dipole mode which is dominated by the top and bottom interfaces of the structure. Furthermore, the low-wavelength resonances on the shoulder of the electric dipole mode correspond to the high-order modes with features inside the gap or on the sidewalls.

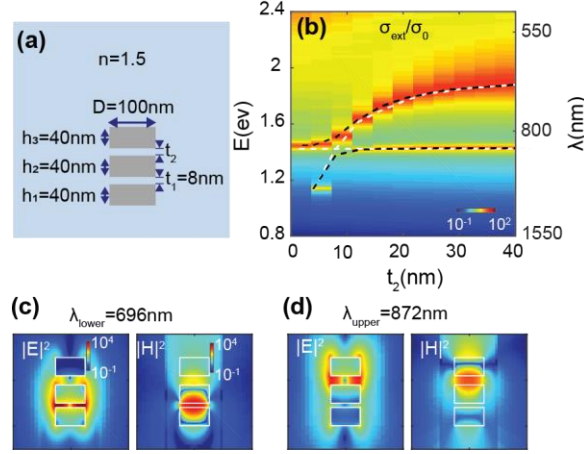


Figure A3. Anti-crossing behavior and spatial overlap condition. (a) To understand how detuning the top and bottom gap modes affect their hybridization, we sweep the thickness of the top nanocavity while keeping the bottom nanocavity thickness constant. (b) Extinction spectra of the system as a function of the top gap thickness (t_2). When two similar modes couple, their common resonance energy splits into two new lower and higher resonance energies. In this regard, the resonance energy loci of the two hybrid modes cannot cross each other. This phenomenon, called the anti-crossing or avoided crossing, evidences the mode coupling event. (c, d) Near-field profiles of the bonding and anti-bonding resonances for $t_2 = 20\text{ nm}$. We see that when the two nanocavities are detuned, their modes have a weak hybridization. This scenario results in a weak spatial overlap between the bonding and antibonding modes. These simulations point out to the following general rule: “To have a good spatial mode overlap between the hybrid modes, their parent modes should both spectrally and spatially overlap”.

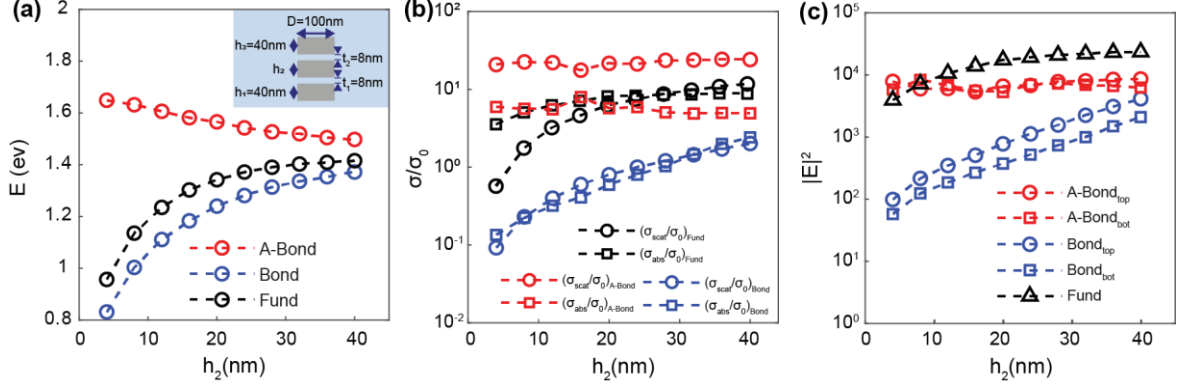


Figure A4. Tuning the optical response by changing the middle metal thickness. (a) Resonance energy of the fundamental mode (one-cavity system), bonding mode (two-cavity system), and the anti-bonding mode (two-cavity system) as a function of h_2 , which represents the bottom metal thickness in the one-cavity system and the middle metal thickness in the two-cavity system. The fundamental mode blueshifts with increasing h_2 which stems from the bonding nature of this mode and weakening of the coupling between the two interfaces of the bottom nanodisk. Changing h_2 affects the modes of the two-cavity system in two manners: 1- shifting the fundamental mode; 2- Modulating the coupling strength between the top and bottom cavities. These factors shift the bonding mode in the same direction while shift the antibonding mode in the opposite directions. In this regard, resonance energy of the bonding mode is much more sensitive to h_2 . (b) scattering and absorption cross sections of the three modes as a function of h_2 . Consistent with part a, the antibonding mode appears less sensitive to h_2 compared to the other two modes. For the fundamental mode, increasing of the scattering cross section as a function of h_2 is due to larger area of the MD mode, which increase its magnetic dipole moment. However, for the bonding mode, this increase is due to the augmented phase retardation between the two nanocavities. Both the fundamental and bonding mode are underdamped²²⁷, which causes their absorption cross-sections to also increase. (c) Maximum intensity enhancement of the three modes (at the edges of the nanocavities) as a function of h_2 . Bonding and anti-bonding modes are evaluated in both the top and bottom nanocavities of the two-cavity system. We see that $|E|^2$ curves generally follow the absorption spectra for each mode. The mismatch between the $|E|^2$ curves of the top and bottom nanocavities are due to interference effects.

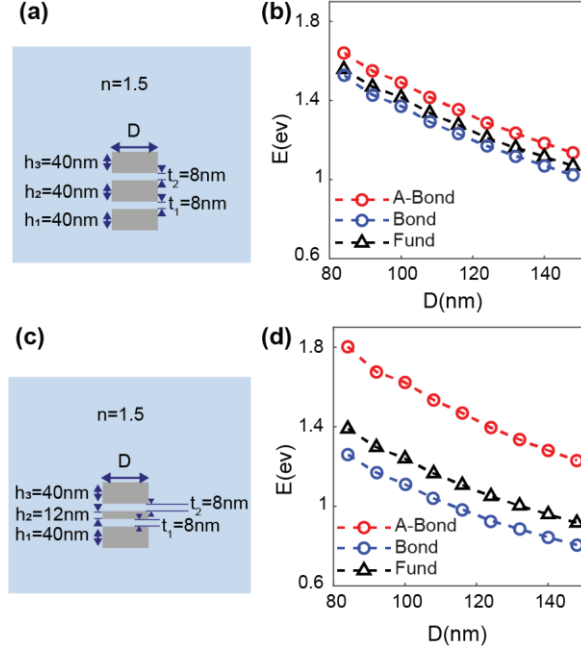


Figure A5. Tuning the modes by changing the diameter (D) for systems with $h_2 = 40 \text{ nm}$ (a) and $h_2 = 12 \text{ nm}$ (b). Increasing the diameter redshifts all the three modes (fundamental, bonding, and anti-bonding) with almost the same slope. This result can be justified if we view the nanocavities as Fabry-Perot resonator with an effective length proportional to the system diameter. In contrast, changing the diameter almost does not affect the energy splitting between the bonding and antibonding modes. This result reveals that the two nanocavities' coupling strength is almost independent of the system diameter.

Chapter 3: Black-Box Coupled-Mode Theory: An Eigenmode Expansion Framework to Analyze Electromagnetic Interactions of Open, Lossy, and Dispersive Resonators

(This is the draft of a paper by Safiabadi Tali SA, Yuan L., and Zhou W. that is under submission.)

Abstract

We present the *Black-box Coupled-Mode Theory (BBCMT)*, an ab initio modal analysis framework based on Maxwell's equations to analyze the electromagnetic interactions of open, lossy, and dispersive resonators. To develop BBCMT, we employ the conjugated Lorentz's reciprocity theorem to normalize the modes and obtain the coupled-mode equations based on conjugated field products. By direct connection to Poynting's theorem, this analysis approach enables defining a resonator's Hamiltonian matrix that characterizes its modes' electromagnetic interactions, energy storage, and absorption. Our approach also generalizes the classic perturbation theory of closed cavities to open resonators. To accurately model both single and coupled resonators, BBCMT considers a resonator's non-resonant behavior in parallel to its resonant response. The non-resonant behavior is captured by treating the resonator as a perturbation to a background structure, which can be flexibly chosen according to the desired accuracy-simplicity trade-off. The modeling complexity can be further adjusted by treating user-defined subcomponents of a resonator system as black-boxes described solely by their input-output transfer characteristics. Under certain constraints and approximations, BBCMT can reduce to either temporal coupled-mode theory (TCMT) or modal analysis of closed resonators. We further demonstrate BBCMT's validity and application in resonator design through two examples of plasmonic metasurfaces, where BBCMT modeling and predictions can match well with finite-difference time-domain (FDTD) simulations while TCMT cannot. Beyond FDTD, BBCMT can offer analytical insights into how electromagnetic interactions among a system's subcomponents can be optimized to maximize the desired response.

3.1. Introduction

Modeling and analyzing the scattering and absorption responses of electromagnetic resonator systems is crucial for designing and developing novel devices in antennas, photonics, plasmonics, and metamaterials/metasurfaces^{58, 89, 227-231}. Numerical methods, such as finite difference time domain (FDTD), method of moments, and finite element method, can precisely solve Maxwell's equations to simulate the electromagnetic responses of resonator systems²³². However, despite providing the far-field and near-field properties of the system, numerical simulations cannot directly analyze the microscopic coupling dynamics between subsystems and interactions of individual modes, constraining their capability for uncovering the underlying design principles. In this regard, complementary analytical methods (Table B1) are required to model and analyze the electromagnetic responses of resonator systems in terms of their resonant modes, i.e., the out-going eigensolutions of sourceless Maxwell's equations under the resonator's boundary conditions²³³. An important modal framework is the temporal coupled-mode theory (TCMT), which is especially powerful in providing intuitive microscopic pictures with simple formulations²³⁴⁻²⁴⁴. TCMT has shown promising applications in studying the optical properties of many systems such as ring resonators^{235, 242}, coupled-cavity systems^{234, 235, 243}, grating, and photonic-crystal structures^{235-237, 239}, and nanoparticles^{240, 244}. Nevertheless, TCMT formulation is largely phenomenological^{234, 237} without a rigorous link to the first-principle Maxwell's equations. Moreover, the TCMT formulation is built upon some restrictive assumptions such as the following: 1) The relationship between the input and output coupling coefficients is acquired following the time-reversal symmetry assumption, which is only applicable to lossless resonators^{234, 236, 237, 239}; 2) Material dispersion effects are neglected^{234-240, 245}; 3) The effects of non-orthogonality between a resonator's modes on its absorption and energy storage are overlooked^{234-237, 239}; 4) Non-resonant absorption is neglected²³⁴⁻²⁴⁰; 5) Despite consideration of non-resonant scattering, no general approach is offered to acquire it for arbitrary resonators²³⁴⁻²⁴⁰; 6) The coupled-resonator formulations are obtained under the assumption of weak coupling between closed (no out-coupling) and lossless resonators^{234, 241}.

The mentioned TCMT shortcomings can be overcome by more rigorous eigenmode expansion approaches that derive the resonators' electromagnetic properties from Maxwell's equations^{58, 233}. Such methods expand the fields as a linear summation of the resonant modes and then use either

the reciprocity theorem^{246, 247} or residue-decomposition of the dyadic Green's function^{58, 248-251} to find the expansion coefficients. Each mode's coefficient is typically calculated as a function of its products with the source (field or current) and all the resonator modes (including itself). Eigenmode expansion analysis is straightforward for closed resonators, and field products can be unconjugated or conjugated in this case^{58, 232}. Using the conjugated field products has the advantage of direct connection to Poynting's theorem, which facilitates expressing the resonator energy-related parameters (e.g., total absorption, stored energy, and a dipole source's dissipation rate) as a summation of different modes contributions⁵⁸. Unlike closed resonators, modal analysis of open resonators is challenging since their modes, called quasi-normal modes (QNMs), exponentially diverge outside the resonator, making their normalization problematic^{233, 245-269}. The diverging nature of QNMs is a direct result of their belonging to non-conservative systems, which makes their eigenfrequencies complex-valued, contrary to normal modes with real-valued eigenfrequencies in conservative (closed and lossless) systems²³³. Three major strategies to tackle the QNMs' normalization issue include: 1) Suppressing the diverging QNM fields using perfectly matched layer (PML) boundary conditions and defining the inner products as volume integrals over the whole computational domain, including the PML domain^{233, 246, 247, 259}; 2) Adding surface-integral terms in the inner product definition to compensate for the exponentially-increasing volume integral over the infinite space^{256, 258}; 3) Defining the inner product integrals over a purely-real finite-domain, without QNM suppression²⁴⁹⁻²⁵¹. Semi-analytical integration-free normalization techniques also exist that utilize the above strategies as their foundation^{257, 262}. These strategies have been successfully utilized to model a variety of optical systems such as photonic crystal cavities^{256, 260, 262}, grating structures^{245, 259, 270}, and plasmonic nanostructures^{246, 247, 257, 260, 262}. Although most QNM works have focused on single resonators, some recent works have analyzed the phenomenon of coupling between QNMs in adjacent resonators as well^{264, 265, 271}. Despite their advantages, reliance of the mentioned QNM analysis strategies on unconjugated field products, absorbing PML layers (strategy 1), and surface integral terms (strategies 2 and 3) hinder direct linking of the mode products to Poynting's theorem. In this regard, it is challenging to unify the existing QNM frameworks with TCMT and the classic modal expansion methods of closed resonators.

This paper establishes the *Black-Box Coupled-Mode Theory (BBCMT)*, an ab initio eigenmode expansion framework based on Maxwell’s equations to model the electromagnetic interactions of open, lossy, and dispersive resonators. To develop BBCMT, we utilize the conjugated form of Lorentz’s reciprocity theorem to define the inner product operation by a volume integral of conjugated field products over the resonator interior. Due to a direct connection to Poynting’s theorem, this approach allows us to define a resonator’s Hamiltonian matrix that, in analogy to quantum mechanics²⁷², governs the modes’ electromagnetic interactions, energy storage, and absorption. The adopted approach also enables generalizing the perturbation theory of closed cavities^{227, 232, 273} to open resonators. The BBCMT framework uniquely captures a resonator’s non-resonant responses to an external source by expressing the scattered fields as perturbations to a background structure’s fields. Consistent with the multiple-scattering picture, our analysis reveals that non-resonant scattering of coupled resonators can modify their resonance and coupling attributes beyond the effects of direct modes’ interaction. By making the background choice flexible and treating user-defined system subcomponents as black-boxes solely described by their input-out relationship, BBCMT allows the user to adjust the models’ complexity and accuracy. Besides the rigorous formulation, we introduce several lemmas to obtain the coupling coefficients in BBCMT models by reverse-engineering the calculated or measured far-field spectra, thus bypassing computationally expensive integrations. Furthermore, we employ the signal flow graphs (SFG) from control engineering²⁷⁴ to solve the BBCMT equations and visually represent the coupling and interaction dynamics they describe.

We show that (1) For cavity resonators with perfect conductor walls, BBCMT formalism is equivalent to the conventional modal analysis of closed resonators with conjugated field products⁵⁸; (2) BBCMT can simplify to TCMT formulations^{234-237, 239} under the TCMT constraints mentioned earlier. To further validate BBCMT’s generality, robustness, and flexibility, we present two examples where BBCMT and TCMT models are side-by-side compared with FDTD simulations. The first example exhibits the application of the background perturbation method in modeling a SiO₂-embedded plasmonic array. The second example uses a nanolaminate plasmonic crystal^{275, 276} to study the non-resonant scattering effects on coupled resonators. In both examples, BBCMT predictions much better match the FDTD simulations than TCMT predictions. Beyond FDTD, the BBCMT analysis reveals how different near-field and radiative coupling pathways

between the system subcomponents contribute to the total absorption. Overall, this paper demonstrates that BBCMT is a versatile theoretical framework for modeling, analyzing, and designing electromagnetic resonator systems, especially in plasmonics and metamaterials/metasurfaces.

The paper is organized as follows: In Sec. 3.2, we discuss the BBCMT formulations for a single resonator. In Sec. 3.3, we discuss the loading effects and the BBCMT formulations for coupled-resonator systems. In Sec. 3.4, we present examples that demonstrate BBCMT's validity and applications. Finally, we conclude our paper in section 3.5.

3.2. BBCMT formulations for a single resonator

This section derives the general BBCMT formulas for a single resonator and discusses their potential impacts. The detailed derivation process is provided in Appendix B. In subsection 3.2.1, we derive the energy-related characteristics and coupling equations for the modes in a generic resonator with loss, dispersion, and mode non-orthogonality. In subsection 3.2.2, we calculate the resonator's scattering and absorption as a summation of different modes' contributions and non-resonant response terms. In subsection 3.2.3, we introduce the background perturbation analysis, which allows removing the non-resonant terms and truncating the number of modes. In subsections 3.2.4 and 3.2.5, we introduce the resonator ports and analyze the resonator perturbation problem in the BBCMT framework, respectively. In subsection 3.2.6, we obtain the resonator's signal flow graph, characteristic equation, and scattering matrix. Finally, in subsection 3.2.7, we introduce the Kappa-estimation and F-estimation lemmas to reverse-engineer BBCMT model parameters of a resonator from its scattering and absorption spectra.

3.2.1. Coupled-mode equation, mode normalization, and energy

We start by considering an arbitrary electromagnetic resonator A lying over an arbitrary medium. For simplicity, we assume that both the resonator and medium materials are non-magnetic and isotropic. We respectively use $\varepsilon_{med}(r, \omega)$ and $\varepsilon_A(r, \omega)$ to label the dielectric function in the absence and presence of the resonator, where r is the position and ω denotes the (angular) frequency. We exclude the perfect electric conductor (PEC) parts of the resonator from $\varepsilon_A(r, \omega)$ and instead treat

them using the surface equivalence principle²³². By definition, the following set of eigenequations can be written for the m^{th} mode:

$$\nabla \times \tilde{E}_{Am}(r) = -j\tilde{\omega}_{Am}\mu_0\tilde{H}_{Am}(r), \quad (1a)$$

$$\nabla \times \tilde{H}_{Am}(r) = j\tilde{\omega}_{Am}\varepsilon_A(r, \tilde{\omega}_m)\tilde{E}_{Am}(r) + \hat{n} \times \tilde{H}_{Am}(r). \quad (1b)$$

where μ_0 is the vacuum permeability and $\hat{n}$ denotes the outward normal unit vector over the resonator's PEC surfaces. $\tilde{\omega}_{Am} = \Omega_{Am} + j\Gamma_{Am}$ is the m^{th} mode's complex resonance frequency²³³ with Ω_{Am} and Γ_{Am} determining the mode oscillation frequency and (total) decay rate, respectively. $\tilde{E}_{Am}(r)$ and $\tilde{H}_{Am}(r)$ respectively denote the mode's normalized electric and magnetic field patterns, which are outgoing outside the resonator but have standing-wave natures inside the resonator (except for the PEC regions over which they are zero). By writing the Poynting's theorem over the resonator interior (PEC parts excluded) and based on Eqs. (1) we can obtain^{233, 277}:

$$\tilde{P}_{Am}^r + \tilde{P}_{Am}^{nr} = 2\Gamma_{Am}\tilde{W}_{Am}, \quad (2)$$

$$\text{where } \tilde{W}_{Am} = \frac{1}{4} \iiint_{V_A} \left[\text{Re} \left(\frac{\partial(\omega\varepsilon_A)}{\partial\omega} \right)_{\omega=\Omega_{Am}} |\tilde{E}_{Am}|^2 + \mu_0 |\tilde{H}_{Am}|^2 \right] d^3r, \quad \tilde{P}_{Am}^{nr} = -\frac{\Omega_{Am}}{2} \iiint_{V_A} \left[\text{Im}[\varepsilon_A(\Omega_{Am})] |\tilde{E}_{Am}|^2 \right] d^3r$$

$$\text{and } \tilde{P}_{Am}^r = \frac{1}{2} \iint_{\partial_A} \text{Re}(\tilde{E}_{Am} \times \tilde{H}_{Am}^*) \cdot d\mathbf{s} \text{ with } V_A / \partial_A \text{ denoting the resonator volume/surface, respectively.}$$

$\tilde{W}_{Am}$ can be interpreted as the normalized and time-averaged electromagnetic energy stored in the m^{th} mode. Also, $\tilde{P}_{Am}^r$ and $\tilde{P}_{Am}^{nr}$ represent the normalized power dissipation by out-ward radiation (Poynting vector flux) and material absorption, respectively. We define the m^{th} mode's radiative decay rate (Γ_{Am}^r), radiative lifetime (τ_{Am}^r), non-radiative decay rate (Γ_{Am}^{nr}), and non-radiative lifetime (τ_{Am}^{nr}) as:

$$\Gamma_{Am}^r = \frac{1}{\tau_{Am}^r} = \frac{\tilde{P}_{Am}^r}{2\tilde{W}_{Am}}, \quad (3a)$$

$$\Gamma_{Am}^{nr} = \frac{1}{\tau_{Am}^{nr}} = \frac{\tilde{P}_{Am}^{nr}}{2\tilde{W}_{Am}}, \quad (3b)$$

which, from Eq. (2), satisfy $\Gamma_{Am} = \Gamma_{Am}^r + \Gamma_{Am}^{nr}$ or equivalently, $\frac{1}{\tau_{Am}} = \frac{1}{\tau_{Am}^r} + \frac{1}{\tau_{Am}^{nr}}$.

Now suppose that resonator A is getting excited by the harmonic electric current source $J(r, \omega)$.

In the resonator's presence, the source creates the total fields $E_A^{tot}(r, \omega)$ and $H_A^{tot}(r, \omega)$ satisfying:

$$\nabla \times E_A^{tot} = -j\omega\mu_0 H_A^{tot}, \quad (4a)$$

$$\nabla \times H_A^{tot} = j\omega\epsilon_A E_A^{tot} + \hat{n} \times H_A^{tot} + J, \quad (4b)$$

where the surface equivalence principle²³² has again been invoked. It is known that when the source resides inside the resonator, the resonant modes form a basis set that can span the total fields in the same region²⁶³. In this regard, two scenarios can be considered (Figure 3.1(a-b)); the source is inside the resonator, which we will briefly discuss, or outside it, which is the focus of this work.

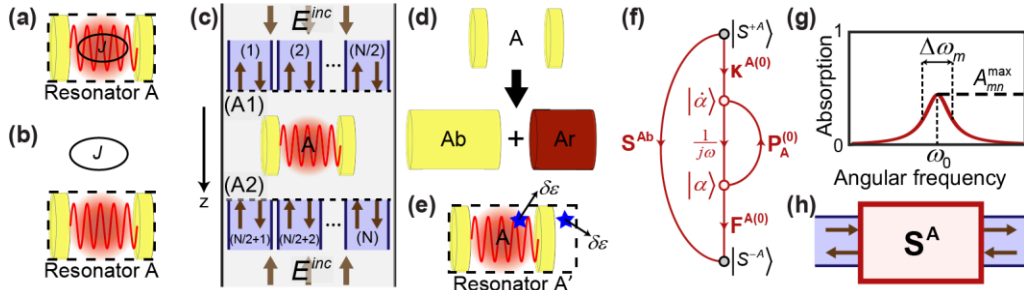


Figure 3.1. BBCMT model for a single resonator. (a, b) Resonator A is getting excited by the current source $J(r, \omega)$ inside (a)/outside (b) of it. (c) Resonator A is getting excited by the incident field E^{inc} . Each waveguide mode in the medium that delivers power to the resonator corresponds to a port. (d) Decomposing a resonator into a background structure (Ab) and a residual structure (Ar). (e) Resonator A' is defined as a combination of resonator A and the dielectric function perturbation $\delta\epsilon$ inside it or in its proximity. (f) The signal flow graph of resonator A showing how its modes are coupled to the input and output power wave vectors. (g, h) Fundamental ideas of Kappa-estimation (g) and F-estimation (h) lemmas to reverse engineer the resonator pole matrix, non-radiative decay rate, and coupling coefficients from the data obtained of numerical simulations or experimental measurements.

- **Source inside the resonator (Figure 3.1(a)).** In this scenario, one can expand the total fields in the resonator's interior as:

$$\left(\begin{array}{c} E_A^{tot}(r, \omega) \\ H_A^{tot}(r, \omega) \end{array} \right) \bigg|_{r \in V_A} = \sum_m \tilde{\alpha}_m(\omega) \begin{pmatrix} \tilde{E}_{Am}(r) \\ \tilde{H}_{Am}(r) \end{pmatrix}, \quad (5)$$

where the unitless term $\tilde{\alpha}_m(\omega)$ is the m^{th} mode's amplitude. By writing the general conjugated form of the Lorentz's reciprocity theorem (Appendix B.1) for Eqs. (1) and (4) over the resonator interior, and considering Eq. (5), we then obtain the steady-state coupled-mode (CM) equation for resonator A (Appendix B.2):

$$\mathbf{H}_A(\omega)(j\omega \mathbf{I} - \mathbf{P}_A)|\tilde{\alpha}\rangle = -\frac{1}{4} \iiint_{J \neq 0} J \cdot |\tilde{E}_A^*\rangle d^3r, \quad (6)$$

where $|\tilde{\alpha}\rangle = [\tilde{\alpha}_i]_{\mathbf{M} \times 1}$ and $|\tilde{E}_A^*\rangle = [\tilde{E}_{Ai}^*]_{\mathbf{M} \times 1}$ with $\mathbf{M}$ being the number of resonator modes, $\mathbf{I}$ is the identity matrix, $\mathbf{P}_A$ is the pole matrix defined as $\mathbf{P}_A = [p_{ij} = \tilde{\omega}_{Ai} \delta_{ij}]_{\mathbf{M} \times \mathbf{M}}$, and $\mathbf{H}_A = [h_{ij}]_{\mathbf{M} \times \mathbf{M}}$ is the *Hamiltonian matrix* with the elements:

$$\begin{aligned} h_{ij} &= \frac{1}{4} (\omega - \tilde{\omega}_{Aj})^{-1} \iiint_{V_A} \{ [\omega \varepsilon_A(\omega) - \tilde{\omega}_{Aj} \varepsilon_A(\tilde{\omega}_{Aj})] (\tilde{E}_{Aj} \cdot \tilde{E}_{Ai}^*) + [\omega \mu_0 - \tilde{\omega}_{Aj} \mu_0] (\tilde{H}_{Aj} \cdot \tilde{H}_{Ai}^*) \} d^3r \\ &\approx \frac{1}{4} \iiint_{V_A} \left\{ \frac{\partial [\omega \varepsilon_A(\omega)]}{\partial \omega} \bigg|_{\omega = \tilde{\omega}_{Aj}} (\tilde{E}_{Aj} \cdot \tilde{E}_{Ai}^*) + \mu_0 (\tilde{H}_{Aj} \cdot \tilde{H}_{Ai}^*) \right\} d^3r \\ &\approx \frac{1}{4} \iiint_{V_A} \left\{ \text{Re} \left[\frac{\partial [\omega \varepsilon_A(\omega)]}{\partial \omega} \right] \bigg|_{\omega = \Omega_{Aj}} (\tilde{E}_{Aj} \cdot \tilde{E}_{Ai}^*) + \mu_0 (\tilde{H}_{Aj} \cdot \tilde{H}_{Ai}^*) \right\} d^3r \\ &\quad - \frac{j}{4} \iiint_{V_A} \text{Im} \left[\frac{\partial [\omega \varepsilon_A(\omega)]}{\partial \omega} \right] \bigg|_{\omega = \Omega_{Aj}} (\tilde{E}_{Aj} \cdot \tilde{E}_{Ai}^*) d^3r. \end{aligned} \quad (7)$$

Eq. (7) indicates that the Hamiltonian matrix is generally non-Hermitian, and its elements have the unit of energy. When the resonator materials are low-dispersion, i.e., $|\partial(\omega \varepsilon_A)/(\varepsilon_A \partial \omega)| \approx 1$, the total energy stored in the resonator modes would be:

$$W_A = \frac{1}{4} \iiint_{V_A} \left[\operatorname{Re} \left(\frac{\partial(\omega \varepsilon_A)}{\partial \omega} \right) \left| \sum_m \tilde{\alpha}_m \tilde{E}_{Am} \right|^2 + \mu_0 \left| \sum_m \tilde{\alpha}_m \tilde{H}_{Am} \right|^2 \right] d^3r = \operatorname{Re}[\langle \tilde{\alpha} | \mathbf{H}_A | \tilde{\alpha} \rangle]. \quad (8)$$

According to Eqs. (2), (7), and (8), we choose the mode normalization condition as:

$$\operatorname{Re}(h_{mm}) = \tilde{W}_{Am} = \frac{1}{4} \iiint_{V_A} \left[\operatorname{Re} \left(\frac{\partial(\omega \varepsilon_A)}{\partial \omega} \right) \left| \tilde{E}_{Am} \right|^2 + \mu_0 \left| \tilde{H}_{Am} \right|^2 \right] d^3r = 1. \quad (9)$$

When the modes are orthogonal, i.e., $h_{ij} \approx 0$ for $i \neq j$, we can use Eq. (9) to simplify Eq. (7) to:

$$h_{ij} \approx \left(1 - \frac{j\Gamma_{Ai}^{nr}}{\Omega_{Ai}} \right) \delta_{ij}. \quad (10)$$

Then, the Hamiltonian matrix becomes diagonal, and Eq. (8) reduces to $W_A = \langle \tilde{\alpha} | \tilde{\alpha} \rangle$, consistent with the stored energy formula in TCMT^{234, 236, 237}. For the special case that the resonator is lossless and closed with perfect conductor walls, the reciprocity theorem gives $h_{ij} = \delta_{ij}$ or $\mathbf{H}_A = \mathbf{I}$. In this scenario, Eq. (6) becomes equivalent to the common eigenmode expansion analysis of closed resonators⁵⁸.

- Source outside the resonator (Figure 3.1(b)). The resonant modes do not span the total fields inside the resonator in this scenario. Hence, a different analysis strategy must be adopted. We define the incident fields $E^{inc}(r, \omega)$ and $H^{inc}(r, \omega)$ as those created by the source when resonator A is absent (Figure 3.1(c)). We also define the scattered fields E_A^{sca} and H_A^{sca} as $E_A^{sca}(r, \omega) = E_A^{tot}(r, \omega) - E^{inc}(r, \omega)$ and $H_A^{sca}(r, \omega) = H_A^{tot}(r, \omega) - H^{inc}(r, \omega)$, respectively. Then, from the volume and surface equivalence principles, we can deduce²³²:

$$\nabla \times E_A^{sca} = -j\omega\mu_0 H_A^{sca}, \quad (11a)$$

$$\nabla \times H_A^{sca} = j\omega\varepsilon_{med} E_A^{sca} + (j\omega\Delta\varepsilon_A E^{inc} + \hat{n} \times H^{inc}) + (j\omega\Delta\varepsilon_A E_A^{sca} + \hat{n} \times H_A^{sca}), \quad (11b)$$

where $\Delta\epsilon_A = \epsilon_A - \epsilon_{med}$. As all the source terms in Eqs. (11) reside inside the resonator, we can write:

$$\left(\begin{matrix} E_A^{sca}(r, \omega) \\ H_A^{sca}(r, \omega) \end{matrix} \right) \bigg|_{r \in V_A} = \sum_m \tilde{\alpha}_m(\omega) \begin{pmatrix} \tilde{E}_{Am}(r) \\ \tilde{H}_{Am}(r) \end{pmatrix}. \quad (12)$$

Then, following Eq. (6)'s derivation process gives the CM equation as follows:

$$\mathbf{H}_A(\omega)(j\omega\mathbf{I} - \mathbf{P}_A)|\tilde{\alpha}\rangle = -\frac{j\omega}{4} \iiint_{\Delta\epsilon_A \neq 0} \Delta\epsilon_A \cdot E^{inc} \cdot |\tilde{E}_A^*\rangle d^3r + \frac{1}{4} \iint_{\partial_A^{PEC}} |\tilde{E}_A^*\rangle \times H^{inc} \cdot ds, \quad (13)$$

where $\partial_{A,PEC}$ denotes the PEC surfaces of the resonator. The only difference between Eq. (6) and Eq. (13) are the source terms on the right-hand side and Eqs. (7)-(10) are still valid. The first and second source terms in Eq. (13) account for the induced volume and surface currents, respectively.

3.2.2. Scattering and absorption

Let us first consider the source to be outside the resonator (Figure 3.1(b)). We use the Lippmann-Schwinger (or Dyson) approach^{262, 263, 278} based on Eqs. (11) and (12) to calculate the scattered fields in the resonator's exterior:

$$E_A^{sca} = E_{Af}^x + \sum_m \tilde{\alpha}_m \tilde{E}_{Am}^{sca}, \quad (14)$$

Where $E_{Af}^x(r, \omega) = \omega^2 \mu_0 \iiint_{\Delta\epsilon_A \neq 0} G_{med}^E \cdot \Delta\epsilon_A \cdot E^{inc} d^3r' + j\omega\mu_0 \iint_{\partial_A^{PEC}} G_{med}^E \times H^{inc} \cdot ds$ and

$$\tilde{E}_{Am}^{sca}(r, \omega) = \omega^2 \mu_0 \iiint_{\Delta\epsilon_A \neq 0} G_{med}^E \cdot \Delta\epsilon_A \cdot \tilde{E}_{Am} d^3r' + j\omega\mu_0 \iint_{\partial_A^{PEC}} G_{med}^E \times \tilde{H}_{Am} \cdot ds \text{ with } G_{med}^E(r, r', \omega) \text{ being the}$$

electric dyadic Green's function of the medium. E_{Af}^x represents the non-resonantly scattered electric field (not mediated by the modes) which is an essential aspect of the Fano effect^{236, 240, 245}.

$\tilde{E}_{Am}^{sca}$ denotes the regularized electric field of the m^{th} mode characterizing its scattering to the

resonator's exterior at the frequency ω and, unlike the quasi-normal field $\tilde{E}_{Am}$, does not diverge.

By writing the Lippmann-Schwinger equation based on Eq. (1), one can obtain

$$\tilde{E}_{Am}^{sca}(r, \tilde{\omega}_m) = \tilde{E}_{Am}(r)^{262}. \text{ Similar expressions can be found for the regularized magnetic field } H_A^{sca}.$$

When the resonator materials are low-dispersion, we can write the resonator absorption (dissipated power) as (Appendix B.2):

$$A_A(\omega) = -\frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im}[\epsilon_A] |E_A^{tot}|^2 d^3r \approx A_{Af}^x - 2\omega \text{Im}[\langle \tilde{\alpha} | \mathbf{H}_A | \tilde{\alpha} \rangle], \quad (15)$$

with $A_{Af}^x(\omega) = -\frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im}(\epsilon_A) |E^{inc}|^2 d^3r$ being the non-resonant absorption. Under the mode

orthogonality condition, we can use Eq. (10) to simplify Eq. (15) to $A_A \approx A_{Af}^x + 2\omega \langle \tilde{\alpha} | \mathbf{\Gamma}_A^{nr} \mathbf{\Omega}_A^{-1} | \tilde{\alpha} \rangle$

where $\mathbf{\Gamma}_A^{nr} = [x_{ij} = \Gamma_{Ai}^{nr} \delta_{ij}]_{\mathbf{M} \times \mathbf{M}}$ and $\mathbf{\Omega}_A = [x_{ij} = \Omega_{Ai} \delta_{ij}]_{\mathbf{M} \times \mathbf{M}}$. Off-resonant modes typically have a small contribution to the resonator's absorption. Therefore, if the modes are also spectrally narrow (quality factors of 10 or higher), Eq. (15) can be further reduced to $A_A = A_{Af}^x + \langle \tilde{\alpha} | 2\mathbf{\Gamma}_A^{nr} | \tilde{\alpha} \rangle$.

When the source is inside the resonator (Figure 3.1(a)), similar analysis procedures give

$$E_A^{sca} = \sum_m \tilde{\alpha}_m \tilde{E}_{Am}^{sca} \text{ and } A_A(\omega) = -2\omega \text{Im}[\langle \tilde{\alpha} | \mathbf{H}_A | \tilde{\alpha} \rangle], \text{ which resemble Eqs. (14) and (15) but without}$$

the non-resonant terms. Throughout the rest of the paper, we consider the source to be outside the resonator. Moreover, for simplicity, we assume that the resonator does not contain any PEC components.

3.2.3. Background perturbation

Calculating the non-resonant terms in Eqs. (14) and (15) is straightforward in certain configurations, e.g., sub-wavelength resonant bodies²⁴⁰, resonators with mirror symmetry in the z-direction²³⁶, or sub-wavelength cavities in large-index slabs^{239, 245}. Nonetheless, evaluating the non-resonant terms is usually quite involved for more complex structures. Furthermore, for design

purposes, one might be exclusively interested in the responses emerging from specific resonator areas (principal areas) such as cavities and protrusions. However, principal areas' contributions to the total scattering and absorption cannot be discerned in Eqs. (14) and (15). We address the mentioned issues by the background-perturbation approach. Assume that the resonator *background*, represented by $\varepsilon_{Ab}(r, \omega)$, is a structure defined such that $\varepsilon_A \neq \varepsilon_{Ab}$ region coincides with the principal areas (Figure 3.1(d)). Incorporating the background structure into the medium ($\varepsilon_{med} \rightarrow \varepsilon_{Ab}$) and following Eq. (13) derivation procedure gives (Appendix B.2)::

$$\mathbf{H}_A(\omega)(j\omega\mathbf{I} - \mathbf{P}_A)|\alpha\rangle = -\frac{j\omega}{4} \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} (\varepsilon_A - \varepsilon_{Ab}) T_{Ab}(E^{inc}) \cdot |\tilde{E}_A^*\rangle d^3r, \quad (17)$$

where $T_{Ab}(E^{inc}) = E^{inc} + E_{Ab}^{sca} = E^{inc} + \omega^2 \mu_0 \iiint_{\Delta\varepsilon_{Ab} \neq 0} G_{Ab}^E \cdot \Delta\varepsilon_{Ab} \cdot E^{inc} d^3r$ is the total electric field that the source creates upon acting on the background structure. Also, $\Delta\varepsilon_{Ab} = \varepsilon_{Ab} - \varepsilon_{med}$, and E_{Ab}^{sca} and $G_{Ab}^E(r, r', \omega)$ represent the scattered electric field and electric dyadic Green's function of the background structure, respectively. Eqs. (13) and (17) have similar forms and even the former can be deduced from the latter by considering a free-space background ($\varepsilon_{Ab} = \varepsilon_{med}$). However, unlike Eq. (13), the modes with small electric fields ($\tilde{E}_{An}^*$) in $\varepsilon_A \neq \varepsilon_{Ab}$ region (non-principal modes) can be neglected in Eq. (17). Following that, we can re-express the resonator's scattering and the absorption (Eqs. (14) and (15)) as a superposition of contributions from the background structure and the modes associated with principal areas (principal modes) (Appendix B.2):

$$E_A^{sca} \approx E_{Ab}^{sca} + \sum_m \alpha_m \tilde{E}_{Am}^{sca}, \quad (18)$$

$$A_A \approx A_{Ab} - 2\omega \text{Im}[\langle \alpha | \mathbf{H}_A | \alpha \rangle], \quad (19)$$

where A_{Ab} is the background structure's absorption. Like Eq. (15), Eq. (19) diminishes to $A_A = A_{Ab} + \langle \alpha | 2\Gamma_A^{nr} | \alpha \rangle$ when the resonator modes are orthogonal and spectrally narrow. The background terms in Eqs. (18) and (19) respectively absorb the scattering and absorption contributions of both the non-resonant components and the non-principal modes. The background

terms can be imported from outside of BBCMT, e.g., from analytical calculations, numerical simulations, or experimental measurements. In such case, the background structure would be like a black-box described by its input-output relationships. The user can determine the background structure according to the selected principal areas in the resonator and the desired accuracy-complexity trade-off level.

3.2.4. Resonator ports

Suppose that the medium is a waveguide with orthogonal modes. The waveguide modes may generally be of any type, e.g., spherical waves, plane waves, and TEM modes over a coaxial cable. However, this paper focuses on the waveguide modes with planar phase fronts, common in photonics²³¹. Taking the z axis as the waveguide axis, we normalize the waveguide modes such that²²⁹:

$$U_{ij} = \frac{1}{4} \iint_{xy \text{ plane}} \left[(E_i^w)^* \times H_j^w + E_j^w \times (H_i^w)^* \right] \cdot \hat{z} dx dy = \pm \delta_{ij}, \quad (20)$$

where $E_n^w(x, y)$ and $H_n^w(x, y)$ are the normalized electric and magnetic fields (over xy plane) of the n^{th} waveguide mode, respectively. Also, the plus/minus sign is for the forward/backward propagating modes. We take β_n as the propagation constant of the n^{th} waveguide mode, with $\beta_n > 0$ for forward-propagating and $\beta_n < 0$ for backward-propagating. Without loss of generality, we set the phase angles of the normalized fields such that $E_i^w = E_j^w$ when $\beta_i = -\beta_j$.

As a scatterer, resonator A disrupts the orthogonality of the different waveguide modes and couples them to each other. However, the orthogonality relation remains preserved in the waveguide regions lying outside the resonator. We divide this region into A1 and A2 (sub)regions with the reference planes $z = z_{A1}$ and $z = z_{A2}$, respectively (Figure 3.1(c)). The waveguide modes can linearly expand the fields in both A1 and A2 regions. Each set of the counterpropagating waveguide modes with β_n and $-\beta_n$ that take the energy to/away from the resonator in the same region (A1 or A2) constitute a resonator port. We index the ports such that the energy-delivering

waveguide mode of the n^{th} port has $\beta_n > 0$ for $1 \leq n \leq \mathbf{N}/2$, and $\beta_n = -\beta_{n-\mathbf{N}/2}$ for $\mathbf{N}/2 + 1 \leq n \leq \mathbf{N}$, where $\mathbf{N}$ is the number of ports (Figure 3.1(c)).

We can expand the total electric field propagating towards and away from resonator A as

$$\sum_n S_{q_n,n}^{+A} E_n^w e^{-j\beta_n(z-z_{q_n})} \text{ and } \sum_n S_{q_n,n}^{-A} E_n^w e^{j\beta_n(z-z_{q_n})}, \text{ where } q_n \text{ is the } n^{th} \text{ port reference plane:}$$

$q_n = A1, A2$ if $\beta_n > 0$ and $\beta_n < 0$, respectively. The unitless coefficients $S_{q_n,n}^{\pm A}$ are called “power

waves”²²⁷, as $|S_{q_n,n}^{+A}|^2$ and $|S_{q_n,n}^{-A}|^2$ are the normalized powers carried by the n^{th} port toward and away

from resonator A, respectively. The input power wave vector of resonator A can be defined as

$$|S^{+A}\rangle = [S_{q_n,n}^{+A}]_{\mathbf{N} \times 1} = \begin{bmatrix} |S_{A1}^{+A}\rangle \\ |S_{A2}^{+A}\rangle \end{bmatrix}, \text{ where } |S_{A1}^{+A}\rangle \text{ and } |S_{A2}^{+A}\rangle \text{ correspond to the ports in A1 and A2 regions,}$$

respectively. The resonator’s output power wave vector can be defined similarly. By assuming that the incident field only has propagating components, we can expand it as

$$E^{inc}(r) = \sum_n S_{q_n,n}^{+A} E_n^w(x,y) e^{-j\beta_n(z-z_{q_n})}. \text{ Inserting this expansion into Eq. (17) breaks the source term in}$$

the CM equation into a summation of different ports’ contributions:

$$j\omega|\alpha\rangle = \mathbf{P}_A|\alpha\rangle + \mathbf{K}^A|S^{+A}\rangle, \quad (21)$$

where the input-coupling matrix $\mathbf{K}^A$ is defined as:

$$\mathbf{K}^A = [\mathbf{K}_{A1}^A \ \mathbf{K}_{A2}^A] = \mathbf{H}_A^{-1} \left[v_{mn} = \left(-\frac{j\omega}{4} \right) \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} (\varepsilon_A - \varepsilon_{Ab}) \cdot T_{Ab} \left(E_n^w e^{-j\beta_n(z-z_{q_n})} \right) \cdot \tilde{E}_{Am}^* d^3r \right]_{\mathbf{M} \times \mathbf{N}}. \quad (22)$$

Elements of the input-coupling matrix have the unit of inverse time.

Just like a dipole antenna²³⁰, the electric field scattered from resonator A (Eq. (18)) can be

decomposed into propagating and non-propagating components as $E_A^{sca} = E_A^{sca,p} + E_A^{sca,np}$. The

propagating component $E_A^{sca,p}$ carries the power radiated away from the resonator, and from Eq.

(18), can be further decomposed as $E_A^{sca,p} = E_{Ab}^{sca,p} + \sum_m \alpha_m \tilde{E}_{Am}^{sca,p}$. The non-propagating component $E_A^{sca,np}$ corresponds to the energy stored in the resonator near-field²³⁰. It is more common to express the total fields radiated away from the resonator rather than expressing the scattered fields^{227, 234}. By expanding $E^{inc} + E_A^{sca,p}$ as a superposition of the waveguide modes and then applying the conjugated Lorentz reciprocity theorem (similar procedure as the CMT for waveguides^{227, 229}), we find the formula for the output power wave vector of the resonator (Appendix B.2):

$$|S^{-A}\rangle \approx \mathbf{S}^{Ab} |S^{+A}\rangle + \mathbf{F}^A |\alpha\rangle. \quad (23)$$

Here, $\mathbf{S}^{Ab} = \begin{bmatrix} \mathbf{S}_{11}^{Ab} & \mathbf{S}_{12}^{Ab} \\ \mathbf{S}_{21}^{Ab} & \mathbf{S}_{22}^{Ab} \end{bmatrix}$ is the scattering matrix²²⁷ of the background structure and $\mathbf{F}^A$ is the output-coupling matrix of the resonator modes:

$$\mathbf{F}^A = \begin{bmatrix} \mathbf{F}_{A1}^A \\ \mathbf{F}_{A2}^A \end{bmatrix} = \mathbf{S}^{Af} \left[v_{nm} = \left(-\frac{j\omega}{4} \right) \iiint_{\Delta\epsilon_A \neq 0} \Delta\epsilon_A \tilde{E}_{Am} \cdot (E_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \right]_{\mathbf{N} \times \mathbf{M}}, \quad (24)$$

where $\mathbf{S}^{Af} = \begin{bmatrix} 0 & \mathbf{D}(z_{A2} - z_{A1}) \\ \mathbf{D}(z_{A2} - z_{A1}) & 0 \end{bmatrix}$ is the scattering matrix of the free space slab between the reference planes and the delay matrix $\mathbf{D}(z_{A2} - z_{A1})$ is defined as the $\mathbf{N}/2 \times \mathbf{N}/2$ diagonal matrix of the elements $d_{nn} = e^{-j\beta_n(z_{A2} - z_{A1})}$ with $1 \leq n \leq \mathbf{N}/2$. $\mathbf{F}^A$ elements are unitless.

Using $A_{Ab} = \langle S^{+A} | S^{+A} \rangle - \langle S^{+A} | (\mathbf{S}^{Ab})^\dagger \mathbf{S}^{Ab} | S^{+A} \rangle$, we can also rewrite the resonator's absorption formula (Eq. (19)) as:

$$A_A = \langle S^{+A} | S^{+A} \rangle - \langle S^{+A} | (\mathbf{S}^{Ab})^\dagger \mathbf{S}^{Ab} | S^{+A} \rangle - 2\omega \text{Im} [\langle \alpha | \mathbf{H}_A | \alpha \rangle]. \quad (25)$$

Moreover, writing the energy balance relations for Eqs. (21) and (23), and then, combining the results with Eq. (25), gives (Appendix B.2):

$$(\mathbf{F}^A)^\dagger \mathbf{F}^A = -\left[\mathbf{H}_A \mathbf{P}_A + (\mathbf{P}_A)^\dagger (\mathbf{H}_A)^\dagger\right] \approx 2\mathbf{\Gamma}_A^r, \quad (26)$$

$$\mathbf{H}_A \mathbf{K}^A = -(\mathbf{F}^A)^\dagger \mathbf{S}^{Ab}. \quad (27)$$

where $\mathbf{\Gamma}_A^r = \left[x_{ij} = \Gamma_{Ai}^r \delta_{ij}\right]_{\mathbf{M} \times \mathbf{M}}$. The approximation in Eq. (26) is valid under the mode orthogonality condition. In this scenario, Eq. (26) translates into $\sum_n |f_{nm}^A|^2 = 2\Gamma_{Am}^r$, implying that the radiative decay rate of the m^{th} mode can be broken as $\Gamma_{Am}^r = \sum_n \Gamma_{Am}^{r,n}$, where $\Gamma_{Am}^{r,n} = |f_{nm}^A|^2 / 2$ is the n^{th} port contribution to Γ_{Am}^r . When the resonator is lossless and its modes are orthogonal, $\mathbf{S}^{Ab}$ becomes unitary²²⁷ and Eq. (10) gives $\mathbf{H}_A = \mathbf{I}$. Under these conditions, combining Eqs. (26) and (27) leads to $\mathbf{K}^A (\mathbf{K}^A)^\dagger = 2\mathbf{\Gamma}_A^r$, consistent with the conventional TCMT models^{234, 236, 237, 239}.

3.2.5. Resonator perturbation and basis set generalization

Suppose that A' is a resonator with the dielectric function $\varepsilon_{A'} = \varepsilon_A + \delta\varepsilon$ where ε_A is the unperturbed resonator's dielectric function and $\delta\varepsilon$ represents a small dielectric function modification inside the resonator or in its proximity (Figure 3.1(c)). By assuming that the unperturbed resonator's modes can expand the scattered fields in $\delta\varepsilon \neq 0$ region, one can obtain (Appendix B.2):

$$\delta\mathbf{H} = \mathbf{H}_{A'} - \mathbf{H}_A = \frac{1}{4} \left[v_{mn} = \iiint_{\delta\varepsilon \neq 0} \delta\varepsilon \tilde{E}_{An} \cdot \tilde{E}_{Am}^* d^3r + \iiint_{\delta V} \mu_0 (\tilde{H}_{Am} \cdot \tilde{H}_{An}^*) d^3r \right]_{\mathbf{M} \times \mathbf{M}} \quad (28)$$

$$\delta\mathbf{P} = \mathbf{P}_{A'} - \mathbf{P}_A = \mathbf{H}_A^{-1} \left[v_{mn} = \left(-\frac{j\omega}{4}\right) \iiint_{\delta\varepsilon \neq 0} \delta\varepsilon \tilde{E}_{An} \cdot \tilde{E}_{Am}^* d^3r \right]_{\mathbf{M} \times \mathbf{M}}, \quad (29)$$

$$\delta\mathbf{K} = \mathbf{K}^{A'} - \mathbf{K}^A = \mathbf{H}_A^{-1} \left[v_{mn} = \left(-\frac{j\omega}{4}\right) \iiint_{\delta\varepsilon \neq 0} \delta\varepsilon \cdot T_{Ab} \left(E_n^w e^{-j\beta_n(z-z_{q_n})}\right) \cdot \tilde{E}_{Am}^* d^3r \right]_{\mathbf{M} \times \mathbf{N}}, \quad (30)$$

$$\delta\mathbf{F} = \mathbf{F}^{A'} - \mathbf{F}^A = \mathbf{S}^{Af} \left[v_{nm} = \left(-\frac{j\omega}{4}\right) \iiint_{\delta\varepsilon \neq 0} \delta\varepsilon \cdot \tilde{E}_{Am} \cdot (E_n^w)^* e^{j\beta_n(z-z_{q_n})} d^3r \right]_{\mathbf{N} \times \mathbf{M}}, \quad (31)$$

where $\delta\mathbf{V}$ is part of $\delta\mathcal{E}$ that lies outside the unperturbed resonator. Eq. (29) indicates that the perturbation $\delta\mathcal{E}$ could couple the different modes, thereby making $\mathbf{P}_A$ non-diagonal. Eqs. (28)-(31) generalize the classic perturbation theory of closed cavities^{227, 232, 273}, which is based on conjugated field products, to open resonators. Unlike the closed resonators, perturbation analysis of open resonators has commonly been based on unconjugated field products^{233, 248, 265-269}.

3.2.6. Signal flow graph, characteristic equation, and scattering matrix

In control engineering, Eqs. (21) and (23) constitute a set of linear state-space equations²⁷⁴ with $|\alpha\rangle$ as the state vector that characterizes the system (resonator A) state and $|S^{-A}\rangle$ as the output vector. A more intuitive way to express the state-space equations is to graphically represent the dynamics they describe using signal flow graphs (SFG)^{227, 274}. To do so, we first rewrite Eq. (21) as:

$$|\dot{\alpha}\rangle = \mathbf{P}_A |\alpha\rangle + \mathbf{K}^A |S^{+A}\rangle, \quad (32a)$$

$$|\alpha\rangle = \frac{1}{j\omega} |\dot{\alpha}\rangle. \quad (32b)$$

Then, by considering $|\alpha\rangle$ and $|\dot{\alpha}\rangle$ as the nodes, we get the SFG shown in Figure 3.1(d). Here, the $\mathbf{P}_A$ arrow is the feedback, and the loop created by the $\mathbf{P}_A$ and the $\frac{1}{j\omega}$ arrows represents the resonant energy circulation inside the resonator. SFGs are very useful for representing and interpreting the electromagnetic interaction dynamics that the CM equations describe. They are also powerful tools to solve the CM equations using Mason's theorem²⁷⁴.

From Eq. (21), we can calculate the amplitude vector of resonator A as follows:

$$|\alpha\rangle = (j\omega\mathbf{I} - \mathbf{P}_A)^{-1} \mathbf{K}^A |S^{+A}\rangle. \quad (33)$$

Equation (33) reveals that we can acquire the resonator poles using the eigenvalue equation $|\mathbf{S}\mathbf{I} - \mathbf{P}_A| = 0$, called the *characteristic equation*²⁷⁴, where $S = j\omega$. Solving the characteristic

equation for ω gives the complex resonance frequencies of the resonator. When the pole matrix is diagonal, the modes are uncoupled and each mode is associated with a single resonance frequency. In contrast, modes' coupling makes their resonance frequencies inseparable.

By plugging Eq. (33) into Eqs. (23) and (25), we can calculate the output power wave vector and the absorption of the resonator. Moreover, by combining Eq. (33) with Eqs. (23) and (27), we can obtain the following expression for the scattering matrix of the resonator:

$$\mathbf{S}^A = \left[\mathbf{I} - \mathbf{F}^A (j\omega\mathbf{I} - \mathbf{P}_A)^{-1} \mathbf{H}_A^{-1} (\mathbf{F}^A)^\dagger \right] \mathbf{S}^{Ab}. \quad (34)$$

An alternative way to obtain Eqs. (33) and (34) is applying Mason's theorem²⁷⁴ to the SFG in Figure 3.1(d).

3.2.7. Parameter retrieval by reverse engineering

The application of Eqs. (21), (23), and (25) requires knowledge of complex resonance frequencies (including the decay rates) and coupling coefficients (input and output) as a pre-requisite. To obtain the complex resonance frequencies, one must solve Maxwell's equations with the resonator boundary conditions²³³. Also, to obtain the coupling coefficients, one must calculate the overlap integrals in Eqs. (22) and (24) from the field distributions of the resonator and the waveguide modes. No matter one performs these calculations analytically or numerically, the computational cost and complexity of such a direct approach is very high. Furthermore, it might be challenging to get the field profiles in experimental situations. To circumvent these difficulties, we introduce two lemmas to acquire the BBCMT parameters of the resonator modes (e.g., m^{th} mode) via reverse-engineering the far-field spectral data. The detailed derivation process of these lemmas can be found in Appendix B.2.

Kappa-estimation lemma. Suppose that resonator A is made of lossy materials, and its absorption spectra (normalized to incident power) around $\omega = \Omega_{Am}$ is known when it is excited from different ports. The absorption spectra around $\omega = \Omega_{Am}$ typically have a Lorentzian-like lineshape superimposed over a non-Lorentzian background. For each port (e.g., n^{th} port), we acquire the Lorentzian lineshape by the background-subtraction (Figure 3.1(e)), from which we can determine

the resonance frequency Ω_{Am} , the full width at half maximum (FWHM) $\Delta\omega_{Am}$, and the peak absorption ($0 < A_{mn}^{\max} \leq 1$) of the m^{th} mode. Ω_{Am} and $\Delta\omega_{Am}$ are independent of the excitation port. Then, we can estimate the m^{th} mode's non-radiative decay rate and the input-coupling coefficients as:

$$\Gamma_{Am}^{nr} = \frac{\Delta\omega_{Am}}{4}(1 \pm \Lambda), \quad (35)$$

$$|K_{mn}^A|^2 = \frac{\Delta\omega_{Am}}{2} \frac{A_{mn}^{\max}}{1 \pm \Lambda}, \quad (36)$$

with $\Lambda = \sqrt{1 - \sum_n A_{nn}^{\max}}$. Eqs. (35) and (36) give us two solution sets. Moreover, the lemma does not directly give us the phase angles of the input-coupling coefficients. We can determine the valid solution set and the phase angles by fitting the scattering spectra. An alternative way is to look at the dominant multipoles and the radiation pattern of the mode. Once the mode input-coupling coefficients are found, its output coupling coefficients can be obtained from Eq. (27).

F-estimation lemma. Suppose that the m^{th} mode's FWHM ($\Delta\omega_{Am}$) and the resonator scattering matrix ($\mathbf{S}^A$) at $\omega = \Omega_{Am}$ are known. One can then estimate the output-coupling coefficients and non-radiative decay rate of the m^{th} mode as follows:

$$\begin{bmatrix} |f_{1m}^A|^2 & \dots & f_{1m}^A (f_{Nm}^A)^* \\ \vdots & \ddots & \vdots \\ f_{Nm}^A (f_{1m}^A)^* & \dots & |f_{Nm}^A|^2 \end{bmatrix} \approx \frac{\Delta\omega_{Am}}{2} \left[\mathbf{I} - \mathbf{S}^A (\mathbf{S}^{Ab})^{-1} \right]_{\omega=\Omega_{Am}}, \quad (37)$$

$$\Gamma_{Am}^{nr} \approx \frac{\Delta\omega_{Am}}{2} - \sum_n \frac{|f_{nm}^A|^2}{2} = \frac{\Delta\omega_{Am}}{2} \left[1 - \frac{1}{2} \text{Tr} \left(\mathbf{I} - \mathbf{S}^A (\mathbf{S}^{Ab})^{-1} \right) \right]_{\omega=\Omega_{Am}}. \quad (38)$$

In Eq. (37), real parts of the diagonal elements of the matrix $\frac{\Delta\omega_{Am}}{2} \left[\mathbf{I} - \mathbf{S}^A (\mathbf{S}^{Ab})^{-1} \right]_{\omega=\Omega_{Am}}$ approximately give us the magnitudes for the output coupling coefficients of the m^{th} mode. We

can estimate the phase angles of the output coupling coefficients using the methods introduced to achieve the same purpose for the Kappa-estimation lemma. After determining the mode output-coupling coefficients, its input-coupling coefficients can be estimated from Eq. (27). Unlike the Kappa-estimation lemma, the F-estimation lemma gives a single solution and does not require the resonator to be lossy. However, this improved versatility is counterbalanced by a higher computational cost as one should first acquire the resonator scattering matrix ($\mathbf{S}^A$) at $\omega = \Omega_{Am}$ to use the F-estimation lemma. $\mathbf{S}^A$ can be acquired by exciting the resonator from each port and measuring the fields scattered into the other ports using numerical simulations or experimental measurements (Figure 3.1(f)).

In summary, section 3.2 established the BBCMT framework for a single resonator from Maxwell's equations for the two scenarios that the source is inside or outside the resonator. We then developed the background perturbation method to capture the non-resonant responses created by an external source and truncate the BBCMT equations by eliminating the non-principal modes. Afterward, the resonator port concept was introduced. We also discussed the subjects of resonator perturbation, basis set generalization, signal flow graph, characteristic equation, and scattering matrix in the BBCMT context. Finally, we introduced the Kappa-estimation and F-estimation lemmas to reverse-engineer a resonator's BBCMT parameters from its far-field spectral response. BBCMT formulations are also helpful for analyzing periodic structures (e.g., nanohole arrays²⁷⁹) under plane wave excitation. Although periodic structures are waveguides with Bloch-type modes²³⁷, an incident plane wave can fix the Bloch vector to make the boundary conditions quasi-3d, thus turning the periodic structure into a quasi-resonator²⁵⁹. Coupling integrations can be done over one unit cell in this case.

3.3. BBCMT formulations for coupled resonators

In this section, we give a brief derivation of the BBCMT formulas for coupled resonators and discuss their potential impacts. In subsection 3.3.1, we derive the CM equations for a system of two coupled resonators. Then, we derive the system's stored energy, scattering, and absorption equations in subsection 3.3.2. Finally, in subsection 3.3.3, we introduce some approximations to simplify the previous subsections' formulations.

3.3.1. Loading effects on coupled resonators

Consider a coupled-resonator system composed of the resonators A and B (Figure 3.2(a)). The fields scattered from the coupled system can be decomposed into a summation of the fields scattered from each of the subsystem resonators as:

$$E^{sca} = E_A^{sca} + E_B^{sca}, \quad (39a)$$

$$H^{sca} = H_A^{sca} + H_B^{sca}, \quad (39b)$$

where E_A^{sca} and H_A^{sca} satisfy:

$$\nabla \times E_A^{sca} = -j\omega\mu_0 H_A^{sca}, \quad (40a)$$

$$\nabla \times H_A^{sca} = j\omega\epsilon_A E_A^{sca} + j\omega\Delta\epsilon_A (E^{inc} + E_B^{sca}), \quad (40b)$$

and, E_B^{sca} and H_B^{sca} satisfy:

$$\nabla \times E_B^{sca} = -j\omega\mu_0 H_B^{sca}, \quad (41a)$$

$$\nabla \times H_B^{sca} = j\omega\epsilon_B E_B^{sca} + j\omega\Delta\epsilon_B (E^{inc} + E_A^{sca}). \quad (41b)$$

ϵ_A/ϵ_B is the dielectric function when only resonator A/B is present and $\Delta\epsilon_A = \epsilon_A - \epsilon_{med}/\Delta\epsilon_B = \epsilon_B - \epsilon_{med}$. Eqs. (40) and (41) resemble Eqs. (11) but now each resonator is excited by the other one's scattered field beside the incident field (Figure 3.2(b)).

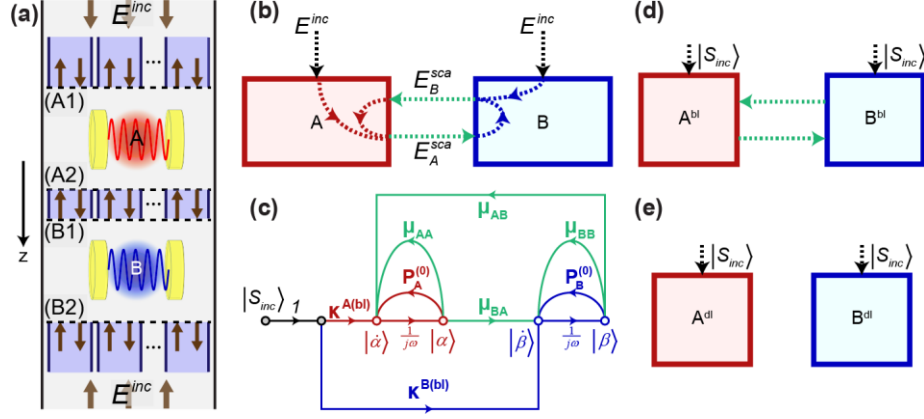


Figure 3.2. BBCMT model for the system of coupled resonators. (a) System of the coupled resonators A and B in the medium. (b) Diagram of energy circulation for the system of coupled resonators reveals the mutual loading effect between them. (c) The SFG for the system of the coupled resonators. Output-coupling of the system modes is not shown in the SFG for simplicity. (d, e) The equivalent scenarios of the coupled background-loaded resonators (d) and the decoupled-loaded resonators (e).

Back-and-forth scattering of fields between the coupled resonators creates new energy circulation routes for their modes, alongside the internal energy circulation routes which exist when the resonators are isolated. This situation is comparable to the self-induced back-action of dipoles in inhomogeneous environments⁵⁸ and modifies the resonance properties of both resonators. By providing an indirect route of interaction with the medium waveguide modes, resonators' coupling also modulates their input and output coupling properties. From Eqs. (40) and (41), and by following the Eq. (18) derivation procedure, we can obtain:

$$E_A^{sca} \approx E_{Ab}^{sca(0)} + \sum_m \alpha_m \tilde{E}_{Am}^{sca(0)} + \omega^2 \mu_0 \iiint_{\Delta \varepsilon_{Ab} \neq 0} G_{Ab}^E \cdot \Delta \varepsilon_{Ab} \cdot E_B^{sca} d^3 r', \quad (42a)$$

$$E_B^{sca} \approx E_{Bb}^{sca(0)} + \sum_k \beta_k \tilde{E}_{Bk}^{sca(0)} + \omega^2 \mu_0 \iiint_{\Delta \varepsilon_{Bb} \neq 0} G_{Bb}^E \cdot \Delta \varepsilon_{Bb} \cdot E_A^{sca} d^3 r', \quad (42b)$$

where $\varepsilon_{Ab}(\varepsilon_{Bb})$ denotes the background dielectric function of resonator A (B) and $\Delta \varepsilon_{Ab} = \varepsilon_{Ab} - \varepsilon_{med}$ ($\Delta \varepsilon_{Bb} = \varepsilon_{Bb} - \varepsilon_{med}$). Also, $E_{Ab}^{sca(0)}$, $\tilde{E}_{Am}^{sca(0)}$, $E_{Bb}^{sca(0)}$ and $\tilde{E}_{Bk}^{sca(0)}$ definitions are same as those of a single resonator in Eq. (18). The notation (0) in the superscripts is added to emphasize the belonging of these parameters to the single-resonator situation. The integral term on the right-hand side of Eq. (42a)/(42b) represents the scattering of E_B^{sca}/E_A^{sca} from the background of resonator A/B, respectively. Although these integral terms make Eqs. (42a) and (42b)

interdependent, one can decouple them through recursive calculations to obtain the following equations for E_A^{sca} and E_B^{sca} :

$$E_A^{sca} = E_{Ab}^{sca(e)} + E_{Bb}^{sca(o)} + \sum_m \alpha_m \tilde{E}_{Am}^{sca(e)} + \sum_k \beta_k \tilde{E}_{Bk}^{sca(o)}, \quad (43a)$$

$$E_B^{sca} = E_{Bb}^{sca(e)} + E_{Ab}^{sca(o)} + \sum_k \beta_k \tilde{E}_{Bk}^{sca(e)} + \sum_m \alpha_m \tilde{E}_{Am}^{sca(o)}, \quad (43b)$$

$$\text{where } E_{Ab}^{sca(e)} = \sum_{i=0}^{\infty} E_{Ab}^{sca(2i)}, E_{Ab}^{sca(o)} = \sum_{i=0}^{\infty} E_{Ab}^{sca(2i+1)}, \tilde{E}_{Am}^{sca(e)} = \sum_{i=0}^{\infty} \tilde{E}_{Am}^{sca(2i)} \text{ and } \tilde{E}_{Am}^{sca(o)} = \sum_{i=0}^{\infty} \tilde{E}_{Am}^{sca(2i+1)}$$

$$\text{with } E_{Ab}^{sca(2i)} = \omega^2 \mu_0 \iiint_{\Delta\epsilon_{Ab} \neq 0} G_{Ab}^E \cdot \Delta\epsilon_{Ab} \cdot E_{Ab}^{sca(2i-1)} d^3r, \text{ and } \tilde{E}_{Am}^{sca(2i)} = \omega^2 \mu_0 \iiint_{\Delta\epsilon_{Ab} \neq 0} G_{Ab}^E \cdot \Delta\epsilon_{Ab} \cdot \tilde{E}_{Am}^{sca(2i-1)} d^3r, \text{ for } i \geq 1,$$

$$\text{and } E_{Ab}^{sca(2i+1)} = \omega^2 \mu_0 \iiint_{\Delta\epsilon_{Bb} \neq 0} G_{Bb}^E \cdot \Delta\epsilon_{Bb} \cdot E_{Ab}^{sca(2i)} d^3r, \text{ and } \tilde{E}_{Am}^{sca(2i+1)} = \omega^2 \mu_0 \iiint_{\Delta\epsilon_{Bb} \neq 0} G_{Bb}^E \cdot \Delta\epsilon_{Bb} \cdot \tilde{E}_{Am}^{sca(2i)} d^3r, \text{ for } i \geq 0.$$

Similar expressions hold for $E_{Bb}^{sca(e)}$, $E_{Bb}^{sca(o)}$, $\tilde{E}_{Bk}^{sca(e)}$ and $\tilde{E}_{Bk}^{sca(o)}$. 0th order fields ($E_{Ab}^{sca(0)}$, $\tilde{E}_{Am}^{sca(0)}$, $E_{Bb}^{sca(0)}$, and $\tilde{E}_{Bk}^{sca(0)}$) account for the E^{inc} direct scattering from each resonator, while the higher-order scattering terms account for multiple back-and-forth scattering of the 0th order fields between the two background structures. Furthermore, $E_{Ab}^{sca(e)} + E_{Bb}^{sca(o)}$ and $E_{Bb}^{sca(e)} + E_{Ab}^{sca(o)}$ respectively represent the electric fields scattered by A and B background structures when they replace the resonators in the medium. This system is the collective background structure corresponding to $\epsilon_b = \epsilon_{med} + \Delta\epsilon_{Ab} + \Delta\epsilon_{Bb}$. The even and odd scattering terms in Eqs. (43) can be calculated in a step-wise manner from their definitions or by solving the integral equations deduced from their definitions:

$$E_{Ab}^{sca(e)} = E_{Ab}^{sca(0)} + \omega^2 \mu_0 \iiint_{\Delta\epsilon_{Ab} \neq 0} G_{Ab}^E \cdot \Delta\epsilon_{Ab} \cdot E_{Ab}^{sca(o)} d^3r = E_{Ab}^{sca(0)} + T_{Ab} \left(E_{Ab}^{sca(o)} \right) - E_{Ab}^{sca(o)}, \quad (44a)$$

$$E_{Ab}^{sca(o)} = \omega^2 \mu_0 \iiint_{\Delta\epsilon_{Bb} \neq 0} G_{Bb}^E \cdot \Delta\epsilon_{Bb} \cdot E_{Ab}^{sca(e)} d^3r = T_{Bb} \left(E_{Ab}^{sca(e)} \right) - E_{Ab}^{sca(e)}, \quad (44b)$$

$$\tilde{E}_{Am}^{sca(e)} = \tilde{E}_{Am}^{sca(0)} + \omega^2 \mu_0 \iiint_{\Delta\epsilon_{Ab} \neq 0} G_{Ab}^E \cdot \Delta\epsilon_{Ab} \cdot \tilde{E}_{Am}^{sca(o)} d^3r = \tilde{E}_{Am}^{sca(0)} + T_{Ab} \left(\tilde{E}_{Am}^{sca(o)} \right) - \tilde{E}_{Am}^{sca(o)}, \quad (44c)$$

$$\tilde{E}_{Am}^{sca(o)} = \omega^2 \mu_0 \iiint_{\Delta \varepsilon_{Bb} \neq 0} G_{Bb}^E \cdot \Delta \varepsilon_{Bb} \tilde{E}_{Am}^{sca(e)} d^3 r = T_{Bb} \left(\tilde{E}_{Am}^{sca(e)} \right) - \tilde{E}_{Am}^{sca(e)}, \quad (44d)$$

and similar expressions for $\tilde{E}_{Bb}^{sca(e)}$, $\tilde{E}_{Bb}^{sca(o)}$, $\tilde{E}_{Bk}^{sca(e)}$ and $\tilde{E}_{Bk}^{sca(o)}$. Here, T_{Ab} and T_{Bb} functions are defined the same as in Eq. (17). By plugging Eq. (43b) and its magnetic counterpart into Eqs. (40), and then following the Eq. (13) derivation procedure, we obtain the CM equation for resonator A:

$$\begin{aligned} \mathbf{H}_A(\omega)(j\omega \mathbf{I} - \mathbf{P}_A)|\alpha\rangle = & -\frac{j\omega}{4} \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} (\varepsilon_A - \varepsilon_{Ab}) T_{Ab} \left(\mathbf{E}^{inc} + \mathbf{E}_{Bb}^{sca(e)} + \mathbf{E}_{Ab}^{sca(o)} \right) \cdot |\tilde{\mathbf{E}}_A^*\rangle d^3 r \\ & -\frac{j\omega}{4} \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} (\varepsilon_A - \varepsilon_{Ab}) T_{Ab} \left(\sum_m \alpha_m \tilde{\mathbf{E}}_{Am}^{sca(o)} \right) \cdot |\tilde{\mathbf{E}}_A^*\rangle d^3 r \\ & -\frac{j\omega}{4} \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} (\varepsilon_A - \varepsilon_{Ab}) T_{Ab} \left(\sum_k \beta_k \tilde{\mathbf{E}}_{Bk}^{sca(e)} \right) \cdot |\tilde{\mathbf{E}}_A^*\rangle d^3 r. \end{aligned} \quad (45)$$

From Eqs. (44), we can write $T_{Ab} \left(\mathbf{E}^{inc} + \mathbf{E}_{Bb}^{sca(e)} + \mathbf{E}_{Ab}^{sca(o)} \right) = \mathbf{E}^{inc} + \mathbf{E}_{Ab}^{sca(e)} + \mathbf{E}_{Ab}^{sca(o)} + \mathbf{E}_{Bb}^{sca(e)} + \mathbf{E}_{Bb}^{sca(o)}$ which is the total electric field created by the collective background structure. Thus, this term can be rewritten as $T_b(\mathbf{E}^{inc}) = \mathbf{E}^{inc} + \omega^2 \mu_0 \iiint_{\Delta \varepsilon_b \neq 0} G_b^E \cdot \Delta \varepsilon_b \cdot \mathbf{E}^{inc} d^3 r$ where G_b^E is the electric dyadic Green's

function of the collective background structure. Furthermore, Eqs. (44) and the definitions of

different scattering terms in (43) give $T_{Ab} \left(\tilde{\mathbf{E}}_{Am}^{sca(o)} \right) = \sum_{i=1}^{\infty} \tilde{\mathbf{E}}_{Am}^{sca(i)}$ and $T_{Ab} \left(\tilde{\mathbf{E}}_{Bk}^{sca(e)} \right) = \sum_{i=0}^{\infty} \tilde{\mathbf{E}}_{Bk}^{sca(i)}$. By

then expanding the incident electric field as $\mathbf{E}^{inc} = \sum_i S_{A1,i}^{+A} \mathbf{E}_i^w e^{-j\beta_i(z-z_{A1})} + \sum_l S_{B2,l}^{+B} \mathbf{E}_l^w e^{-j\beta_l(z-z_{B2})}$,

where $\beta_i > 0$ and $\beta_l < 0$, one can express Eq. (45) based on the system ports as:

$$j\omega|\alpha\rangle = \left(\mathbf{P}_A^{(0)} + \boldsymbol{\mu}_{AA} \right) |\alpha\rangle + \mathbf{K}^{A(b)} |S^{+T}\rangle + \boldsymbol{\mu}_{AB} |\beta\rangle, \quad (46)$$

where $\mathbf{P}_A^{(0)}$ is similar to that in Eq. (21) and $|S^{+T}\rangle = \begin{bmatrix} |S_{A1}^{+A}\rangle \\ |S_{B2}^{+B}\rangle \end{bmatrix}$ denotes the input power wave vector

for the collective system of resonators. Moreover, $\boldsymbol{\mu}_{AA}$, $\mathbf{K}^{A(b)}$ and $\boldsymbol{\mu}_{AB}$ are defined as:

$$\boldsymbol{\mu}_{AA} = \sum_{i=1}^{\infty} \mathbf{H}_A^{-1} \left[x_{mn} = \left(-\frac{j\omega}{4} \right) \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} (\varepsilon_A - \varepsilon_{Ab}) \tilde{E}_{An}^{sca(i)} \tilde{E}_{Am}^* d^3r \right]_{\mathbf{M} \times \mathbf{M}}, \quad (47)$$

$$\mathbf{K}^{A(bi)} = [\mathbf{K}_{A1}^{A(bi)} \mathbf{K}_{B2}^{A(bi)}] = \mathbf{H}_A^{-1} \left[v_{mn} = \left(-\frac{j\omega}{4} \right) \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} (\varepsilon_A - \varepsilon_{Ab}) T_b \left(E_n^w e^{-j\beta_n(z-z_{qn})} \right) \tilde{E}_{Am}^* d^3r \right]_{\mathbf{M} \times \mathbf{N}}, \quad (48)$$

$$\boldsymbol{\mu}_{AB} = \sum_{i=0}^{\infty} \mathbf{H}_A^{-1} \left[x_{mk} = \left(-\frac{j\omega}{4} \right) \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} (\varepsilon_A - \varepsilon_{Ab}) \tilde{E}_{Bk}^{sca(i)} \tilde{E}_{Am}^* d^3r \right]_{\mathbf{M} \times \mathbf{K}}, \quad (49)$$

with $\mathbf{K}$ being the number of resonator B modes and $q_n = A1, B2$ for $\beta_n > 0$ and $\beta_n < 0$, respectively. $\boldsymbol{\mu}_{AA}$ and $\mathbf{K}^{A(bi)}$ denote the self-coupling and modified input-coupling matrices of resonator A, respectively. These matrices capture the modification of the input-coupling and resonance behavior for resonator A due to scattering from resonator B background. The B-to-A cross-coupling matrix $\boldsymbol{\mu}_{AB}$ captures the energy transfer from resonator B modes to resonator A modes. Both $\boldsymbol{\mu}_{AA}$ and $\boldsymbol{\mu}_{AB}$ have the units of inverse time. Please note that the summation index in Eq. (47) starts from $i = 1$ while in Eq. (49) starts from $i = 0$. This shows that, generally, self-coupling is a higher order process than cross-coupling. By decomposing $\tilde{E}_{An}^{sca(i)}$ in Eq. (47) and $\tilde{E}_{Bk}^{sca(i)}$ in Eq. (49) into near-field (non-propagating) and radiative (propagating) components, one can also break $\boldsymbol{\mu}_{AA}$ and $\boldsymbol{\mu}_{AB}$ into near-field and radiative components as $\boldsymbol{\mu}_{AA} = \boldsymbol{\mu}_{AA}^n + \boldsymbol{\mu}_{AA}^r$ and $\boldsymbol{\mu}_{AB} = \boldsymbol{\mu}_{AB}^n + \boldsymbol{\mu}_{AB}^r$, respectively. Parallel to resonator A, we can obtain the CM equation of resonator B as follows:

$$j\omega|\beta\rangle = (\mathbf{P}_B^{(0)} + \boldsymbol{\mu}_{BB})|\beta\rangle + \mathbf{K}^{B(bi)}|S^{+T}\rangle + \boldsymbol{\mu}_{BA}|\alpha\rangle, \quad (50)$$

where $\mathbf{P}_B^{(0)}$, $\boldsymbol{\mu}_{BB}$, $\mathbf{K}^{B(bi)}$ and $\boldsymbol{\mu}_{BA}$ are defined similarly as Eqs. (47)-(49). The SFG in Figure 3.2(c) visualizes the Eqs. (46) and (50) dynamics. The SFG reveals that in addition to the original feedback arrows $\mathbf{P}_A^{(0)}$ and $\mathbf{P}_B^{(0)}$, resonators A and B have the additional feedback branches $\boldsymbol{\mu}_{AA}$ and $\boldsymbol{\mu}_{BB}$, respectively. Moreover, their input-coupling matrices have changed from $\mathbf{K}^{A(0)}$ and $\mathbf{K}^{B(0)}$ (i.e., those of the isolated resonators) to $\mathbf{K}^{A(bi)}$ and $\mathbf{K}^{B(bi)}$, respectively. Resonators' coupling can be

interpreted as their mutual loading, just as cascaded circuit networks²⁸⁰. We define A^{bl} , the background-loaded resonator A, as the resonator with the pole matrix $\mathbf{P}_A^{(\text{bl})} = \mathbf{P}_A^{(0)} + \boldsymbol{\mu}_{AA}$ and the input-coupling matrix $\boldsymbol{\kappa}^{A(\text{bl})}$. A^{bl} is a black-box that captures the loading effects on resonator A due to non-resonant and non-principal (modes) scattering from resonator B. A^{bl} can also be viewed as a Fabry-Perot-like resonator with resonator A and the background structure of resonator B as its end mirrors. Unlike $\mathbf{P}_A^{(0)}$, the matrix $\mathbf{P}_A^{(\text{bl})}$ is generally frequency-dependent and non-diagonal, as a result of which, each A^{bl} mode associates with multiple resonance frequencies. When resonator B has a free space background (negligible non-resonant and non-principal scattering), we get $\mathbf{P}_A^{(\text{bl})} = \mathbf{P}_A^{(0)}$, $\boldsymbol{\kappa}_{A1}^{A(\text{bl})} = \boldsymbol{\kappa}_{A1}^{A(0)}$, and $\boldsymbol{\kappa}_{B2}^{A(\text{bl})} = \boldsymbol{\kappa}_{A2}^{A(0)} \mathbf{D}(Z_{B2} - Z_{A2}) = \boldsymbol{\kappa}_{B2}^{A(0)}$. Hence, in this scenario, A^{bl} becomes equivalent to A and only the second reference plane changes from A2 to B2. B^{bl} , the background-loaded resonator B, can be defined the same as A^{bl} .

Besides the background-loading effects, the coupling terms $\boldsymbol{\mu}_{AB}$ and $\boldsymbol{\mu}_{BA}$ modify each resonator's input-coupling and resonance behaviors by creating extra self-coupling and input-coupling channels. As Figure 3.2(c) manifests, the extra self-coupling channel for resonator A includes $\boldsymbol{\mu}_{BA}$, $1/j\omega$ (blue) and $\boldsymbol{\mu}_{AB}$ arrows, and for resonator B, it includes $\boldsymbol{\mu}_{AB}$, $1/j\omega$ (red) and $\boldsymbol{\mu}_{BA}$ arrows. Moreover, the extra input-coupling route for resonator A includes $\boldsymbol{\kappa}^{B(\text{L})}$, $1/j\omega$ (blue) and $\boldsymbol{\mu}_{AB}$ arrows, and for resonator B, it includes $\boldsymbol{\kappa}^{A(\text{L})}$, $1/j\omega$ (red) and $\boldsymbol{\mu}_{BA}$ arrows. The input-coupling and resonance behavior modifications due to $\boldsymbol{\mu}_{AB}$ and $\boldsymbol{\mu}_{BA}$ represent the resonant loading effects of the coupled resonators due to interaction of their principal modes. The background and resonant loading effects become more apparent by decoupling Eqs. (46) and (50):

$$j\omega|\alpha\rangle = \left[\mathbf{P}_A^{(\text{bl})} + \boldsymbol{\mu}_{AB} (j\omega\mathbf{I} - \mathbf{P}_B^{(\text{bl})})^{-1} \boldsymbol{\mu}_{BA} \right] |\alpha\rangle + \left[\boldsymbol{\kappa}^{A(\text{bl})} + \boldsymbol{\mu}_{AB} (j\omega\mathbf{I} - \mathbf{P}_B^{(\text{bl})})^{-1} \boldsymbol{\kappa}^{B(\text{bl})} \right] |S^{+T}\rangle, \quad (51a)$$

$$j\omega|\beta\rangle = \left[\mathbf{P}_B^{(\text{bl})} + \boldsymbol{\mu}_{BA} (j\omega\mathbf{I} - \mathbf{P}_A^{(\text{bl})})^{-1} \boldsymbol{\mu}_{AB} \right] |\beta\rangle + \left[\boldsymbol{\kappa}^{B(\text{bl})} + \boldsymbol{\mu}_{BA} (j\omega\mathbf{I} - \mathbf{P}_A^{(\text{bl})})^{-1} \boldsymbol{\kappa}^{A(\text{bl})} \right] |S^{+T}\rangle. \quad (51b)$$

Corresponding to Eq. (51a), we define A^{dl} , the decoupled-loaded resonator A, as the resonator with the pole matrix $\mathbf{P}_A^{(\text{dl})} = \mathbf{P}_A^{(\text{bl})} + \boldsymbol{\mu}_{AB} (j\omega\mathbf{I} - \mathbf{P}_B^{(\text{bl})})^{-1} \boldsymbol{\mu}_{BA}$ and the input-coupling matrix $\boldsymbol{\kappa}^{A(\text{dl})} = \boldsymbol{\kappa}^{A(\text{bl})} + \boldsymbol{\mu}_{AB} (j\omega\mathbf{I} - \mathbf{P}_B^{(\text{bl})})^{-1} \boldsymbol{\kappa}^{B(\text{bl})}$. A^{dl} is a black-box that captures the total loading effects of resonator B on resonator A. We define the resonator B^{dl} the same as A^{dl} . A-B, $A^{\text{bl}}\text{-}B^{\text{bl}}$, and $A^{\text{dl}}\text{-}B^{\text{dl}}$ systems have similar mode amplitudes and resonance behaviors (Figure 3.2(d-e)). However, unlike A and B, A^{bl} and B^{bl} only resonantly load each other while A^{dl} and B^{dl} do not load each other at all.

Upon coupling, the resonance frequencies of the resonators A and B become inseparable. From Eqs. (46) and (50), one can obtain the characteristic equation for the collective system of resonators as:

$$\left| j\omega\mathbf{I} - (\mathbf{P}^{(0)} + \boldsymbol{\mu}) \right| = 0, \quad (52)$$

where $\mathbf{P}^{(0)} = \begin{bmatrix} \mathbf{P}_A^{(0)} & \mathbf{0} \\ \mathbf{0} & \mathbf{P}_B^{(0)} \end{bmatrix}$ and $\boldsymbol{\mu} = \begin{bmatrix} \boldsymbol{\mu}_{AA} & \boldsymbol{\mu}_{AB} \\ \boldsymbol{\mu}_{BA} & \boldsymbol{\mu}_{BB} \end{bmatrix}$. The resonance frequencies can also be found by solving the characteristic equations for A^{dl} and B^{dl} .

3.3.2. Energy, scattering, and absorption of the coupled resonators

From Eqs. (39) and (43), and by following the Eq. (23) derivation procedure, one obtains the output power wave vector for the collective system of the resonators:

$$\left| S^{-T} \right\rangle = \mathbf{S}^b \left| S^{+T} \right\rangle + \mathbf{F} \begin{bmatrix} |\alpha\rangle \\ |\beta\rangle \end{bmatrix}, \quad (53)$$

where $\left| S^{-T} \right\rangle = \begin{bmatrix} \left| S_{A1}^{-A} \right\rangle \\ \left| S_{B2}^{-B} \right\rangle \end{bmatrix}$, $\mathbf{S}^b$ is the scattering matrix of the collective background structure and

$\mathbf{F} = \begin{bmatrix} \mathbf{F}^A & \mathbf{F}^B \end{bmatrix}$ is the collective output-coupling matrix with:

$$\begin{aligned}
\mathbf{F}^A &= \begin{bmatrix} \mathbf{F}_{A1}^A \\ \mathbf{F}_{B2}^A \end{bmatrix} = \mathbf{S}^f \left[v_{nm} = \left(-\frac{j\omega}{4} \right) \iiint_{\text{space}} \left[\Delta\epsilon_A \cdot (\tilde{E}_{Am} + \tilde{E}_{Am}^{sca(o)}) + \Delta\epsilon_B \tilde{E}_{Am}^{sca(e)} \right] \cdot (E_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \right]_{N \times M} \\
&= \begin{bmatrix} \mathbf{F}_{A1}^{A(0)} \\ \mathbf{F}_{B2}^{A(0)} \end{bmatrix} + \mathbf{S}^f \left[v_{nm} = \left(-\frac{j\omega}{4} \right) \iiint_{\Delta\epsilon_A \neq 0} \Delta\epsilon_A \cdot \tilde{E}_{Am}^{sca(o)} \cdot (E_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \right]_{N \times M} \\
&\quad + \mathbf{S}^f \left[v_{nm} = \left(-\frac{j\omega}{4} \right) \iiint_{\Delta\epsilon_B \neq 0} \Delta\epsilon_B \cdot \tilde{E}_{Am}^{sca(e)} \cdot (E_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \right]_{N \times M},
\end{aligned} \tag{54a}$$

$$\begin{aligned}
\mathbf{F}^B &= \begin{bmatrix} \mathbf{F}_{A1}^B \\ \mathbf{F}_{B2}^B \end{bmatrix} = \mathbf{S}^f \left[v_{nk} = \left(-\frac{j\omega}{4} \right) \iiint_{\text{space}} \left[\Delta\epsilon_B \cdot (\tilde{E}_{Bk} + \tilde{E}_{Bk}^{sca(o)}) + \Delta\epsilon_A \tilde{E}_{Bk}^{sca(e)} \right] \cdot (E_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \right]_{N \times K} \\
&= \begin{bmatrix} \mathbf{F}_{A1}^{B(0)} \\ \mathbf{F}_{B2}^{B(0)} \end{bmatrix} + \mathbf{S}^f \left[v_{nk} = \left(-\frac{j\omega}{4} \right) \iiint_{\Delta\epsilon_B \neq 0} \Delta\epsilon_B \cdot \tilde{E}_{Bk}^{sca(o)} \cdot (E_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \right]_{N \times K} \\
&\quad + \mathbf{S}^f \left[v_{nk} = \left(-\frac{j\omega}{4} \right) \iiint_{\Delta\epsilon_A \neq 0} \Delta\epsilon_A \cdot \tilde{E}_{Bk}^{sca(e)} \cdot (E_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \right]_{N \times K},
\end{aligned} \tag{54b}$$

where $\mathbf{S}^f$ is the scattering matrix of the free space slab between A1 and B2 reference planes and q_n definition is the same as in Eq. (48). Eq. (53) has a similar form as its single resonator counterpart (Eq. (23)).

To find the collective stored energy and absorption of the coupled resonators, we assume that the high-order resonant fields inside each resonator are negligible (weak-coupling regime). Then, by following the Eqs. (8), (19), and (25) derivation procedures, we can obtain:

$$W \approx \text{Re}[\langle \alpha | \mathbf{H}_A | \alpha \rangle] + \text{Re}[\langle \beta | \mathbf{H}_B | \beta \rangle], \tag{55}$$

$$\begin{aligned}
A &\approx A_b - 2\omega \text{Im}[\langle \alpha | \mathbf{H}_A | \alpha \rangle] - 2\omega \text{Im}[\langle \beta | \mathbf{H}_B | \beta \rangle] \\
&= \langle S_{inc} | S_{inc} \rangle - \langle S_{inc} | (\mathbf{S}^b)^\dagger \mathbf{S}^b | S_{inc} \rangle - 2\omega \text{Im}[\langle \alpha | \mathbf{H}_A | \alpha \rangle] - 2\omega \text{Im}[\langle \beta | \mathbf{H}_B | \beta \rangle],
\end{aligned} \tag{56}$$

with A_b being the absorption of the collective background structure. Eqs. (51)-(56) indicate that in the weak-coupling regime, the resonators' Hamiltonian matrices and non-radiative decay properties are preserved while their resonance and input/output-coupling properties get altered. This result can be interpreted as the mutual Purcell effect⁵⁸ of the coupled resonators on each other. Eqs. (51)-(56) further reveal that upon mutual coupling of resonators, both the non-resonant

and resonant loading phenomena are responsible for the modifications of each resonator's resonance and input/output coupling behaviors. Non-resonant loading effects are not captured by the common LCAO-type (LCAO: linear combination of atomic orbitals) approaches of QNM coupling analysis^{264, 271}.

The different coupling matrices are not entirely independent of each other. From Eqs. (46), (50), (53), and (56), and by following the Eq. (26) derivation procedure, one can deduce (Appendix B.3):

$$\mathbf{F}^\dagger \mathbf{F} \approx 2\mathbf{\Gamma}^r - (\boldsymbol{\mu} + \boldsymbol{\mu}^\dagger), \quad (57)$$

where $\mathbf{\Gamma}^r = \begin{bmatrix} \mathbf{\Gamma}_A^r & \mathbf{0} \\ \mathbf{0} & \mathbf{\Gamma}_B^r \end{bmatrix}$. In the weak-coupling regime, Eq. (57) can be split into two simpler equations (Appendix B.3):

$$\boldsymbol{\mu}^r + (\boldsymbol{\mu}^r)^\dagger \approx 2\mathbf{\Gamma}^r - \mathbf{F}^\dagger \mathbf{F}, \quad (58a)$$

$$\boldsymbol{\mu}^n + (\boldsymbol{\mu}^n)^\dagger = 0, \quad (58b)$$

where $\boldsymbol{\mu}^r = \begin{bmatrix} \boldsymbol{\mu}_{AA}^r & \boldsymbol{\mu}_{AB}^r \\ \boldsymbol{\mu}_{BA}^r & \boldsymbol{\mu}_{BB}^r \end{bmatrix}$ and $\boldsymbol{\mu}^n = \begin{bmatrix} \boldsymbol{\mu}_{AA}^n & \boldsymbol{\mu}_{AB}^n \\ \boldsymbol{\mu}_{BA}^n & \boldsymbol{\mu}_{BB}^n \end{bmatrix}$. Eqs. (57) and (58) are a generalization to the coupling coefficients' relationship in the TCMT formulation of coupled resonators²³⁴.

3.3.3. Non-resonant background approximation

Suppose that the resonators do not overlap in the propagation direction of waveguide modes (Figure 3.2(a)) and their background structures are off-resonant in the operating frequency range. The latter condition allows approximating that the background structures scatter the propagating incident fields as propagating fields, and evanescent incident fields as evanescent fields. Then, based on the system geometry and from Eqs. (23), (43) and (44), one can write the following equations for the scattering of fields between the two resonators:

$$\begin{bmatrix} |S_{A1}^{-A}\rangle \\ |S_{A2}^{-A}\rangle \end{bmatrix} = \mathbf{S}^{Ab} \begin{bmatrix} |S_{A1}^{+A}\rangle \\ |S_{A2}^{+A}\rangle \end{bmatrix} + \begin{bmatrix} \mathbf{F}_{A1}^{A(0)} \\ \mathbf{F}_{A2}^{A(0)} \end{bmatrix} |\alpha\rangle = \begin{bmatrix} \mathbf{S}_{11}^{Ab} & \mathbf{S}_{12}^{Ab} \\ \mathbf{S}_{21}^{Ab} & \mathbf{S}_{22}^{Ab} \end{bmatrix} \begin{bmatrix} |S_{A1}^{+A}\rangle \\ |S_{A2}^{+A}\rangle \end{bmatrix} + \begin{bmatrix} \mathbf{F}_{A1}^{A(0)} \\ \mathbf{F}_{A2}^{A(0)} \end{bmatrix} |\alpha\rangle, \quad (59a)$$

$$\begin{bmatrix} |S_{B1}^{-B}\rangle \\ |S_{B2}^{-B}\rangle \end{bmatrix} = \mathbf{S}^{Bb} \begin{bmatrix} |S_{B1}^{+B}\rangle \\ |S_{B2}^{+B}\rangle \end{bmatrix} + \begin{bmatrix} \mathbf{F}_{B1}^{B(0)} \\ \mathbf{F}_{B2}^{B(0)} \end{bmatrix} |\beta\rangle = \begin{bmatrix} \mathbf{S}_{11}^{Bb} & \mathbf{S}_{12}^{Bb} \\ \mathbf{S}_{21}^{Bb} & \mathbf{S}_{22}^{Bb} \end{bmatrix} \begin{bmatrix} |S_{B1}^{+B}\rangle \\ |S_{B2}^{+B}\rangle \end{bmatrix} + \begin{bmatrix} \mathbf{F}_{B1}^{B(0)} \\ \mathbf{F}_{B2}^{B(0)} \end{bmatrix} |\beta\rangle, \quad (59b)$$

$$|S_{A2}^{+A}\rangle = \mathbf{D}(z_{B1} - z_{A2}) |S_{B1}^{-B}\rangle, \quad (59c)$$

$$|S_{B1}^{+B}\rangle = \mathbf{D}(z_{B1} - z_{A2}) |S_{A2}^{-A}\rangle, \quad (59d)$$

where $|S_{A2}^{+A}\rangle$, $|S_{B1}^{+B}\rangle$, $|S_{A1}^{-A}\rangle$ and $|S_{B2}^{-B}\rangle$ are the unknown terms. Eqs. (59a) and (59b) represent the formulas for the output power wave vectors of the two resonators, same as Eq. (23). On the other hand, Eqs. (59c) and (59d) describe the back-and-forth scattering of the propagating fields between the two resonators.

By solving Eqs. (59) for $|S_{A2}^{+A}\rangle$ and $|S_{B1}^{+B}\rangle$, we can obtain:

$$|S_{A2}^{+A}\rangle = \mathbf{D}(z_{B1} - z_{A2}) [\mathbf{I} - \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2})]^{-1} [\mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) |S_{A2}^{-A(0)}\rangle + |S_{B1}^{-B(0)}\rangle], \quad (60a)$$

$$|S_{B1}^{+B}\rangle = \mathbf{D}(z_{B1} - z_{A2}) [\mathbf{I} - \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2})]^{-1} [|S_{A2}^{-A(0)}\rangle + \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) |S_{B1}^{-B(0)}\rangle], \quad (60b)$$

where $|S_{A2}^{-A(0)}\rangle = \mathbf{S}_{21}^{Ab} |S_{A1}^{+A}\rangle + \mathbf{F}_{A2}^{A(0)} |\alpha\rangle$ is the 0th order output power wave vector of resonator A in region A2 when the incident field is from region A1. Also, $|S_{B1}^{-B(0)}\rangle = \mathbf{S}_{12}^{Bb} |S_{B2}^{+B}\rangle + \mathbf{F}_{B1}^{B(0)} |\beta\rangle$ is the 0th order output power wave vector of resonator B in region B1 when the incident field is from region B2. From Eqs. (22), (45), (59) and (60), and by decomposing $\mathbf{E}_B^{sca} = \mathbf{E}_B^{sca,p} + \mathbf{E}_B^{sca,np}$, we can estimate the radiative components of the input-coupling, self-coupling, and cross-coupling matrices (Eqs. (47)-(49)) in terms of the uncoupled resonators' parameters as:

$$\boldsymbol{\mu}_{AA}^r = \boldsymbol{\kappa}_{A2}^{A(0)} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{F}_{A2}^{A(0)}, \quad (61a)$$

$$\boldsymbol{\kappa}_{A1}^{A(b)} = \boldsymbol{\kappa}_{A1}^{A(0)} + \boldsymbol{\kappa}_{A2}^{A(0)} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{21}^{Ab}, \quad (61b)$$

$$\boldsymbol{\kappa}_{B2}^{A(b)} = \boldsymbol{\kappa}_{A2}^{A(0)} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{S}_{12}^{Bb}, \quad (61c)$$

$$\boldsymbol{\mu}_{AB}^r = \boldsymbol{\kappa}_{A2}^{A(0)} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{F}_{B1}^{B(0)}, \quad (61d)$$

with $\boldsymbol{\kappa}_{A1}^{A(0)}$ and $\boldsymbol{\kappa}_{A2}^{A(0)}$ being the same as in Eq. (21). Similar equations as Eqs. (61) exist for $\boldsymbol{\mu}_{BB}^r, \boldsymbol{\kappa}_{A1}^{B(b)}$, $\boldsymbol{\kappa}_{B2}^{B(b)}$, and $\boldsymbol{\mu}_{BA}^r$. From Eqs. (61), we can rewrite the CM equations (46) and (50) as:

$$\begin{aligned} j\omega|\alpha\rangle &= (\mathbf{P}_A^{(0)} + \boldsymbol{\mu}_{AA}^n + \boldsymbol{\mu}_{AA}^r)|\alpha\rangle + \boldsymbol{\kappa}_{A1}^{A(b)}|S_{A1}^{+A}\rangle + \boldsymbol{\kappa}_{B2}^{A(b)}|S_{B2}^{+B}\rangle + (\boldsymbol{\mu}_{AB}^n + \boldsymbol{\mu}_{AB}^r)|\beta\rangle \\ &= (\mathbf{P}_A^{(0)} + \boldsymbol{\mu}_{AA}^n)|\alpha\rangle + \boldsymbol{\kappa}_{A1}^{A(0)}|S_{A1}^{+A}\rangle + \boldsymbol{\kappa}_{A2}^{A(0)}|S_{A2}^{+A}\rangle + \boldsymbol{\mu}_{AB}^n|\beta\rangle, \end{aligned} \quad (62a)$$

$$\begin{aligned} j\omega|\beta\rangle &= (\mathbf{P}_B^{(0)} + \boldsymbol{\mu}_{BB}^n + \boldsymbol{\mu}_{BB}^r)|\beta\rangle + \boldsymbol{\kappa}_{A1}^{B(b)}|S_{A1}^{+A}\rangle + \boldsymbol{\kappa}_{B2}^{B(b)}|S_{B2}^{+B}\rangle + (\boldsymbol{\mu}_{BA}^n + \boldsymbol{\mu}_{BA}^r)|\alpha\rangle \\ &= (\mathbf{P}_B^{(0)} + \boldsymbol{\mu}_{BB}^n)|\beta\rangle + \boldsymbol{\kappa}_{B1}^{B(0)}|S_{B1}^{+B}\rangle + \boldsymbol{\kappa}_{B2}^{B(0)}|S_{B2}^{+B}\rangle + \boldsymbol{\mu}_{BA}^n|\alpha\rangle, \end{aligned} \quad (62b)$$

which resemble the CM equations of the uncoupled resonators except for the near-field coupling terms $\boldsymbol{\mu}_{AB}^n$ and $\boldsymbol{\mu}_{BA}^n$.

By solving Eqs. (59) for $|S_{A1}^{-A}\rangle$ and $|S_{B2}^{-B}\rangle$, one can also estimate the scattering matrix of the collective background structure and the output-coupling matrix (in Eq. (53)) of the coupled system in terms of the uncoupled resonators' parameters:

$$\mathbf{S}_{11}^b = \mathbf{S}_{11}^{Ab} + \mathbf{S}_{12}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{21}^{Ab}, \quad (63a)$$

$$\mathbf{S}_{12}^b = \mathbf{S}_{12}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{S}_{12}^{Bb}, \quad (63b)$$

$$\mathbf{S}_{21}^b = \mathbf{S}_{21}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{S}_{21}^{Ab}, \quad (63c)$$

$$\mathbf{S}_{22}^b = \mathbf{S}_{22}^{Bb} + \mathbf{S}_{21}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{12}^{Bb}, \quad (63d)$$

$$\mathbf{F}_{A1}^A = \mathbf{F}_{A1}^{A(0)} + \mathbf{S}_{12}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{F}_{A2}^{A(0)}, \quad (63e)$$

$$\mathbf{F}_{B2}^A = \mathbf{S}_{21}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{F}_{A2}^{A(0)}, \quad (63f)$$

$$\mathbf{F}_{A1}^B = \mathbf{S}_{12}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{F}_{B1}^{B(0)}, \quad (63g)$$

$$\mathbf{F}_{B2}^B = \mathbf{F}_{B2}^{B(0)} + \mathbf{S}_{21}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \left[\mathbf{I} - \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{S}_{11}^{Bb} \mathbf{D}(z_{B1} - z_{A2}) \right]^{-1} \mathbf{S}_{22}^{Ab} \mathbf{D}(z_{B1} - z_{A2}) \mathbf{F}_{B1}^{B(0)}. \quad (63h)$$

Eqs. (60) and (63) can also be deduced from Eqs. (44). A_b , the absorption of the collective background structure (in Eq. (56)) can also be estimated as:

$$A_b \approx \langle S^{+A} | S^{+A} \rangle - \langle S^{+A} | (\mathbf{S}^{Ab})^\dagger \mathbf{S}^{Ab} | S^{+A} \rangle + \langle S^{+B} | S^{+B} \rangle - \langle S^{+B} | (\mathbf{S}^{Bb})^\dagger \mathbf{S}^{Bb} | S^{+B} \rangle, \quad (64)$$

$$\text{where } |S^{+A}\rangle = \begin{bmatrix} |S_{A1}^{+A}\rangle \\ |S_{A2}^{+A}\rangle \end{bmatrix} \text{ and } |S^{+B}\rangle = \begin{bmatrix} |S_{B1}^{+B}\rangle \\ |S_{B2}^{+B}\rangle \end{bmatrix}.$$

In summary, section 3.3 thoroughly analyzed the resonator-to-resonator coupling phenomenon in the BBCMT framework and based on the multiple scattering picture. Notably, the analysis reveals that the non-resonant scattering of coupled resonators can alter their coupling and resonance behavior beyond the effects of direct interaction between their modes. When resonator B is replaced by a non-resonant scatterer (e.g., a ground plane), the section's formulations convert into another version of the resonator perturbation analysis. Although for simplicity we only discussed the coupling between two resonators in this section, the approach is similar when coupling among three or more resonators is considered.

3.4. Applications and numerical validation

To signify our theory's validity, we compare BBCMT predictions and FDTD simulations in two examples. Section 3.4.1 example demonstrates the usefulness of the background perturbation method to express the optical responses for a single resonator. On the other hand, section 3.4.2 example shows the significance of considering the non-resonant loading effects in accurate

modeling of coupled optical resonators. In addition to BBCMT numerical validation, both examples exhibit the BBCMT generality over conventional TCMT by closely comparing their predictions.

3.4.1. Background perturbation example

Figure 3.3(a) shows an array of Ag-SiO₂-Ag nanodisks embedded in a SiO₂ slab (Appendices B.4 and B.5) and normally illuminated by an x-polarized plane wave from the top. The FDTD-simulated far-field spectra of the system in Figure 3.3(b-d) show that its response in the frequency range $\omega = 1.8 \times 10^{15}$ rad/s to $\omega = 2.6 \times 10^{15}$ rad/s is dominated by a single resonance at $\Omega_A = 2.19 \times 10^{15}$ rad/s. Furthermore, the near-field analysis of the system reveals that this resonance belongs to a localized surface plasmon (LSP) mode in the nanogap between the silver nanodisks (details in SI Appendix B.5).

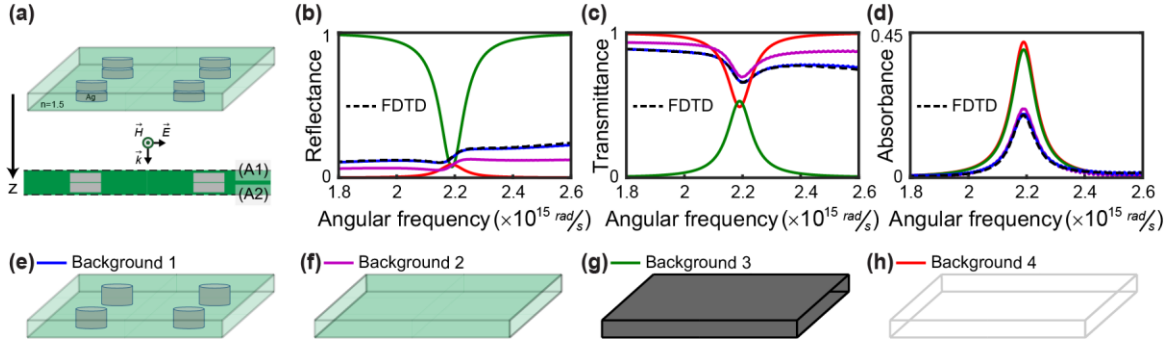


Figure 3.3. An example to clarify the concept of a proper background structure and numerically validate the background perturbation method. (a) The resonator geometry: An MIM nanodisk array embedded in an SiO₂ slab. (b) Reflectance, (c) transmittance, and (d) absorbance spectra over the designated frequency. The dashed lines represent the spectra calculated from the FDTD simulation. The solid lines represent the spectra calculated by BBCMT models with (e) background 1: a metal nanodisk array embedded in the SiO₂ slab, (f) background 2: the embedding SiO₂ slab, (g) background 3: a PEC ground plane slab, and (h) background 4: a free space slab. Backgrounds 3 and 4 correspond to the directly-coupled and the side-coupled TCMT versions, respectively.

We now use BBCMT to model the system spectral response in the determined frequency range. Although each Ag-SiO₂-Ag nanodisk can be treated as an individual resonator, we avoid such an approach for simplicity. Instead, we consider the nanodisk array and its embedding SiO₂ layer to represent a single resonator (A) collectively. Since the array has a subwavelength periodicity in the spectral range of interest ($P = 400 \text{ nm} < \lambda$), the phase-matching condition only allows for the

0th order backscattering (or reflection) and forward-scattering (or transmission) of the normally-incident plane wave²²⁹. Moreover, the system does not convert x-polarization to y-polarization or vice versa. Therefore, we can take resonator A to have two ports (top and bottom). By choosing the embedding SiO₂ slab's top and bottom interfaces as the ports' reference planes (A1 and A2) and from Eqs. (21)-(27), we can write:

$$j\omega\alpha = P_A\alpha + \begin{bmatrix} \kappa_{A1}^A & \kappa_{A2}^A \end{bmatrix} \begin{bmatrix} S_{A1}^{+A} \\ S_{A2}^{+A} \end{bmatrix}, \quad (65a)$$

$$\begin{bmatrix} S_{A1}^{-A} \\ S_{A2}^{-A} \end{bmatrix} = \mathbf{S}^{\text{Ab}} \begin{bmatrix} S_{A1}^{+A} \\ S_{A2}^{+A} \end{bmatrix} + \begin{bmatrix} f_{A1}^{A(0)} \\ f_{A2}^{A(0)} \end{bmatrix} \alpha, \quad (65b)$$

$$\begin{bmatrix} \kappa_{A1}^A & \kappa_{A2}^A \end{bmatrix} = - \begin{bmatrix} (f_{A1}^A)^* & (f_{A2}^A)^* \end{bmatrix} \mathbf{S}^{\text{Ab}}, \quad (65c)$$

$$A_A = 2\Gamma_A^{nr} |\alpha|^2, \quad (65d)$$

where α is the mode amplitude and $P_A = j\Omega_A - \Gamma_A^{nr} - \Gamma_A^r$ is the mode pole with Γ_A^{nr} and Γ_A^r being the non-radiative and radiative decay rates, respectively. $\begin{bmatrix} \kappa_{A1}^A & \kappa_{A2}^A \end{bmatrix}$ is the mode input-coupling

matrix and $\begin{bmatrix} S_{A1}^{+A} \\ S_{A2}^{+A} \end{bmatrix}$ is the input power wave vector. Moreover, $\begin{bmatrix} f_{A1}^A \\ f_{A2}^A \end{bmatrix}$ is the mode output-coupling

matrix and $\mathbf{S}^{\text{Ab}}$ is the scattering matrix of the resonator's background structure. We do the BBCMT modeling with two background structures (Figure 3.3(e-f)): 1) A silver nanodisk array (like the original nanodisks but without the gap) embedded in the SiO₂ slab; 2) The SiO₂ slab. For each background structure, we use the F-estimation lemma to acquire the parameters in Eqs. (65) (Appendix B.5). Then, by putting $S_{A1}^{+A} = 1$ and $S_{A2}^{+A} = 0$, the system's reflectance, transmittance, and absorbance spectra can be calculated (Figure 3.3(b-d)). The BBCMT-predicted spectra for background 1 match the FDTD-calculated results very well. The BBCMT-predicted spectra for background 2 are less accurate but still correctly capture the overall spectral trends. Furthermore, background 2 has the virtue of being less complex, leading to a reduced computational cost for finding the background scattering matrix.

In addition to the background structures 1 and 2, we perform the modeling for Background 3, a PEC ground-plane slab (Figure 3.3(g)), and Background 4, a Free-space slab (Figure 3.3(h)) (Appendix B.5). BBCMT analyses with these background structures are equivalent to the directly-coupled²³⁴ and side-coupled²³⁵ versions of the classic TCMT, respectively (demonstrated in the next section). Figure 3.3(b-d) reveal that none of these TCMT versions can properly model the resonator's spectral behavior. The reason is that the SiO₂ slab is neither as transparent as a free-space slab nor as reflective as a ground plane but has a reflectivity between these two cases.

3.4.2. BBCMT-aided resonator design

By providing simple analytic models and a microscopic understanding of how different system parameters interact to construct the total response, BBCMT can help uncover the design rules of complex resonator systems. In this subsection, we use BBCMT to optimize a plasmonic metastructure for the highest absorption. Figure 3.4(a) shows a nanolaminate plasmonic crystal^{275, 276} consisting of an array of tapered Ag-SiO₂-Ag nanodomes over an Ag-SiO₂-Ag nanohole array with tapered nanoholes (Appendix B.5). The incident wave is an x-polarized plane wave normally illuminated from the top.

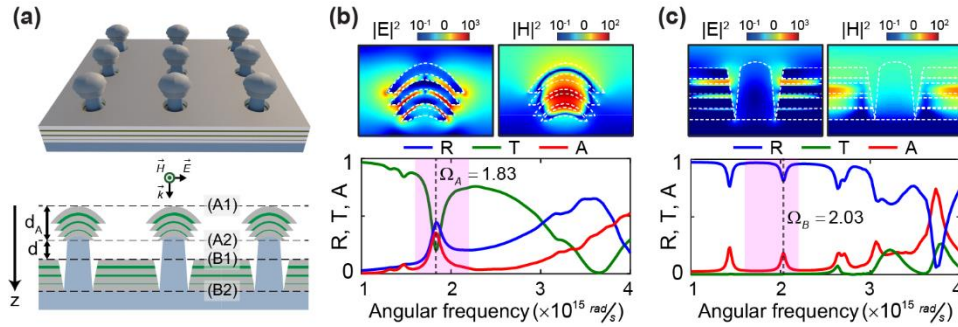


Figure 3.4. The nanolaminate plasmonic crystal and its constituent nanodome and nanohole arrays. (a) The geometry of the nanolaminate plasmonic crystal. d represents the distance between the nanodome and nanohole arrays. The system is illuminated with an x-polarized plane wave incident from the top side. (b, c) The FDTD-simulated reflectance, transmittance, and absorbance spectra of the uncoupled nanodome array (b) and the uncoupled nanohole array (c). The figures also show the near-field distributions of the dominant mode for each subsystem (at resonance) in the designated frequency range of interest ($\omega = 1.6 \times 10^{15}$ rad/s to $\omega = 2.2 \times 10^{15}$ rad/s) shaded in purple.

Our goal is to find the optimal distance between the nanodome and nanohole arrays ($d = z_{B1} - z_{A2}$ in Figure 3.4(a)), that maximizes the magnitude and bandwidth of light absorption in the frequency

range $\omega = 1.6 \times 10^{15}$ rad/s to $\omega = 2.2 \times 10^{15}$ rad/s (purple-shaded area in Figure 3.4(b-c)). To achieve the goal, we first find the proper BBCMT models for the uncoupled nanodome and nanohole arrays and then build the plasmonic crystal BBCMT model by analyzing the coupling between the nanodome and nanohole arrays. Next, we extract the BBCMT model parameters by fitting the FDTD-simulated absorbance spectra of the uncoupled and coupled arrays. After that, we find the d optimal value from the BBCMT analysis. Finally, we verify the design and analysis by comparing the BBCMT-calculated and FDTD-simulated far-field spectra.

BBCMT model of the system

We start by finding the BBCMT model for the uncoupled nanodome array (resonator A). As the nanodomains have subwavelength dimensions, their non-resonant absorption and scattering are negligible²⁴⁰, such that the incident light entirely transmits through the nanodome array unless it gets resonantly scattered or absorbed by the nanodomains' LSP modes. This fact is manifested by the coincidence of the nanodome array's absorbance peaks and transmittance dips (Figure 3.4(b)). Moreover, the array has a subwavelength periodicity ($P = 400 \text{ nm} < \lambda$) and preserves the incident wave's polarization. Accordingly, we can take resonator A to have two-ports (top and bottom

ports) and a free space background with the scattering matrix $\mathbf{S}^{\text{Ab}} = \mathbf{S}^{\text{Af}} = \begin{bmatrix} 0 & e^{-jk d_A} \\ e^{-jk d_A} & 0 \end{bmatrix}$, where

k is the free-space wavenumber and $d_A = |z_{A2} - z_{A1}| = 150 \text{ nm}$ displays the distance between the resonator's top and bottom reference planes (A1 and A2 in Figure 3.4(a)).

Far-field spectra of resonator A reveal that the mode resonant at $\Omega_A = 1.83 \times 10^{15}$ rad/s dominates the resonator response in the designated frequency range (Figure 3.4(b)). Near-field distributions of this mode in Figure 3.4(b) indicate that it is a plasmonic gap mode with a dominant magnetic dipole nature^{281, 282}. From Eqs. (21)-(27), we get the following equations for resonator A:

$$j\omega\alpha = P_A^{(0)}\alpha + \begin{bmatrix} \kappa_{A1}^{A(0)} & \kappa_{A2}^{A(0)} \end{bmatrix} \begin{bmatrix} S_{A1}^{+A} \\ S_{A2}^{+A} \end{bmatrix} = \left(j\Omega_A - \Gamma_A^{nr} - \Gamma_A^{r,1} - \Gamma_A^{r,2} \right) \alpha + \kappa_{A1}^{A(0)} S_{A1}^{+A} + \kappa_{A2}^{A(0)} S_{A2}^{+A}, \quad (66a)$$

$$\begin{bmatrix} S_{A1}^{-A} \\ S_{A2}^{-A} \end{bmatrix} = \begin{bmatrix} 0 & e^{-jkd_A} \\ e^{-jkd_A} & 0 \end{bmatrix} \begin{bmatrix} S_{A1}^{+A} \\ S_{A2}^{+A} \end{bmatrix} - \begin{bmatrix} 0 & e^{-jkd_A} \\ e^{-jkd_A} & 0 \end{bmatrix} \begin{bmatrix} \left(\kappa_{A1}^{A(0)} \right)^* \\ \left(\kappa_{A2}^{A(0)} \right)^* \end{bmatrix} \alpha, \quad (66b)$$

$$\left| \kappa_{A1}^{A(0)} \right| = \sqrt{2\Gamma_A^{r,2}}, \left| \kappa_{A2}^{A(0)} \right| = \sqrt{2\Gamma_A^{r,1}}, \quad (66c)$$

$$A_A = 2\Gamma_A^{nr} |\alpha|^2, \quad (66d)$$

where α is the mode amplitude, $P_A^{(0)}$ is the pole matrix, and $\Gamma_A^{r,1}$ and $\Gamma_A^{r,2}$ represent the decay rates of the mode into the resonator top and bottom ports, respectively. We have considered the decay rates and the coupling coefficients to have the units of 1/s in Eq. (66c). Eqs. (66) match the equations derived for side-coupled resonators in the TCMT framework²³⁵.

Next, we find the BBCMT model for the MIM nanohole array. The nanohole array is essentially a planar MIM structure perforated with a regular array of subwavelength nanoholes. Such structures support several Bloch SPP modes in their gaps/interfaces²⁷⁶. The nanoholes' subwavelength size does not allow for the non-resonant transmission of the incident light through them. Therefore, when the incident light's frequency shifts away from the Bloch SPP modes' resonances, the nanohole array behaves almost exactly as the underlying planar MIM structure, and most of the incident light gets reflected. However, as shown in Figure 3.4(c), resonant excitation of the Bloch SPP modes causes reflectance dips coinciding with absorbance peaks. Resonant transmittance peaks also appear when the Bloch SPP modes on the bottom interface get excited²⁷⁹. Moreover, the array has a subwavelength periodicity ($P = 400 \text{ nm} < \lambda$) and preserves the incident polarization. Accordingly, we can consider the nanohole array to be a two-port resonator B with the underlying planar MIM structure as the background. Since the planar MIM structure behaves almost like a PEC ground plane, we can write $\mathbf{S}^{\text{Bb}} \approx \mathbf{S}^{\text{ground plane}} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$,

where the reference planes are chosen to overlap with the resonator's top and bottom surfaces (Figure 3.4(a)).

Far-field spectra of resonator B reveal that the mode resonant at $\Omega_B = 2.03 \times 10^{15}$ rad/s dominates the resonator response in the designated frequency range (Figure 3.4(c)). Near-field distributions of this mode in Figure 3.4(c) indicate that it is a Bloch SPP mode associated with the dielectric gaps. From Eqs. (21)-(27), we get the following equations for resonator B:

$$j\omega\beta = P_B^{(0)}\beta + \begin{bmatrix} \kappa_{B1}^{B(0)} & \kappa_{B2}^{B(0)} \end{bmatrix} \begin{bmatrix} S_{B1}^{+B} \\ S_{B2}^{+B} \end{bmatrix} = \left(j\Omega_B - \Gamma_B^{nr} - \Gamma_B^{r,1} - \Gamma_B^{r,2} \right) \beta + \kappa_{B1}^{B(0)} S_{B1}^{+B} + \kappa_{B2}^{B(0)} S_{B2}^{+B}, \quad (67a)$$

$$\begin{bmatrix} S_{B1}^{-B} \\ S_{B2}^{-B} \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} S_{B1}^{+B} \\ S_{B2}^{+B} \end{bmatrix} - \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \left(\kappa_{B1}^{B(0)} \right)^* \\ \left(\kappa_{B2}^{B(0)} \right)^* \end{bmatrix} \beta, \quad (67b)$$

$$\left| \kappa_{B1}^{B(0)} \right| = \sqrt{2\Gamma_B^{r,1}}, \quad \left| \kappa_{B2}^{B(0)} \right| = \sqrt{2\Gamma_B^{r,2}}, \quad (67c)$$

$$A_B = 2\Gamma_B^{nr} |\beta|^2, \quad (67d)$$

where β is the mode amplitude, and $P_B^{(0)}$ is the pole matrix, and $\Gamma_B^{r,1}$ and $\Gamma_B^{r,2}$ are defined same as in Eqs. (66). Eqs. (67) match the equations derived for directly-coupled resonators in the TCMT framework^{234, 237}.

Figure 3.5(a) schematic represents the BBCMT model of the nanolaminate plasmonic crystal, where resonators A and B are coupled through near-field and radiative interactions. Here, we have neglected the effect of polymer pillars between the nanodome and nanohole arrays as they are both non-resonant and have a negligible scattering due to subwavelength cross-section.

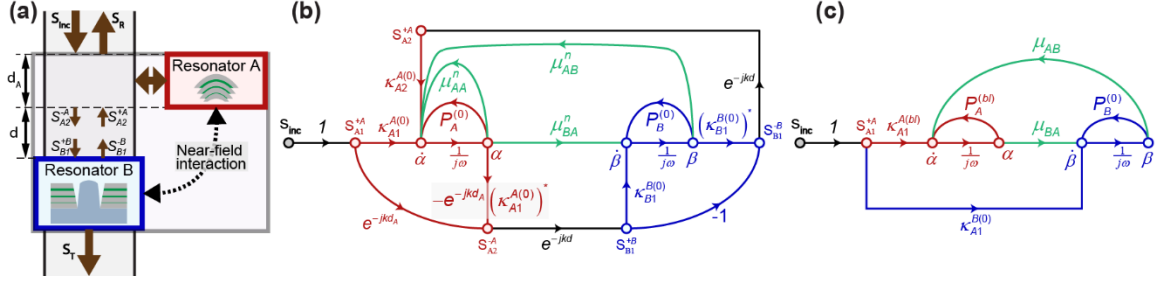


Figure 3.5. (a) BBCMT model for the nanolaminate plasmonic crystal. (b) The SFG of the system when we assume a free space background structure for the nanodome array and a background structure of the PEC ground plane for the nanohole array. (c) The SFG resulted from the simplification of the SFG in part (b) by the SFG decomposition rules.

Since the background structures of the resonators A and B are non-resonant, and they do not overlap in the wave propagation direction, we may use the section 3.3.3 approximations. From Eq. (62), the coupled system's CM equations would be:

$$j\omega\alpha = \left[P_A^{(0)} + \mu_{AA}^n \right] \alpha + \kappa_{A1}^{A(0)} S_{inc} + \kappa_{A2}^{A(0)} S_{A2}^{+A} + \mu_{AB}^n \beta, \quad (68a)$$

$$j\omega\beta = P_B^{(0)} \beta + \kappa_{B1}^{B(0)} S_{B1}^{+B} + \mu_{BA}^n \alpha, \quad (68b)$$

where $S_{B2}^{+B} = 0$ and $S_{A1}^{+A} = S_{inc}$ as the excitation wave is incident from the top side. Since resonator B background structure is a ground plane, the self-coupling term μ_{AA}^n can be interpreted as the near-field interaction between resonator A and its image in the ground plane. As resonator A has a negligible non-resonant scattering, we have not considered any self-coupling term for resonator B. Furthermore, considering that a resonator's near-field components exponentially decay with the distance away from it, we can approximate the near-field coupling terms in Eqs. (68) as follows:

$$\mu_{AA}^n = \mu_{AA}^{n0} e^{-\alpha_{AA} kd}, \quad (69a)$$

$$\mu_{AB}^n = \mu_{AB}^{n0} e^{-\alpha_{AB} kd}, \quad (69b)$$

$$\mu_{BA}^n = \mu_{BA}^{n0} e^{-\alpha_{BA} kd}, \quad (69c)$$

with μ_{AA}^{n0} , μ_{AB}^{n0} and μ_{BA}^{n0} being the near-field coupling terms for $d=0$ and α_{AA} , α_{AB} and α_{BA} being the normalized decay lengths.

From Eqs. (59), (66), and (67) and considering the coupled system's geometry, we can write:

$$\begin{bmatrix} S_R \\ S_{A2}^{-A} \end{bmatrix} = \begin{bmatrix} 0 & e^{-jkd_A} \\ e^{-jkd_A} & 0 \end{bmatrix} \begin{bmatrix} S_{inc} \\ S_{A2}^{+A} \end{bmatrix} - \begin{bmatrix} 0 & e^{-jkd_A} \\ e^{-jkd_A} & 0 \end{bmatrix} \begin{bmatrix} \left(\kappa_{A1}^{A(0)} \right)^* \\ \left(\kappa_{A2}^{A(0)} \right)^* \end{bmatrix} \alpha, \quad (70a)$$

$$\begin{bmatrix} S_{B1}^{-B} \\ S_T \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} S_{B1}^{+B} \\ 0 \end{bmatrix} - \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} \left(\kappa_{B1}^{B(0)} \right)^* \\ \left(\kappa_{B2}^{B(0)} \right)^* \end{bmatrix} \beta, \quad (70b)$$

$$S_{A2}^{+A} = e^{-jkd} S_{B1}^{-B}, \quad (70c)$$

$$S_{B1}^{+B} = e^{-jkd} S_{A2}^{-A}, \quad (70d)$$

where $S_R = S_{A1}^{-A}$ and $S_T = S_{B2}^{-B}$ represent the reflected and transmitted power waves of the coupled system, respectively. Figure 3.5(b) SFG illustrates the electromagnetic interaction dynamics associated with Eqs. (68) and (70c-d). Via applying the SFG decomposition rules^{227, 274} to Figure 3.5(b), we can simplify it to Figure 3.5(c) SFG, corresponding to the following equations:

$$j\omega\alpha = P_A^{(bl)}\alpha + \kappa_{A1}^{A(bl)}S_{inc} + \mu_{AB}\beta, \quad (71a)$$

$$j\omega\beta = P_B^{(0)}\beta + \kappa_{A1}^{B(0)}S_{inc} + \mu_{BA}\alpha, \quad (71b)$$

where $P_A^{(bl)} = P_A^{(0)} + \mu_{AA}^n + \mu_{AA}^r$, $\mu_{AB} = \mu_{AB}^n + \mu_{AB}^r$ and $\mu_{BA} = \mu_{BA}^n + \mu_{BA}^r$. Also:

$$\mu_{AA}^r = \kappa_{A2}^{A(0)} e^{-jk(d_A+2d)} \left(\kappa_{A1}^{A(0)} \right)^*, \quad (72a)$$

$$\kappa_{A1}^{A(bl)} = \kappa_{A1}^{A(0)} - \kappa_{A2}^{A(0)} e^{-jk(d_A+2d)}, \quad (72b)$$

$$\mu_{AB}^r = \kappa_{A2}^{A(0)} e^{-jkd} \left(\kappa_{B1}^{B(0)} \right)^*, \quad (72c)$$

$$\kappa_{A1}^{B(0)} = e^{-jk(d_A+d)} \kappa_{B1}^{B(0)}, \quad (72d)$$

$$\mu_{BA}^r = -\kappa_{B1}^{B(0)} e^{-jk(d_A+d)} \left(\kappa_{A1}^{A(0)} \right)^*. \quad (72e)$$

The red arrows combination in Figure 3.5(c) describes the signal flow dynamics for A^{bl} , i.e., resonator A loaded with resonator B's background structure. A^{bl} CM equation is similar to Eq. (71a) but without the term $\mu_{AB}\beta$. Resonator A^{bl} can be considered as a Fabry-Perot-like cavity between resonator A and resonator B ground-plane-like background. From Eq. (71a), A^{bl} characteristic equation is $|j\omega - P_A^{(bl)}| = 0$, which has multiple roots in the complex plane since $P_A^{(bl)}$ is frequency-dependent. Hence, despite resonator A being single-resonant, resonator A^{bl} has multiple resonance frequencies. As resonator A has a free-space background, resonator B does not experience any background loading effect (B and B^{bl} are equivalent). Only, the top reference plane has shifted from B1 in resonator B to A1 in resonator B^{bl} . From Eqs. (71), one can obtain the mode amplitudes as follows:

$$\alpha = \frac{\kappa_{A1}^{A(dl)} S_{inc}}{j\omega - P_A^{(dl)}}, \quad (73a)$$

$$\beta = \frac{\kappa_{A1}^{B(dl)} S_{inc}}{j\omega - P_B^{(dl)}}, \quad (73b)$$

Where $P_A^{(dl)} = P_A^{(bl)} + \mu_{AB}\mu_{BA}/(j\omega - P_B^{(0)})$, $\kappa_{A1}^{A(dl)} = \kappa_{A1}^{A(bl)} + \mu_{AB}\kappa_{A1}^{B(0)}/(j\omega - P_B^{(0)})$, $P_B^{(dl)} = P_B^{(0)} + \mu_{BA}\mu_{AB}/(j\omega - P_A^{(bl)})$, and $\kappa_{A1}^{B(dl)} = \kappa_{A1}^{B(0)} + \mu_{BA}\kappa_{A1}^{A(bl)}/(j\omega - P_A^{(bl)})$. After that, from Eqs. (70), or from Eqs. (53) and (63), one can calculate output power waves of the coupled system:

$$\begin{bmatrix} S_R \\ S_T \end{bmatrix} = \mathbf{S}^b \begin{bmatrix} S_{inc} \\ 0 \end{bmatrix} + \mathbf{F} \begin{bmatrix} \alpha \\ \beta \end{bmatrix} = \begin{bmatrix} -e^{-jk(2d_A+2d)} & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} S_{inc} \\ 0 \end{bmatrix} + \begin{bmatrix} e^{-jk(2d_A+2d)} (\kappa_{A1}^{A(0)})^* - e^{-jkd_A} (\kappa_{A2}^{A(0)})^* & e^{-jk(d_A+d)} (\kappa_{B1}^{B(0)})^* \\ 0 & (\kappa_{B2}^{B(0)})^* \end{bmatrix} \begin{bmatrix} \alpha \\ \beta \end{bmatrix}. \quad (74)$$

By considering $\mathbf{\Gamma}^r = \begin{bmatrix} \Gamma_A^{r,1} + \Gamma_A^{r,2} & 0 \\ 0 & \Gamma_B^{r,1} + \Gamma_B^{r,2} \end{bmatrix}$ and $\mathbf{\mu}^r = \begin{bmatrix} \mu_{AA}^r & \mu_{AB}^r \\ \mu_{BA}^r & 0 \end{bmatrix}$, Eqs. (66c), (67c), (72a), and (74) reveal that $\mathbf{\mu}^r + (\mathbf{\mu}^r)^\dagger = 2\mathbf{\Gamma}^r - \mathbf{F}^\dagger \mathbf{F}$ which corroborates Eq. (58a) validity. By finding the

output power waves, the reflection and transmission can be obtained from $|S_R|^2$ and $|S_T|^2$, respectively. Furthermore, from Eqs. (64), (66d), and (67d), the coupled system's absorption would be:

$$A = 2\Gamma_A^{nr} |\alpha|^2 + 2\Gamma_B^{nr} |\beta|^2. \quad (75)$$

From Eq. (75), it is possible to calculate the individual contributions of resonators A and B to the total absorption from $2\Gamma_A^{nr} |\alpha|^2$ and $2\Gamma_B^{nr} |\beta|^2$, respectively.

Reverse-engineering the parameters in the BBCMT model

As the next step, we use the kappa-estimation lemma (section 3.2.7) to reverse-engineer the parameters in the CM equations of the uncoupled resonators by fitting the FDTD-simulated absorbance curves (background-subtracted) for top-side and bottom-side illuminations (Appendix B.5). We find the following parameters for the nanodome array (Figure 3.6(a-b)):

$$P_A^{(0)} = (1.83 \times 10^{15} j - 8.10 \times 10^{13}) 1/s, \quad \kappa_{A1}^{A(0)} = 6.05 \times 10^6 1/s \quad \text{and} \quad \kappa_{A2}^{A(0)} = -8.30 \times 10^6 1/s. \quad \text{Also, we find the nanohole array parameters as follows (Figure 3.6(c-d)):$$

$$P_B^{(0)} = (2.03 \times 10^{15} j - 3.31 \times 10^{13}) 1/s, \quad \kappa_{B1}^{B(0)} = 1.60 \times 10^6 1/s \quad \text{and} \quad \kappa_{B2}^{B(0)} = -8.19 \times 10^5 1/s.$$

Interestingly, we find that $|\kappa_{A1}^{A(0)}| \neq |\kappa_{A2}^{A(0)}|$ and $|\kappa_{B1}^{B(0)}| \neq |\kappa_{B2}^{B(0)}|$, which aligns with the bianisotropic behaviors of the resonators observed in Figure 3.6(a, c). From Eq. (22), the resonators' bianisotropic behaviors are caused by their lossy materials and non-symmetric structures. After finding the uncoupled parameters, we can easily calculate the background-loaded input-coupling parameters and the coefficients of radiative coupling between the two resonators from Eqs. (72). Nevertheless, to find the near-field coupling parameters (in Eqs. (69)), we fit the FDTD-simulated absorbance spectra of the nanolaminate plasmonic crystal for $d=80$ and $d=120$ nm (Figure 3.6(e)). The fitting process can be simplified by utilizing Eq. (58b): $\mu_{AA}^n + (\mu_{AA}^n)^* = 0$ indicates that μ_{AA}^{n0} is a purely imaginary number and $\mu_{AB}^n + (\mu_{BA}^n)^* = 0$ gives $\mu_{BA}^{n0} = -(\mu_{AB}^{n0})^*$ and $\alpha_{BA} = \alpha_{AB}$. Then, by fitting, we get: $\mu_{AA}^{n0} = 5.7 \times 10^{13} e^{j\pi/2} 1/s$, $\mu_{AB}^{n0} = -(\mu_{BA}^{n0})^* = 8.7 \times 10^{13} e^{j\pi/2} 1/s$, $\alpha_{AA} = 0.5$ and $\alpha_{AB} = \alpha_{BA} = 2.9$.

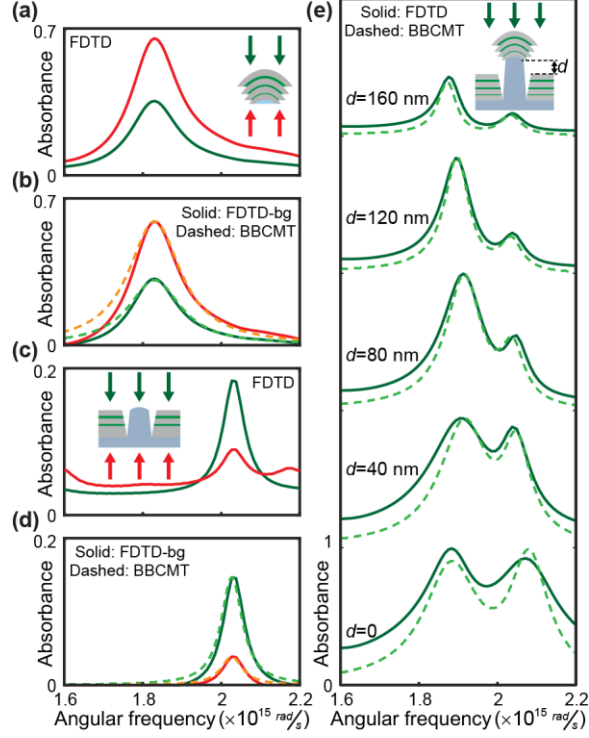


Figure 3.6. Reverse-engineering the parameters in the BBCMT model of the nanolaminate plasmonic crystal from the FDTD-simulated absorbance spectra. (a-d) finding the parameters of the uncoupled resonators by the Kappa-estimation lemma. We used the FDTD-simulated absorbance spectra of the nanodome array (a) and nanohole array (c) for top-side and bottom-side illuminations as the data for the Kappa-estimation lemma. The parameters obtained from the lemma are such that the BBCMT-calculated absorbance spectra for top-side and bottom-side illuminations can fit the background-subtracted absorbance spectra from the FDTD simulations, as illustrated for the nanodome array (b) and the nanohole array (d). (e) We found the parameters of coupling between the resonators by fitting the absorbance spectra of the nanolaminate plasmonic crystal for $d=80$ nm and $d=120$ nm. Nevertheless, the BBCMT-calculated spectra for several other values of d also show a decent match to the FDTD-simulated spectra.

Now, by putting the estimated parameters back into Eqs. (73)-(75) and considering $S_{inc} = 1$, we can obtain the reflectance, transmittance, and absorbance spectra of the nanolaminate plasmonic crystal for different values of d . Interestingly, Figure 3.6(e) reveals that the BBCMT-calculated absorbance spectra for several values of d decently match the FDTD-simulated absorbance spectra, although we only used two values of d ($d=80$ and $d=120$ nm) to retrieve the coupling coefficients. This observation demonstrates that the BBCMT model accurately captures the microscopic dynamics in the plasmonic crystal system.

Finding the optimal d value

Figure 3.7(a-c) represent the absorbance spectra of the nanolaminate plasmonic crystal and each of its subsystems' contributions for $d=0$ up to $d=2000$ nm as colormaps in the $d-\omega$ plane. The corresponding FDTD-simulated colormaps are shown in Figure 3.7(d-f).

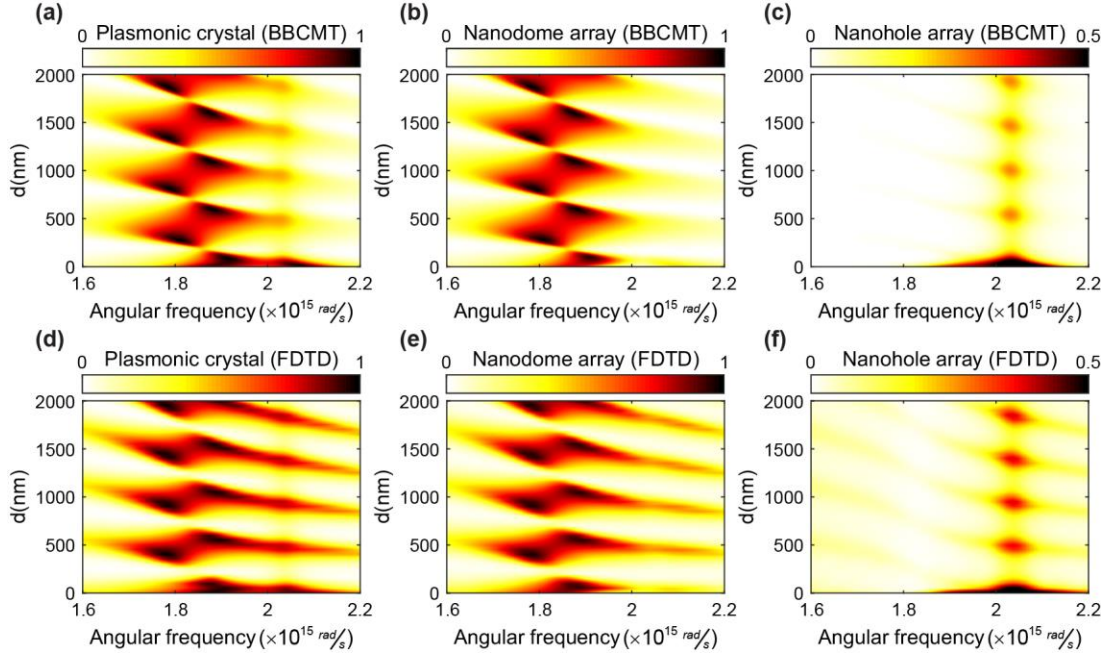


Figure 3.7. Side-by-side comparison between the BBCMT calculations and FDTD simulations for the absorbance spectra of the nanolaminate plasmonic crystal and its sub-arrays for $d=0$ up to $d=2000$ nm. The resulting spectra are shown as colormaps in the $d-\omega$ plane. (a, d) Absorbance colormap of the nanolaminate plasmonic crystal from BBCMT (a) and FDTD (d). (b, e) Absorbance colormap of the coupled nanodome array from BBCMT (b) and FDTD (e). (c, f) Absorbance colormap of the coupled nanohole array from BBCMT (c) and FDTD (f).

For each d value, we define the absorption figure of merit (FOM_{abs}) as the area under the absorbance curve from $\omega = 1.6 \times 10^{15}$ rad/s up to $\omega = 2.2 \times 10^{15}$ rad/s (Figure B3(a-c)). Both the BBCMT-calculated and FDTD-simulated $FOM_{abs}-d$ curves indicate that the absorption performance of the plasmonic crystal and its nanohole array subsystem get maximized at $d=0$. However, the nanodome array subsystem shows about 75% of its maximum performance at $d=0$. The BBCMT-calculated and FDTD-simulated colormaps in Figure 3.7 share a plethora of other features as well. For instance: 1) For $d=0$, the peak absorbance of the nanodome array is 2.5 times that of the uncoupled nanodome array for top-side excitation, while this ratio is 4.5 for the nanohole

array; 2) As d goes up, both the peak absorbance and FOM_{abs} of the nanohole array considerably drop and do not recover again, but this is not the case for the nanodome array; 3) Absorbance of the plasmonic crystal and its sub-arrays asymptotically approach a periodic function of d with the periodicity being $\lambda/2 = \pi c/\omega$ at each frequency (Figure B3(d-f)).

Unlike FDTD, BBCMT offers a microscopic picture that helps us understand the enabling factors behind the described features. The term $-\kappa_{A2}^{A(0)} e^{-jk(d_A+2d)}$ in Eq. (72b) introduces an indirect channel for coupling of the nanodome array to the incident light through interaction with the non-resonantly backscattered light from the nanohole array. In addition, magnetic dipole and bianisotropic natures of the nanodome array cause $\text{sign}(\kappa_{A1}^{A(0)}) \neq \text{sign}(\kappa_{A2}^{A(0)})$ and $|\kappa_{A2}^{A(0)}| > |\kappa_{A1}^{A(0)}|$, respectively (Appendix B.5). These factors make $\kappa_{A1}^{A(dl)}$ in Eq. (73a) much larger than the intrinsic $\kappa_{A1}^{A(0)}$ value in a broad frequency range when $d \sim 0$ (Figure B4(b)), leading to an enhanced absorbance for the nanodome array in this regime (Figure B4(a)). Yet, the bandwidth of this enhancement is limited by the resonance factor $1/(j\omega - P_A^{(dl)})$ (Figure B4(c)). From Eq. (73b), high absorbance enhancement of the nanohole array for $d \sim 0$ (Figure B4(d)) is due to the strong coupling between the two resonators (large μ_{AB} and μ_{BA}) in this regime, which enhances $\kappa_{A1}^{B(dl)}$ much beyond the intrinsic $\kappa_{A1}^{B(0)}$ value (Figure B4(e)). The near-field coupling terms μ_{AB}^n and μ_{BA}^n have the dominant contribution to the resonators' strong coupling for $d \sim 0$. As d goes up, μ_{AB}^n and μ_{BA}^n exponentially decay, leading to a conspicuous absorption reduction in the nanohole array. Moreover, from Eqs. (72) and (73), the mode amplitudes α and β become periodic functions of d with the periodicity of $\lambda/2$ at each frequency. From Eq. (75), the mode amplitudes' periodic behavior for large d values is the reason for the absorbance spectra periodic behavior in this regime. The microscopic picture offered by the BBCMT model allows us to definitively conclude that the nanolaminate plasmonic crystal has the highest absorption performance for $d=0$. In addition to absorbance, we have calculated the reflectance and transmittance spectra of the plasmonic crystal for $d=0$ up to $d=2000$ nm from Eq. (74) (Figure B5). The resulting $d - \omega$ plane colormaps are again highly similar to the FDTD-calculated reflectance and transmittance colormaps (Appendix B.5). The small discrepancies between the BBCMT and FDTD results, e.g., the spectral linewidths, are

primarily due to assumption of a free-space background for the nanodome array, which neglects the broadband scattering from its electric dipole mode^{281, 282}. A gap-filled nanodome array could be a more accurate background structure (like section 3.4.1).

As the final remark on this part, we exhibit the importance of the non-resonant loading effects by eliminating them from the model (putting $P_A^{(bl)} = P_A^{(0)}$ in Eqs. (71)) and re-evaluating the model performance (Figure B6). We have re-adjusted the mode-coupling coefficients ($\mu_{AB}^{n0} = -(\mu_{BA}^{n0})^* = 2 \times 10^{13} e^{(j7\pi/8)} 1/s$) to fit the FDTD-simulated absorption spectrum of the nanolaminate plasmonic crystal for $d=80\text{ nm}$ as best as possible. As Figure B6 reveals, the results predicted from this simplified model are highly off from FDTD calculations, revealing that accounting for the non-resonant loading effect is vital for accurate modeling. The non-resonant loading effects are not considered in the TCMT framework.

3.5. Summary and Outlook

In summary, this work presented the *Black-box Coupled-Mode Theory (BBCMT)*, an ab initio eigenmode expansion framework based on Maxwell's equations to model the electromagnetic interactions of open, lossy, and dispersive resonators. The key to BBCMT development is invoking the conjugated Lorentz's reciprocity theorem to normalize the modes and acquire the coupled-mode equation. By directly connecting the field products to Poynting's theorem, the BBCMT analysis approach enables the definition of a resonator's Hamiltonian matrix that, as in quantum mechanics, characterizes the modes' electromagnetic interactions and energy. Furthermore, the analysis framework generalizes the perturbation theory of microwave cavities to open resonators. To accurately model the resonators' interactions, both their non-resonant and resonant responses are taken into account in the BBCMT framework. The resonant responses are expanded as a summation of different modes' contributions, while the non-resonant responses are treated by the background perturbation method. BBCMT models' complexity and accuracy can be arbitrarily adjusted by flexibly choosing the background structures and black-boxing user-defined subcomponents of the system. Besides the formal formulation, we offered several lemmas that allow retrieval of coupling coefficients from the calculated or measured far-field spectra, relieving the user from computationally expensive integrations. Furthermore, we introduced the signal flow

graphs from control engineering to solve the BBCMT equations and visually represent the electromagnetic interactions they describe.

BBCMT can reduce to either TCMT or common modal analysis of closed resonators under proper constraints and approximations. To further demonstrate BBCMT's validity and versatility, we studied two examples of plasmonic metastructures where BBCMT and TCMT predictions were side-by-side compared with FDTD simulations and found the BBCMT results to be a much better match. Moreover, we showed how the BBCMT-driven insight over different pathways of coupling and interaction can facilitate the design and analysis of electromagnetic resonant systems, especially in plasmonics and metamaterials. BBCMT is valid for linear systems across the whole electromagnetic spectrum, and although non-magnetic and isotropic materials were assumed for simplicity, the framework can easily be extended to address these constraints. As future work, BBCMT can be further generalized to handle non-linear systems as well.

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Appendix B

B.1. Conjugated form of Lorentz's reciprocity theorem

In this section, we derive the general conjugated form of Lorentz's reciprocity theorem^{232, 246} under the isotropic materials assumption. Assume that ω_1 , $E_1(r)$, $H_1(r)$, $J_1(r)$, $\varepsilon_1(r, \omega)$, and $\mu_1(r, \omega)$ constitute a solution set for Maxwell's equations such that:

$$\nabla \times E_1 = -j\omega_1\mu_1(\omega_1)H_1, \quad (\text{B1a})$$

$$\nabla \times H_1 = j\omega_1\varepsilon_1(\omega_1)E_1 + J_1, \quad (\text{B1b})$$

in the volume V enclosed by the surface S . We have omitted the components' position dependency for brevity. Also, Assume that ω_2 , $E_2(r)$, $H_2(r)$, $J_2(r)$, $\varepsilon_2(r, \omega)$, and $\mu_2(r, \omega)$ represent another solution set for Maxwell's equations in the volume V . By taking the complex conjugate of the Maxwell's equations for the second solution set we get:

$$\nabla \times E_2^* = -j\omega_2^*\mu_2^*(\omega_2)(-H_2^*), \quad (\text{B2a})$$

$$\nabla \times (-H_2^*) = j\omega_2^*\varepsilon_2^*(\omega_2)E_2^* - J_2^*. \quad (\text{B2b})$$

Then, by applying the divergence theorem to the vector $E_1 \times H_2^* + E_2^* \times H_1$ and using Eqs. (B1) and (B2), we obtain the general conjugated form of Lorentz's reciprocity theorem as follows:

$$\begin{aligned} & \iint_S (E_1 \times H_2^* + E_2^* \times H_1) \cdot d\mathbf{s} = \\ & j \iiint_V \left\{ [\omega_2^*\varepsilon_2^*(\omega_2) - \omega_1\varepsilon_1(\omega_1)] (E_1 \cdot E_2^*) + [\omega_2^*\mu_2^*(\omega_2) - \omega_1\mu_1(\omega_1)] (H_1 \cdot H_2^*) \right\} d^3r \\ & - \iiint_V (E_1 \cdot J_2^* + E_2^* \cdot J_1) d^3r. \end{aligned} \quad (\text{B3})$$

B.2. Single resonator BBCMT formulations

B.2.1. Mode amplitudes and energy

Suppose an electromagnetic resonator A lies over the medium and gets excited by the harmonic current source $J(r, \omega)$. For simplicity, we assume non-magnetic materials for both the medium and resonator. Also, we consider two scenarios where the source is inside the resonator or outside it.

- **Source inside the resonator (Figure 1(a)).** The total fields $E_A^{tot}(r, \omega)$ and $H_A^{tot}(r, \omega)$ satisfy:

$$\nabla \times E_A^{tot} = -j\omega\mu_0 H_A^{tot}, \quad (B4a)$$

$$\nabla \times H_A^{tot} = j\omega\varepsilon_A E_A^{tot} + \hat{n} \times H_A^{tot} + J, \quad (B4b)$$

where μ_0 is the vacuum permeability. When the source resides inside the resonator, the resonant modes form a basis set that can span the total fields in the same region²⁶³. Hence, we can write:

$$\left(\begin{array}{c} E_A^{tot}(r, \omega) \\ H_A^{tot}(r, \omega) \end{array} \right) \Big|_{r \in V_A} = \sum_m \tilde{\alpha}_m(\omega) \left(\begin{array}{c} \tilde{E}_{Am}(r) \\ \tilde{H}_{Am}(r) \end{array} \right), \quad (B5)$$

where $\tilde{\alpha}_m(\omega)$, $\tilde{E}_{Am}(r)$, and $\tilde{H}_{Am}(r)$ represent the m^{th} mode amplitude (unitless) and normalized electric and magnetic field patterns, respectively. We denote the complex resonance frequency of the mode by $\tilde{\omega}_{Am} = \Omega_{Am} + j\Gamma_{Am}$, where Ω_{Am} and Γ_{Am} determine the mode oscillation frequency and (total) decay rate, respectively. By definition, the field patterns and the resonance frequency of the m^{th} mode satisfy the following set of eigenequations:

$$\nabla \times \tilde{E}_{Am}(r) = -j\tilde{\omega}_{Am}\mu_0 \tilde{H}_{Am}(r), \quad (B6a)$$

$$\nabla \times \tilde{H}_{Am}(r) = j\tilde{\omega}_{Am}\varepsilon_A(r, \tilde{\omega}_m) \tilde{E}_{Am}(r) + \hat{n} \times \tilde{H}_{Am}(r). \quad (B6b)$$

We take the m^{th} and n^{th} QNMs as the first and second solution sets of Maxwell's equations, respectively. Then, by applying the conjugated form of Lorentz's reciprocity theorem over the resonator's interior and simple algebraic manipulations we obtain:

$$\begin{aligned} & \iint_{\partial_A - \partial_{A,PEC}} (\tilde{\mathbf{E}}_{Am} \times \tilde{\mathbf{H}}_{An}^* + \tilde{\mathbf{E}}_{An}^* \times \tilde{\mathbf{H}}_{Am}) \cdot d\mathbf{s} = \\ & j \iiint_{V_A} \left\{ [\tilde{\omega}_{An}^* \varepsilon_A^* (\tilde{\omega}_{An}) - \tilde{\omega}_{Am} \varepsilon_A (\tilde{\omega}_{Am})] (\tilde{\mathbf{E}}_{Am} \cdot \tilde{\mathbf{E}}_{An}^*) + [\tilde{\omega}_{An}^* \mu_0 - \tilde{\omega}_{Am} \mu_0] (\tilde{\mathbf{H}}_{Am} \cdot \tilde{\mathbf{H}}_{An}^*) \right\} d^3r, \end{aligned} \quad (\text{B7})$$

where the components spatial dependence is not shown for brevity. Next, we apply the conjugated form of Lorentz's reciprocity theorem over the resonator's interior with the total fields (Eq. (B4)) as the first solution, and n^{th} QNM (Eq. (B6)) as the second solution:

$$\begin{aligned} & \iint_{\partial_A - \partial_{A,PEC}} (\mathbf{E}_A^{\text{tot}} \times \tilde{\mathbf{H}}_{An}^* + \tilde{\mathbf{E}}_{An}^* \times \mathbf{H}_A^{\text{tot}}) \cdot d\mathbf{s} = \\ & j \iiint_{V_A} \left\{ [\tilde{\omega}_{An}^* \varepsilon_A^* (\tilde{\omega}_{An}) - \omega \varepsilon_A (\omega)] (\mathbf{E}_A^{\text{tot}} \cdot \tilde{\mathbf{E}}_{An}^*) + [\tilde{\omega}_{An}^* \mu_0 - \omega \mu_0] (\mathbf{H}_A^{\text{tot}} \cdot \tilde{\mathbf{H}}_{An}^*) \right\} d^3r - \iiint_{V_A} J \cdot \tilde{\mathbf{E}}_{An}^* d^3r. \end{aligned} \quad (\text{B8})$$

Combining Eqs. (B5), (B7), and (B8) then gives:

$$j \sum_m \tilde{\alpha}_m \iiint_{V_A} \left\{ [\omega \varepsilon_A (\omega) - \tilde{\omega}_{Am} \varepsilon_A (\tilde{\omega}_{Am})] (\tilde{\mathbf{E}}_{Am} \cdot \tilde{\mathbf{E}}_{An}^*) + [\omega \mu_0 - \tilde{\omega}_{Am} \mu_0] (\tilde{\mathbf{H}}_{Am} \cdot \tilde{\mathbf{H}}_{An}^*) \right\} d^3r = - \iiint_{V_A} J \cdot \tilde{\mathbf{E}}_{An}^* d^3r. \quad (\text{B9})$$

Now, by writing Eq. (B9) for different values of n , multiplying both sides by $\frac{1}{4}$, and combining all the resulting equations into a single matrix equation, we can acquire the resonator's CM equation as follows:

$$\mathbf{H}_A(\omega)(j\omega \mathbf{I} - \mathbf{P}_A) |\tilde{\alpha}\rangle = -\frac{1}{4} \iiint_{J \neq 0} J \cdot |\tilde{\mathbf{E}}_A^*\rangle d^3r, \quad (\text{B10})$$

where $|\tilde{\alpha}\rangle = [\tilde{\alpha}_i]_{\mathbf{M} \times 1}$ and $|\tilde{\mathbf{E}}_A^*\rangle = [\tilde{\mathbf{E}}_{Ai}^*]_{\mathbf{M} \times 1}$ with $\mathbf{M}$ being the number of resonator modes, $\mathbf{I}$ is the identity matrix, $\mathbf{P}_A$ is the pole matrix defined as $\mathbf{P}_A = [p_{ij} = \tilde{\omega}_{Ai} \delta_{ij}]_{\mathbf{M} \times \mathbf{M}}$, and $\mathbf{H}_A = [h_{ij}]_{\mathbf{M} \times \mathbf{M}}$ is the *Hamiltonian matrix* with the elements:

$$\begin{aligned}
h_{ij} &= \frac{1}{4} (\omega - \tilde{\omega}_{Aj})^{-1} \iiint_{V_A} \left\{ [\omega \varepsilon_A(\omega) - \tilde{\omega}_{Aj} \varepsilon_A(\tilde{\omega}_{Aj})] (\tilde{E}_{Aj} \cdot \tilde{E}_{Ai}^*) + [\omega \mu_0 - \tilde{\omega}_{Aj} \mu_0] (\tilde{H}_{Aj} \cdot \tilde{H}_{Ai}^*) \right\} d^3r \\
&\approx \frac{1}{4} \iiint_{V_A} \left\{ \frac{\partial [\omega \varepsilon_A(\omega)]}{\partial \omega} \bigg|_{\omega=\tilde{\omega}_{Aj}} (\tilde{E}_{Aj} \cdot \tilde{E}_{Ai}^*) + \mu_0 (\tilde{H}_{Aj} \cdot \tilde{H}_{Ai}^*) \right\} d^3r \\
&\approx \frac{1}{4} \iiint_{V_A} \left\{ \text{Re} \left[\frac{\partial [\omega \varepsilon_A(\omega)]}{\partial \omega} \right] \bigg|_{\omega=\Omega_{Aj}} (\tilde{E}_{Aj} \cdot \tilde{E}_{Ai}^*) + \mu_0 (\tilde{H}_{Aj} \cdot \tilde{H}_{Ai}^*) \right\} d^3r \\
&\quad - \frac{j}{4} \iiint_{V_A} \left\{ \text{Im} \left[\frac{\partial [\omega \varepsilon_A(\omega)]}{\partial \omega} \right] \bigg|_{\omega=\Omega_{Aj}} (\tilde{E}_{Aj} \cdot \tilde{E}_{Ai}^*) \right\} d^3r.
\end{aligned} \tag{B11}$$

The reason for including the $(\omega - \tilde{\omega}_{Aj})^{-1}$ in h_{ij} definition is that the integral term is zero for $\omega = \tilde{\omega}_{Aj}$. When the resonator materials are low-dispersion ($|\partial(\omega \varepsilon_A)/(\varepsilon_A \partial \omega)| \approx 1$), Eq. (B11) leads to the following formula for the total energy stored in the resonator modes:

$$W_A = \frac{1}{4} \iiint_{V_A} \left[\text{Re} \left(\frac{\partial(\omega \varepsilon_A)}{\partial \omega} \right) \left| \sum_m \tilde{\alpha}_m \tilde{E}_{Am} \right|^2 + \mu_0 \left| \sum_m \tilde{\alpha}_m \tilde{H}_{Am} \right|^2 \right] d^3r = \text{Re}[\langle \tilde{\alpha} | \mathbf{H}_A | \tilde{\alpha} \rangle]. \tag{B12}$$

In this regard, we choose the mode normalization condition as:

$$\text{Re}(h_{mm}) = \tilde{W}_{Am} = \frac{1}{4} \iiint_{V_A} \left[\text{Re} \left(\frac{\partial(\omega \varepsilon_A)}{\partial \omega} \right) \bigg|_{\omega=\Omega_{Am}} |\tilde{E}_{Am}|^2 + \mu_0 |\tilde{H}_{Am}|^2 \right] d^3r = 1. \tag{B13}$$

We say the i^{th} and j^{th} modes are orthogonal when $h_{ij} = 0$ for $i \neq j$. In this scenario, combining Eqs. (B11), (B13), and definition of the decay rates (Eqs. (3) in the main text) gives:

$$h_{ij} \approx \left(1 - \frac{j \Gamma_{Ai}^{nr}}{\Omega_{Ai}} \right) \delta_{ij}. \tag{B14}$$

- **Source outside the resonator (Figure 1(b)).** The resonant modes do not span the total fields inside the resonator in this scenario. Hence, we adopt a different strategy. We define the incident fields $E^{\text{inc}}(r, \omega)$ and $H^{\text{inc}}(r, \omega)$ as those created by the source when resonator A is absent (Figure 3.1(c)). We also define the scattered fields E_A^{sca} and H_A^{sca} as $E_A^{\text{sca}}(r, \omega) = E_A^{\text{tot}}(r, \omega) - E^{\text{inc}}(r, \omega)$ and $H_A^{\text{sca}}(r, \omega) = H_A^{\text{tot}}(r, \omega) - H^{\text{inc}}(r, \omega)$, respectively. Then, from the volume and surface equivalence principles, we can deduce²³²:

$$\nabla \times E_A^{sca} = -j\omega\mu_0 H_A^{sca}, \quad (B15a)$$

$$\nabla \times H_A^{sca} = j\omega\varepsilon_{med} E_A^{sca} + (j\omega\Delta\varepsilon_A E^{inc} + \hat{n} \times H^{inc}) + (j\omega\Delta\varepsilon_A E_A^{sca} + \hat{n} \times H_A^{sca}), \quad (B15b)$$

where $\Delta\varepsilon_A = \varepsilon_A - \varepsilon_{med}$. As all the source terms in Eqs. (B15) reside inside the resonator, we can write:

$$\left(\begin{array}{c} E_A^{sca}(r, \omega) \\ H_A^{sca}(r, \omega) \end{array} \right) \Big|_{r \in V_A} = \sum_m \tilde{\alpha}_m(\omega) \left(\begin{array}{c} \tilde{E}_{Am}(r) \\ \tilde{H}_{Am}(r) \end{array} \right). \quad (B16)$$

Then, following Eq. (B10)'s derivation process gives the CM equation as follows:

$$\mathbf{H}_A(\omega)(j\omega\mathbf{I} - \mathbf{P}_A)|\tilde{\alpha}\rangle = -\frac{j\omega}{4} \iiint_{\Delta\varepsilon_A \neq 0} \Delta\varepsilon_A E^{inc} \cdot |\tilde{E}_A^*\rangle d^3r + \frac{1}{4} \iint_{\partial_A^{PEC}} |\tilde{E}_A^*\rangle \times H^{inc} \cdot ds. \quad (B17)$$

By assuming that the incident fields do not have any non-propagating waveguide components, we can expand them as a summation of propagating waveguide modes:

$$E^{inc}(r) = \sum_n S_{q_n, n}^{+A} E_n^w(x, y) e^{-j\beta_n(z-z_{qn})}, \quad (B18a)$$

$$H^{inc}(r) = \sum_n S_{q_n, n}^{+A} H_n^w(x, y) e^{-j\beta_n(z-z_{qn})} \quad (B18b)$$

where $q_n = A1, A2$ for $\beta_n > 0$ and $\beta_n < 0$, respectively. By plugging Eqs. (B18) into Eq. (B17), we can obtain the matrix form of the CM equation:

$$j\omega|\tilde{\alpha}\rangle = \mathbf{P}_A|\tilde{\alpha}\rangle + \mathbf{K}^{A(f)}|S^{+A}\rangle, \quad (B19)$$

where $\mathbf{K}^{A(f)} = [\mathbf{K}_{A1}^{A(f)} \ \mathbf{K}_{A2}^{A(f)}]$ is the *input-coupling matrix* defined as:

$$\mathbf{K}^{A(f)} = \mathbf{H}_A^{-1} \left[\mathbf{v}_{mn} = \left(-\frac{j\omega}{4} \right) \iiint_{\Delta\varepsilon_A \neq 0} \Delta\varepsilon_A E_n^w \cdot \tilde{E}_{Am}^* e^{-j\beta_n(z-z_{qn})} d^3r \right]_{M \times N} \\ + \mathbf{H}_A^{-1} \left[\mathbf{v}_{mn} = \frac{1}{4} \iint_{\partial_A^{PEC}} \tilde{E}_{Am}^* \times H_n^w e^{-j\beta_n(z-z_{qn})} \cdot ds \right]_{M \times N}. \quad (B20)$$

B.2.2. Scattering and absorption

First assume that the source is outside the resonator (Figure 3.1(b)). We use the Lippmann-Schwinger (or Dyson) approach^{262, 263, 278} to calculate the scattered fields in the resonator's exterior. Eqs. (S15) indicates that $(j\omega\Delta\epsilon_A E^{inc} + \hat{n} \times H^{inc}) + (j\omega\Delta\epsilon_A E_A^{sca} + \hat{n} \times H_A^{sca})$ is the source that generates the scattered fields. Also, as $\Delta\epsilon_A = 0$ outside the resonator, we can expand E_A^{sca} and H_A^{sca} in the source term based on Eq. (B16). Accordingly, we can write:

$$E_A^{sca} = E_{Af}^x + \sum_m \tilde{\alpha}_m \tilde{E}_{Am}^{sca} \quad (B21)$$

where $E_{Af}^x(r, \omega) = \omega^2 \mu_0 \iiint_{\Delta\epsilon_A \neq 0} G_{med}^E \cdot \Delta\epsilon_A \cdot E^{inc} d^3 r' + j\omega\mu_0 \iint_{\partial_A^{PEC}} G_{med}^E \times H^{inc} \cdot ds$ represents the non-resonantly scattered electric field and

$\tilde{E}_{Am}^{sca}(r, \omega) = \omega^2 \mu_0 \iiint_{\Delta\epsilon_A \neq 0} G_{med}^E \cdot \Delta\epsilon_A \cdot \tilde{E}_{Am} d^3 r' + j\omega\mu_0 \iint_{\partial_A^{PEC}} G_{med}^E \times \tilde{H}_{Am} \cdot ds$ denotes the regularized scattered

electric field of the m^{th} mode. $G_{med}^E(r, r', \omega)$ is the electric dyadic Green's function of the medium.

The resonator's scattered fields can be decomposed into non-propagating and propagating components as $E_A^{sca} = E_A^{sca,np} + E_A^{sca,p} = E_A^{sca,np} + E_{Af}^{x,p} + \sum_m \tilde{\alpha}_m \tilde{E}_{Am}^{sca,p}$ and a similar relation for the magnetic field. In each of the A1 and A2 regions, the propagating scattering components can be expanded as a superposition of the waveguide modes as:

$$\begin{aligned} E_A^{sca,p} \Big|_{r \in A1} &= \sum_l S_{A1,l}^{-A,sca} E_l^w e^{-j\beta_l(z-z_{A1})} \\ &= \sum_l S_{A1,l}^{-A,x} E_l^w e^{-j\beta_l(z-z_{A1})} + \sum_m \tilde{\alpha}_m \sum_l f_{A1,lm}^{A(0)} E_l^w e^{-j\beta_l(z-z_{A1})}, \end{aligned} \quad (B22a)$$

$$\begin{aligned} E_A^{sca,p} \Big|_{r \in A2} &= \sum_i S_{A2,i}^{-A,sca} E_i^w e^{-j\beta_i(z-z_{A2})} \\ &= \sum_i S_{A2,i}^{-A,x} E_i^w e^{-j\beta_i(z-z_{A2})} + \sum_m \tilde{\alpha}_m \sum_i f_{A2,im}^{A(0)} E_i^w e^{-j\beta_i(z-z_{A2})}, \end{aligned} \quad (B22b)$$

where $\beta_l < 0$ and $\beta_i > 0$. Magnetic fields in A1 and A2 regions can also be similarly expanded. To find the expansion coefficients in Eqs. (B22), we apply the reciprocity theorem between the A1 and A2 planes with the scattered fields (Eq. (B15)) as the first solution, and n^{th} QNM (Eq. (B6)) as the second solution to obtain:

$$\begin{aligned}
S_{q'_n, n}^{-A, sca} = & \left(-\frac{j\omega}{4} \right) e^{-j|\beta_n|(z_{A2}-z_{A1})} \iiint_{\Delta\epsilon_A \neq 0} \Delta\epsilon_A \cdot (E^{inc} + E_A^{sca}) \cdot (E_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \\
& + \frac{1}{4} e^{-j|\beta_n|(z_{A2}-z_{A1})} \iint_{\partial_A^{PEC}} (E_n^w)^* \times (H^{inc} + H_A^{sca}) e^{j\beta_n(z-z_{qn})} \cdot ds,
\end{aligned} \tag{B23}$$

where $q_n = A1$ and $q'_n = A2$ for $\beta_n > 0$, and $q_n = A2$ and $q'_n = A1$ for $\beta_n < 0$. Eq. (B23) shows how the resonator couples different waveguide modes to each other as a scatterer. It is more common to express the total fields radiated away from the resonator rather than the scattered fields. By adding E^{inc} to both sides of Eqs. (B22) and combining the result with Eqs. (B16), (B18), and (B23), we can obtain the following formula for the outward radiation of the resonator:

$$|S^{-A}\rangle = \mathbf{S}^{Af} |S^{+A}\rangle + \mathbf{X}^{Af} |S^{+A}\rangle + \mathbf{F}^A |\tilde{\alpha}\rangle, \tag{B24}$$

where $\mathbf{S}^{Af} = \begin{bmatrix} 0 & \mathbf{D}(z_{A2} - z_{A1}) \\ \mathbf{D}(z_{A2} - z_{A1}) & 0 \end{bmatrix}$ is the scattering matrix for the free space slab between

the reference planes with the delay matrix $\mathbf{D}(z_{A2} - z_{A1})$ defined as the $\mathbf{N}/2 \times \mathbf{N}/2$ diagonal matrix of the elements $d_{nn} = e^{-j\beta_n(z_{A2}-z_{A1})}$ with $1 \leq n \leq \mathbf{N}/2$. $\mathbf{X}^{Af} |S^{+A}\rangle$ represents the non-resonant scattering of the incident field with $\mathbf{X}^{Af}$ defined as:

$$\begin{aligned}
\mathbf{X}^{Af} = \mathbf{S}^{Af} & \left[x_{nk} = \left(-\frac{j\omega}{4} \right) e^{j(\beta_k z_{qk} - \beta_n z_{qn})} \iiint_{\epsilon_A \neq \epsilon_{med}} \Delta\epsilon_A \cdot E_k^w \cdot (E_n^w)^* e^{j(\beta_n - \beta_k)z} d^3r \right]_{\mathbf{N} \times \mathbf{N}} \\
& + \mathbf{S}^{Af} \left[x_{nk} = \frac{1}{4} e^{j(\beta_k z_{qk} - \beta_n z_{qn})} \iint_{\partial_A^{PEC}} (E_n^w)^* \times H_k^w e^{j(\beta_n - \beta_k)z} \cdot ds \right]_{\mathbf{N} \times \mathbf{N}}.
\end{aligned} \tag{B25}$$

Furthermore, $\mathbf{F}^A = \begin{bmatrix} \mathbf{F}_{A1}^A \\ \mathbf{F}_{A2}^A \end{bmatrix}$ is the *output-coupling matrix* of the modes:

$$\begin{aligned}
\mathbf{F}^A = \mathbf{S}^{Af} & \left[v_{nm} = \left(-\frac{j\omega}{4} \right) \iiint_{\Delta\epsilon_A \neq 0} \Delta\epsilon_A \cdot \tilde{E}_{Am} \cdot (E_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \right]_{\mathbf{N} \times \mathbf{M}} \\
& + \mathbf{S}^{Af} \left[v_{nm} = \frac{1}{4} \iint_{\partial_A^{PEC}} (E_n^w)^* \times \tilde{H}_{Am} e^{j\beta_n(z-z_{qn})} \cdot ds \right]_{\mathbf{N} \times \mathbf{M}}.
\end{aligned} \tag{B26}$$

Now we determine the resonator absorption ²⁷⁷:

$$\begin{aligned}
A_A(\omega) &= -\frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im}[\epsilon_A(r, \omega)] |E^{inc}(r, \omega) + E_A^{sca}(r, \omega)|^2 d^3r = -\frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im} \left[\epsilon_A \left| E^{inc} + \sum_m \tilde{\alpha}_m \tilde{E}_{Am} \right|^2 \right] d^3r \\
&= -\frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im}(\epsilon_A) |E^{inc}|^2 d^3r - \frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im} \left[\epsilon_A \sum_m \sum_n \tilde{\alpha}_m^* \tilde{\alpha}_n (\tilde{E}_{Am}^* \cdot \tilde{E}_{An}) \right] d^3r \\
&\quad - \frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im} \left[\Delta\epsilon_A \sum_m \tilde{\alpha}_m^* (E^{inc} \cdot \tilde{E}_{Am}) \right] d^3r - \frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im} \left\{ \Delta\epsilon_A \sum_m \tilde{\alpha}_m \left[(E^{inc})^* \cdot \tilde{E}_{Am} \right] \right\} d^3r,
\end{aligned} \tag{B27}$$

where the change of ϵ_A to $\Delta\epsilon_A$ is due to our initial assumption of having a lossless medium. The

integral term $-\frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im}(\epsilon_A) |E^{inc}|^2 d^3r$ corresponds to the non-resonant absorption of the incident

field and shall be represented by A_{Af}^x . The term $-\frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im} \left[\epsilon_A \sum_m \sum_n \tilde{\alpha}_m^* \tilde{\alpha}_n (\tilde{E}_{Am}^* \cdot \tilde{E}_{An}) \right] d^3r$ shows

the resonant absorption mediated by the resonator modes and when the resonator materials are low-dispersion ($|\partial(\omega\epsilon_A)/(\epsilon_A \partial\omega)| \approx 1$) we can use Eq. (B11) to approximate it as

$$\begin{aligned}
2\omega \text{Im}[\langle \tilde{\alpha} | \mathbf{H}_A | \tilde{\alpha} \rangle]. \quad \text{The terms} \quad & -\frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im} \left[\Delta\epsilon_A \sum_m \tilde{\alpha}_m^* (E^{inc} \cdot \tilde{E}_{Am}) \right] d^3r \quad \text{and} \\
& -\frac{\omega}{2} \iiint_{\Delta\epsilon_A \neq 0} \text{Im} \left\{ \Delta\epsilon_A \sum_m \tilde{\alpha}_m \left[(E^{inc})^* \cdot \tilde{E}_{Am} \right] \right\} d^3r
\end{aligned}$$

describe the absorption due to the cross product of the resonator modes and the incident field. We can typically neglect the cross-product terms as they almost cancel out when the materials are low-loss, i.e., $\tan(\delta_A) = -\text{Im}[\epsilon_A]/\text{Re}[\epsilon_A] \ll 1$.

Considering the above analyses, we can rewrite Eq. (B27) as:

$$A_A \approx A_{Af}^x - 2\omega \text{Im}[\langle \tilde{\alpha} | \mathbf{H}_A | \tilde{\alpha} \rangle]. \tag{B28}$$

When the source is inside the resonator (Figure 1(a)), we get similar scattering and absorption formulas but without the non-resonant terms. In what follows, we assume that the resonator does not contain any PEC components for simplicity.

B.2.3. Background perturbation

We consider a *background structure* with the dielectric function $\epsilon_{Ab}(r, \omega)$ such that $\epsilon_A(r, \omega) \neq \epsilon_{Ab}(r, \omega)$ region coincides with the resonator's principal areas. Like Eqs. (B15), Maxwell's equations for the scattered fields of the background structure can be written as:

$$\nabla \times E_{Ab}^{sca} = -j\omega\mu_0 H_{Ab}^{sca}, \quad (B29a)$$

$$\nabla \times H_{Ab}^{sca} = j\omega\epsilon_{Ab} E_{Ab}^{sca} + j\omega\Delta\epsilon_{Ab} E^{inc}, \quad (B29b)$$

where $\Delta\epsilon_{Ab} = \epsilon_{Ab} - \epsilon_{med}$. By writing the right-hand-side of Eq. (B29b) as $j\omega\epsilon_{med} E_{Ab}^{sca} + j\omega\Delta\epsilon_{Ab} (E^{inc} + E_{Ab}^{sca})$, we can get the following equation for the field scattered from the background structure:

$$E_{Ab}^{sca} = \omega^2 \mu_0 \iiint_{\epsilon_{Ab} \neq \epsilon_{med}} G_{med}^E \cdot \Delta\epsilon_{Ab} \cdot T_{Ab}(E^{inc}) d^3 r', \quad (B30)$$

where $T_{Ab}(E^{inc}) = E^{inc} + E_{Ab}^{sca} = E^{inc} + \omega^2 \mu_0 \iiint_{\Delta\epsilon_{Ab} \neq 0} G_{Ab}^E \cdot \Delta\epsilon_{Ab} \cdot E^{inc} d^3 r'$ is the total electric field that the sources create when the background structure replaces the resonator in the medium, with $G_{Ab}^E(r, r', \omega)$ being the electric dyadic Green's function of the background structure.

By combining Eqs. (B15) and (B29) we can get:

$$\nabla \times E_{Ar}^{sca} = -j\omega\mu_0 H_{Ar}^{sca}, \quad (B31a)$$

$$\nabla \times H_{Ar}^{sca} = j\omega\epsilon_A E_{Ar}^{sca} + j\omega(\epsilon_A - \epsilon_{Ab})(E^{inc} + E_{Ab}^{sca}). \quad (B31b)$$

where $E_{Ar}^{sca} = E_A^{sca} - E_{Ab}^{sca}$ and $H_{Ar}^{sca} = H_A^{sca} - H_{Ab}^{sca}$. By assuming $E_{Ar}^{sca}|_{r \in V_A} = \sum_m \alpha_m \tilde{E}_{Am}$ and $H_{Ar}^{sca}|_{r \in V_A} = \sum_m \alpha_m \tilde{H}_{Am}$ like Eq. (B16), and then following the Eq. (B17) derivation procedure, we obtain the CM equation as follows:

$$\begin{aligned} \mathbf{H}_A(\omega)(j\omega\mathbf{I} - \mathbf{P}_A)|\alpha\rangle &= -\frac{j\omega}{4} \iiint_{\epsilon_A \neq \epsilon_{Ab}} (\epsilon_A - \epsilon_{Ab})(E^{inc} + E_{Ab}^{sca}) \cdot |\tilde{E}_A^*\rangle d^3 r \\ &= -\frac{j\omega}{4} \iiint_{\epsilon_A \neq \epsilon_{Ab}} (\epsilon_A - \epsilon_{Ab}) T_{Ab}(E^{inc}) \cdot |\tilde{E}_A^*\rangle d^3 r. \end{aligned} \quad (B32)$$

By inserting Eqs. (B18) into Eq. (B32), we can rewrite it in matrix format as:

$$j\omega|\alpha\rangle = \mathbf{P}_A|\alpha\rangle + \mathbf{K}^A|S^{+A}\rangle, \quad (B33)$$

which has a similar form as Eq. (B19). However, the input-coupling matrix has changed from $\mathbf{\kappa}^{A(f)}$ (Eq. (B20)) to $\mathbf{\kappa}^A$ defined as:

$$\mathbf{\kappa}^A = \mathbf{H}_A^{-1} \left[\mathbf{v}_{mn} = \left(-\frac{j\omega}{4} \right) \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} (\varepsilon_A - \varepsilon_{Ab}) \cdot \mathbf{T}_{Ab} \left(\mathbf{E}_n^w e^{-j\beta_n(z-z_{qn})} \right) \cdot \tilde{\mathbf{E}}_{Am}^* d^3r \right]_{\mathbf{M} \times \mathbf{N}}. \quad (\text{B34})$$

By writing the right-hand-side of Eq. (B31b) as $j\omega\varepsilon_{med}\mathbf{E}_{Ar}^{sca} + j\omega\Delta\varepsilon_A\mathbf{E}_{Ar}^{sca} + j\omega(\varepsilon_A - \varepsilon_{Ab})(\mathbf{E}^{inc} + \mathbf{E}_{Ab}^{sca})$ and then following the Eq. (B21) derivation process, we can express the scattered electric field of resonator A as a perturbation to the background's scattered field:

$$\mathbf{E}_A^{sca} = \mathbf{E}_{Ab}^x + \mathbf{E}_{Ab}^{sca} + \sum_m \alpha_m \tilde{\mathbf{E}}_{Am}^{sca} \approx \mathbf{E}_{Ab}^{sca} + \sum_m \alpha_m \tilde{\mathbf{E}}_{Am}^{sca}, \quad (\text{B35})$$

where $\mathbf{E}_{Ab}^x = \omega^2 \mu_0 \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} \mathbf{G}_{med}^E \cdot (\varepsilon_A - \varepsilon_{Ab}) \cdot \mathbf{T}_{Ab}(\mathbf{E}^{inc}) d^3r$ is the modified term for the non-resonantly scattered electric field and $\tilde{\mathbf{E}}_{Am}^{sca}$ has a similar definition as in Eq. (B21).

By decomposing $\mathbf{E}_A^{sca}$ in Eq. (B35) into non-propagating and propagating components as

$$\mathbf{E}_A^{sca} = (\mathbf{E}_{Ab}^{sca,np} + \mathbf{E}_{Ar}^{sca,np}) + \left(\mathbf{E}_{Ab}^{sca,p} + \sum_m \alpha_m \tilde{\mathbf{E}}_{Am}^{sca,p} \right), \text{ and then following the Eq. (B24) derivation}$$

procedure, we get the following equation for the output power wave vector of the resonator:

$$|S^{-A}\rangle = \mathbf{X}^{Ab} |S^{+A}\rangle + \mathbf{S}^{Ab} |S^{+A}\rangle + \mathbf{F}^A |\alpha\rangle \approx \mathbf{S}^{Ab} |S^{+A}\rangle + \mathbf{F}^A |\alpha\rangle, \quad (\text{B36})$$

where $\mathbf{S}^{Ab} = \begin{bmatrix} \mathbf{S}_{11}^{Ab} & \mathbf{S}_{12}^{Ab} \\ \mathbf{S}_{21}^{Ab} & \mathbf{S}_{22}^{Ab} \end{bmatrix}$ is the scattering matrix of the background structure defined as:

$$\begin{bmatrix} |S_{A1}^{-Ab}\rangle \\ |S_{A2}^{-Ab}\rangle \end{bmatrix} = \mathbf{S}^{Ab} \begin{bmatrix} |S_{A1}^{+A}\rangle \\ |S_{A2}^{+A}\rangle \end{bmatrix}, \quad (\text{B37})$$

with the vectors $|S_{A1}^{-Ab}\rangle$ and $|S_{A2}^{-Ab}\rangle$ representing the output power wave vectors of the background structure in regions A1 and A2, respectively. Also, $\mathbf{X}^{Ab}$ is the modified non-resonant scattering matrix:

$$\mathbf{X}^{Ab} = \mathbf{S}^{Af} \left[x_{p,nk} = \left(-\frac{j\omega}{4} \right) e^{-j\beta_n(z_{A2}-z_{A1})} \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} (\varepsilon_A - \varepsilon_{Ab}) T_{Ab} \left(E_k^w e^{-j\beta_k(z-z_{qk})} \right) \cdot (E_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \right]_{N \times N}. \quad (\text{B38})$$

By considering E_{Ar}^{sca} and H_{Ar}^{sca} definitions and following the Eq. (B28) derivation process, we can also express the resonator's absorption as a perturbation to the background's absorption:

$$A_A(\omega) \approx A_{Ab}^x(\omega) + A_{Ab}(\omega) - 2\omega \text{Im}[\langle \alpha | \mathbf{H}_A | \alpha \rangle] \approx A_{Ab}(\omega) - 2\omega \text{Im}[\langle \alpha | \mathbf{H}_A | \alpha \rangle], \quad (\text{B39})$$

where $A_{Ab}^x(\omega) = -\frac{\omega}{2} \iiint_{\varepsilon_A \neq \varepsilon_{Ab}} \text{Im}(\varepsilon_A - \varepsilon_{Ab}) |T_{Ab}(E^{inc})|^2 d^3r$ is the modified non-resonant absorption.

When $V_{\varepsilon_A \neq \varepsilon_{Ab}} \ll V_A$ or $T_{Ab}(E^{inc}) \ll E_{Ar}^{sca}$ in $\varepsilon_A \neq \varepsilon_{Ab}$ region, the non-resonant terms in Eq. (B35), (B36), and (B39) can be neglected.

Considering the energy conservation, one can express the resonator and background absorption as $A_A = \langle S^{+A} | S^{+A} \rangle - \langle S^{-A} | S^{-A} \rangle$ and $A_{Ab} = \langle S^{+A} | S^{+A} \rangle - \langle S^{-Ab} | S^{-Ab} \rangle$, respectively. By combining these relations with Eqs. (B33) and (B34), we obtain:

$$A_A = \langle S^{+A} | S^{+A} \rangle - \langle S^{+A} | (\mathbf{S}^{Ab})^\dagger \mathbf{S}^{Ab} | S^{+A} \rangle - \langle \alpha | (\mathbf{F}^A)^\dagger \mathbf{F}^A | \alpha \rangle - \langle S^{+A} | (\mathbf{S}^{Ab})^\dagger \mathbf{F}^A | \alpha \rangle - \langle \alpha | (\mathbf{F}^A)^\dagger \mathbf{S}^{Ab} | S^{+A} \rangle = A_{Ab}(\omega) - \langle \alpha | (\mathbf{F}^A)^\dagger \mathbf{F}^A | \alpha \rangle - 2\text{Re}[\langle \alpha | (\mathbf{F}^A)^\dagger \mathbf{S}^{Ab} | S^{+A} \rangle], \quad (\text{B40})$$

where $\dagger$ denotes the conjugate transpose operation. Also, from Eqs. (B33) and (B39) we can get:

$$A_A(\omega) = A_{Ab}(\omega) + 2\text{Re}[\langle \alpha | \mathbf{H}_A \mathbf{P}_A | \alpha \rangle] + 2\text{Re}[\langle \alpha | \mathbf{H}_A \mathbf{K}^A | S^{+A} \rangle]. \quad (\text{B41})$$

Combining Eqs. (B40) and (B41) then gives us:

$$(\mathbf{F}^A)^\dagger \mathbf{F}^A = -[\mathbf{H}_A \mathbf{P}_A + (\mathbf{P}_A)^\dagger (\mathbf{H}_A)^\dagger], \quad (\text{B42a})$$

$$\mathbf{H}_A \mathbf{K}^A = -(\mathbf{F}^A)^\dagger \mathbf{S}^{Ab}. \quad (\text{B42b})$$

Eq. (B42) can be simplified to $(\mathbf{F}^A)^\dagger \mathbf{F}^A \approx 2\mathbf{\Gamma}_A^r$ under the mode orthogonality condition (Eq. (B14)).

When the background structure is the free-space, the coupled-mode, scattering, and absorption equations derived in this section become same as their counterparts in sections B.2.1 and B.2.2. In

this regard, choosing a free-space background structure is equivalent to not using the background perturbation in the first place.

B.2.4. Resonator perturbation and basis set generalization

We consider a resonator A' with the dielectric function $\varepsilon_{A'} = \varepsilon_A + \delta\varepsilon$, where $\delta\varepsilon$ is small and lies close to or inside resonator A, such that resonator A modes can approximately expand the scattered fields inside $\delta\varepsilon$. Then, by following the Eq. (B32) derivation procedure we would get:

$$\begin{aligned} \mathbf{H}_A(\omega)(j\omega\mathbf{I} - \mathbf{P}_A)|\alpha\rangle = & -\frac{j\omega}{4} \iiint_{\varepsilon_{A'} \neq \varepsilon_{Ab}} (\varepsilon_{A'} - \varepsilon_{Ab}) T_{Ab}(E^{inc}) \cdot |\tilde{E}_A^*\rangle d^3r \\ & + \sum_n \alpha_n \left(-\frac{j\omega}{4} \right) \iiint_{\delta\varepsilon \neq 0} \delta\varepsilon \tilde{E}_{An} \cdot |\tilde{E}_A^*\rangle d^3r, \end{aligned} \quad (\text{B43})$$

which can be rearranged in matrix format as:

$$j\omega|\alpha\rangle = \mathbf{P}_{A'}|\alpha\rangle + \mathbf{K}^{A'}|S^{+A}\rangle = (\mathbf{P}_A + \delta\mathbf{P})|\alpha\rangle + (\mathbf{K}^A + \delta\mathbf{K})|S^{+A}\rangle, \quad (\text{B44})$$

where $\mathbf{P}_{A'} = \mathbf{P}_A + \delta\mathbf{P}$ and $\mathbf{K}^{A'} = \mathbf{K}^A + \delta\mathbf{K}$ are the perturbed pole and input-coupling matrices, respectively. Also:

$$\delta\mathbf{P} = \mathbf{H}_A^{-1} \left[v_{mn} = \left(-\frac{j\omega}{4} \right) \iiint_{\delta\varepsilon \neq 0} \delta\varepsilon \tilde{E}_{An} \cdot \tilde{E}_{Am}^* d^3r \right]_{\mathbf{M} \times \mathbf{M}}, \quad (\text{B45})$$

$$\delta\mathbf{K} = \mathbf{H}_A^{-1} \left[v_{mn} = \left(-\frac{j\omega}{4} \right) \iiint_{\delta\varepsilon \neq 0} \delta\varepsilon \cdot T_{Ab} \left(E_n^w e^{-j\beta_n(z-z_{qn})} \right) \cdot \tilde{E}_{Am}^* d^3r \right]_{\mathbf{M} \times \mathbf{N}}. \quad (\text{B46})$$

To calculate the stored energy and absorption (Eqs. (B12) and (B39)), we should also modify the Hamiltonian matrix to $\mathbf{H}_{A'} = \mathbf{H}_A + \delta\mathbf{H}$, where:

$$\delta\mathbf{H} = \left[v_{mn} = \frac{1}{4} \iiint_{\delta\varepsilon \neq 0} \delta\varepsilon \tilde{E}_{An} \cdot \tilde{E}_{Am}^* d^3r + \frac{1}{4} \iiint_{\partial V} \mu_0 (\tilde{H}_{Am} \cdot \tilde{H}_{An}^*) d^3r \right]_{\mathbf{M} \times \mathbf{M}}, \quad (\text{B47})$$

where we have considered $\delta\varepsilon$ has a low dispersion for simplicity.

Finally, resonator perturbation modifies the output-coupling matrix to $\mathbf{F}^{A'} = \mathbf{F}^A + \delta\mathbf{F}$, where $\delta\mathbf{F}$ can be calculated from Eq. (B26) as:

$$\delta \mathbf{F} = \mathbf{S}^{\text{Af}} \left[\mathbf{v}_{nm} = \left(-\frac{j\omega}{4} \right) \iiint_{\delta \varepsilon \neq 0} \delta \varepsilon \cdot \tilde{\mathbf{E}}_{Am} \cdot (\mathbf{E}_n^w)^* e^{j\beta_n(z-z_{qn})} d^3r \right]_{\mathbf{N} \times \mathbf{M}}. \quad (\text{B47})$$

B.2.5. Parameter retrieval by reverse engineering

Kappa-estimation lemma:

The primary goal of Kappa-estimation lemma is estimation of the non-radiative decay rate and input-coupling coefficients for the m^{th} mode of the resonator. Suppose that: 1) Resonator A is made of low-dispersion and lossy ($\text{Im}[\varepsilon_A] \neq 0$) materials; 2) Resonator A's QNMs are orthogonal and are used as the mode basis set; 3) the background structure is lossless. Moreover, assume that the resonator absorption spectra around $\omega = \Omega_{Am}$ is known when it is excited from different ports.

Consider that the resonator is being excited from the n^{th} port while all the other ports are matched. We can then write the CM equation for the m^{th} resonator mode as follows:

$$j\omega\alpha_m = P_{Am}\alpha_m + \kappa_{mn}^A S_n^{+A} = j\Omega_{Am}\alpha_m - (\Gamma_{Am}^{nr} + \sum_n \Gamma_{Am}^{r,n})\alpha_m + \kappa_{mn}^A S_n^{+A}, \quad (\text{B49})$$

from which, we can calculate the m^{th} mode amplitude as follows:

$$\alpha_m = \frac{\kappa_{mn}^A S_n^{+A}}{j(\omega - \Omega_{Am}) + (\Gamma_{Am}^{nr} + \sum_n \Gamma_{Am}^{r,n})}. \quad (\text{B50})$$

From Eq. (B39), we can use the formula $A_A(\omega) = A_{Ab}(\omega) + \langle \alpha | 2\mathbf{\Gamma}_A^{nr} | \alpha \rangle$ to calculate the absorption of resonator A in the spectral vicinity of $\omega = \Omega_{Am}$. This formula reveals that the absorption spectrum would approximately consist of the Lorentzian curve $A_{mn} = 2\Gamma_{Am}^{nr} |\alpha_m|^2$ on top of a non-resonant background spectrum in the vicinity of $\omega = \Omega_{Am}$. A_{mn} can be considered to be the absorption of the m^{th} resonator mode when it is excited from the n^{th} port, and from Eq. (B50) can be rewritten as:

$$A_{mn} = \frac{2\Gamma_{Am}^{nr} |\kappa_{mn}^A|^2 |S_n^{+A}|^2}{(\omega - \Omega_{Am})^2 + (\Gamma_{Am}^{nr} + \sum_n \Gamma_{Am}^{r,n})^2}. \quad (\text{B51})$$

From Eq. (B51), the maximum normalized absorption (at $\omega = \Omega_{Am}$) and full width at half maximum (FWHM) for the m^{th} resonator mode and n^{th} port would be:

$$A_{mn}^{\max} = \frac{2\Gamma_{Am}^{nr} |\kappa_{mn}^A|^2}{(\Gamma_{Am}^{nr} + \sum_n \Gamma_{Am}^{r,n})^2}, \quad (\text{B52a})$$

$$\Delta\omega_{Am} = 2\left(\Gamma_{Am}^{nr} + \sum_n \Gamma_{Am}^{r,n}\right), \quad (\text{B52b})$$

where we have dropped the superscript normalized for brevity. We have also dropped the subscript n for the FWHM as it appears to be independent of the excitation port.

From Eqs. (B42) together with our initial assumptions of orthogonal resonator modes and a lossless background structure, we can deduce that $\sum_n |\kappa_{mn}^A|^2 = 2\sum_n \Gamma_{Am}^{r,n}$. Combining this result with Eqs. (B52) gives us:

$$\sum_n A_{mn}^{\max} = \frac{2\Gamma_{Am}^{nr} \left(\sum_i |\kappa_{mn}^A|^2\right)}{(\Gamma_{Am}^{nr} + \sum_n \Gamma_{Am}^{r,n})^2} = \frac{2\Gamma_{Am}^{nr} (\Delta\omega_{Am} - 2\Gamma_{Am}^{nr})}{\Delta\omega_{Am}^2 / 4}, \quad (\text{B53a})$$

$$\left(\Gamma_{Am}^{nr}\right)^2 - \left(\frac{\Delta\omega_{Am}}{2}\right)\Gamma_{Am}^{nr} + \left(\frac{\Delta\omega_{Am}}{4}\right)^2 \sum_n A_{mn}^{\max} = 0. \quad (\text{B53b})$$

By solving Eq. (B53b) for Γ_{Am}^{nr} , we would obtain:

$$\Gamma_{Am}^{nr} = \frac{\Delta\omega_{Am}}{4} \pm \frac{\Delta\omega_{Am}}{4} \sqrt{1 - \sum_n A_{mn}^{\max}} = \frac{\Delta\omega_{Am}}{4} (1 \pm \Lambda), \quad (\text{B54})$$

where $\Lambda = \sqrt{1 - \sum_n A_{mn}^{\max}}$. From Eqs. (B52b) and (B53a) we can deduce that $\sum_n A_{mn}^{\max} \leq 1$, which guarantees Λ to always be a real number between 0 and 1. Furthermore, From Eqs. (B52) and (B54), we can obtain the following formula for the input-coupling coefficients of the m^{th} mode:

$$|\kappa_{mn}^A|^2 = \frac{\Delta\omega_{Am}}{2} \frac{A_{mn}^{\max}}{1 \pm \Lambda}. \quad (\text{B55})$$

Eqs. (B54) and (B55) give us two sets of solutions; The solution with “+” sign indicates that the resonator behaves like a closed resonator. On the other hand, the solution with “-” sign indicates that the resonator has a negligible material loss. Moreover, the lemma does not directly give us any information on the phase angles of the input-coupling coefficients, except an arbitrary one of them which can be set zero as the reference phase angle (e.g. $\text{angle}(\kappa_{m1}^A) = 0$). We can determine the valid set of solution and the rest of the phase angles by fitting the scattering spectra of the resonator around $\omega = \Omega_{Am}$. An alternative way is to look at the dominant multipoles and the radiation pattern of the mode. Once the input-coupling coefficients of the mode are found, its output coupling coefficients can be obtained from Eq. (B42b).

Kappa-estimation lemma is primarily useful when the resonator materials are lossy. When the resonator materials are lossless, we would get $\Lambda = 1$. In such scenario, Eq. (B54) correctly gives us $\Gamma_{Am}^{nr} = 0$ for the “-” sign. However, Eq. (B55) fails to give us the input-coupling coefficients as both the numerator and denominator on the right-hand-side of the equation become zero. To use the Kappa-estimation lemma for lossless resonators, one can first introduce a small loss into the system and then use the lemma. For example, small imaginary components can be artificially added to the permittivities of the materials or small fractions of lossy materials can be introduced into the system.

F-estimation lemma

The primary goal of the F-estimation lemma is estimation of the non-radiative decay rate and output-coupling coefficients for the m^{th} mode of the resonator. We assume that the FWHM ($\Delta\omega_{Am}$) for the m^{th} mode is known. We first find the scattering matrix ($\mathbf{S}^A$) of the resonator at the frequency $\omega = \Omega_{Am}$ by exciting the resonator from each port and measuring the fields scattered into the other ports.

When the resonator QNMs are orthogonal and used as the mode basis set, we can rewrite Eq. (34) of the main text as:

$$\mathbf{S}^A = \left\{ \mathbf{I} - \sum_m \begin{bmatrix} f_{1m}^A \\ \vdots \\ f_{Nm}^A \end{bmatrix} \frac{\begin{bmatrix} (f_{1m}^A)^* \cdots (f_{Nm}^A)^* \end{bmatrix}}{j(\omega - \Omega_{Am}) + (\Gamma_{Am}^{nr} + \sum_n \Gamma_{Am}^{r,n})} \right\} \mathbf{S}^{Ab}, \quad (\text{B56})$$

from which, we can approximate the resonator scattering matrix at the frequency of $\omega = \Omega_{Am}$ as:

$$\mathbf{S}^A(\omega = \Omega_{Am}) \approx \left\{ \mathbf{I} - \begin{bmatrix} f_{1m}^A \\ \vdots \\ f_{Nm}^A \end{bmatrix} \frac{\begin{bmatrix} (f_{1m}^A)^* \cdots (f_{Nm}^A)^* \end{bmatrix}}{(\Gamma_{Am}^{nr} + \sum_n \Gamma_{Am}^{r,n})} \right\} \mathbf{S}^{Ab}(\omega = \Omega_{Am}). \quad (\text{B57})$$

By combining Eqs. (B52b) and (B57) and some algebraic manipulations, we would then obtain:

$$\begin{bmatrix} |f_{1m}^A|^2 & \cdots & f_{1m}^A (f_{Nm}^A)^* \\ \vdots & \ddots & \vdots \\ f_{Nm}^A (f_{1m}^A)^* & \cdots & |f_{Nm}^A|^2 \end{bmatrix} \approx \frac{\Delta\omega_{Am}}{2} \left[\mathbf{I} - \mathbf{S}^A (\mathbf{S}^{Ab})^{-1} \right]_{\omega=\Omega_{Am}}, \quad (\text{B58})$$

which tells that one can estimate the magnitudes of the output-coupling coefficients for the m^{th} mode from the diagonal elements of the matrix $\frac{\Delta\omega_{Am}}{2} \left[\mathbf{I} - \mathbf{S}^A (\mathbf{S}^{Ab})^{-1} \right]_{\omega=\Omega_{Am}}$. For the phase angles of the output coupling coefficients, we can set $\text{angle}(f_{1m}^A) = 0$ as the phase reference, and then determine the rest of the phase angles using the methods explained for the Kappa-estimation lemma. We can also estimate the input-coupling coefficients from Eq. (B42b). After that, from Eqs. (B42a), (B52b) and (B58), we can estimate the non-radiative decay rate as:

$$\Gamma_{Am}^{nr} \approx \frac{\Delta\omega_{Am}}{2} - \sum_n \frac{|f_{nm}^A|^2}{2} = \frac{\Delta\omega_{Am}}{2} \left[1 - \frac{1}{2} \text{Tr} \left(\mathbf{I} - \mathbf{S}^A (\mathbf{S}^{Ab})^{-1} \right) \right]_{\omega=\Omega_{Am}}. \quad (\text{B59})$$

As the final remark on the F-estimation lemma, please note that although the off-diagonal elements in Eq. (B58) can apparently give us the phase angles for the output coupling coefficients, it is not always a trustable procedure. The reason is that the phase angles of the off-diagonal are highly affected by the choice of background structure and unless the scattering matrix of the background structure closely resembles that of the resonator itself, the phase angles could be highly off their ideal values.

B.3. Relationships between the resonators' coupling parameters

This section derives Eqs. (57) and (58) in section 3.2 of the main text. By concatenating the CM equations of the coupled resonators (Eqs. (46) and (50) of the main text), we can write the CM equation for the collective system of the resonators as:

$$j\omega \begin{bmatrix} |\alpha\rangle \\ |\beta\rangle \end{bmatrix} = \mathbf{P} \begin{bmatrix} |\alpha\rangle \\ |\beta\rangle \end{bmatrix} + \mathbf{\kappa} |S^{+inc}\rangle, \quad (\text{B60})$$

where $\mathbf{\kappa} = \begin{bmatrix} \mathbf{\kappa}^{A(bl)} \\ \mathbf{\kappa}^{B(bl)} \end{bmatrix}$ and $\mathbf{P} = \mathbf{P}^{(0)} + \mathbf{\mu}$ with $\mathbf{P}^{(0)} = \begin{bmatrix} \mathbf{P}_A^{(0)} & \mathbf{0} \\ \mathbf{0} & \mathbf{P}_B^{(0)} \end{bmatrix}$ and $\mathbf{\mu} = \begin{bmatrix} \mu_{AA} & \mu_{AB} \\ \mu_{BA} & \mu_{BB} \end{bmatrix}$. The superscript

(0) indicates belonging to the uncoupled case. We also define the collective Hamiltonian matrix

as $\mathbf{H} = \begin{bmatrix} \mathbf{H}_A & \mathbf{0} \\ \mathbf{0} & \mathbf{H}_B \end{bmatrix}$. Then, by following the procedure used to derive Eqs. (B42a), we can get

$\mathbf{F}^\dagger \mathbf{F} = -[\mathbf{P}^\dagger \mathbf{H}^\dagger + \mathbf{H} \mathbf{P}]$, where $\mathbf{F}$ is defined in Eq. (54) of the main text. When the resonator modes are orthogonal, and the materials are low-dispersion and low-loss, this equation can be simplified to:

$$\mathbf{F}^\dagger \mathbf{F} \approx 2\mathbf{\Gamma}^r - (\mathbf{\mu} + \mathbf{\mu}^\dagger), \quad (\text{B61})$$

with $\mathbf{\Gamma}^r = \begin{bmatrix} \mathbf{\Gamma}_A^r & \mathbf{0} \\ \mathbf{0} & \mathbf{\Gamma}_B^r \end{bmatrix}$. In the limit that the two resonators are infinitely far, all the near-field components of the coupling matrices vanish. Accordingly, Eq. (B61) turns into:

$$\mathbf{F}^\dagger \mathbf{F} \approx 2\mathbf{\Gamma}^r - [\mathbf{\mu}^r + (\mathbf{\mu}^r)^\dagger]. \quad (\text{B62})$$

Now, by approximating that Eq. (B62) is also valid in the weak-coupling regime, we can combine it with Eq. (B61) to obtain the following relationship between the near-field coupling matrices:

$$\mathbf{\mu}^n + (\mathbf{\mu}^n)^\dagger = \mathbf{0}. \quad (\text{B63})$$

B.4. Simulation settings and materials

The FDTD simulations in this work are done using the Lumerical FDTD software. The medium refractive index is set to 1 and the mesh size to 3 nm in all the simulations. For the boundary

conditions, we have chosen perfectly matched layer (PML) in the z direction, and periodic boundary conditions in x and y directions.

The materials used in the examples of the main text include Palik silver model ²⁸³ and SiO₂ with the constant refractive index of $n=1.5$. The considered constant and real refractive index of SiO₂ indicates that it has zero loss and dispersion. For the silver, we can check these factors from its dielectric function. Figure B1 shows the dielectric function, dispersion factor ($|\partial(\omega\epsilon)/(\epsilon\partial\omega)|$), and loss tangent ($\tan(\delta) = -\text{Im}[\epsilon]/\text{Re}[\epsilon]$) of the silver in the frequency range corresponding to the main text examples.

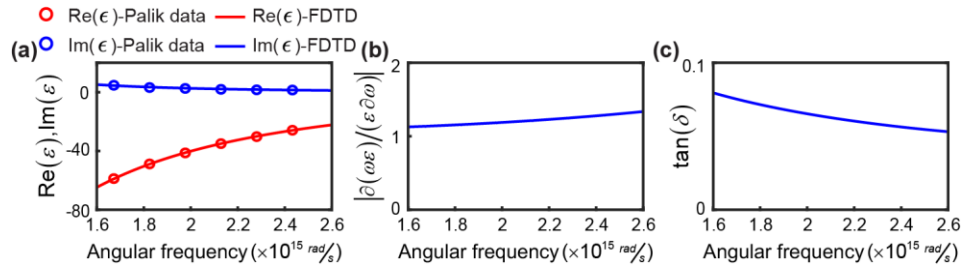


Figure B1. (a) Dielectric function, (b) dispersion factor, and (c) loss tangent of the Palik silver model.

Figures B1(b-c) indicate that Palik silver can be considered low-dispersion (almost) and low-loss in the frequency range of interest.

B.5. Calculations of section 3.4 examples in the main text

B.5.1. MIM nanodisk array embedded in a SiO₂ slab

The spatial period of the array is $P=400$ nm and the diameter of the nanodisks is 100 nm. Also, we have chosen the thicknesses of 30 nm, 12 nm, and 80 nm for the nanodisks, the nanogap, and the embedding layer, respectively. FDTD simulations revealed that in the frequency range of $\omega = 1.8 \times 10^{15} \text{ rad/s}$ to $\omega = 2.6 \times 10^{15} \text{ rad/s}$, the resonator response is dominated by a gap mode with the resonance frequency of $\Omega_A = 2.19 \times 10^{15} \text{ rad/s}$. Figure B2 illustrates the near-field distributions of the mode.

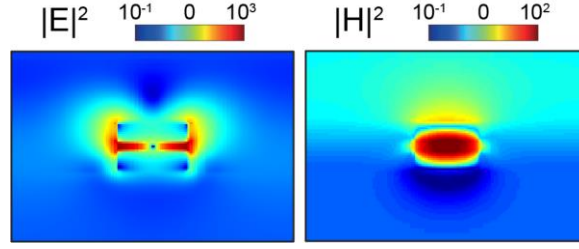


Figure B2. Near field distributions of the resonator at the resonance frequency of $\Omega_A = 2.19 \times 10^{15}$ rad/s reveals that the dominant mode belongs to the gap between the nanodisks.

We use the F-estimation lemma to obtain the parameters of the resonator BBCMT models corresponding to each of the background structures mentioned in section 3.4.1 of the main text. From the FDTD-simulated absorbance spectrum of the resonator in Figure 3D of the main text, we can obtain $P_A^{(0)} = j\Omega_A - \Delta\omega_A/2 = 2.19 \times 10^{15} j - 5.05 \times 10^{13} 1/s$. By putting appropriate monitors in the

FDTD simulations, we can also find $\mathbf{S}^A(\omega = \Omega_A) = \begin{bmatrix} -0.27-0.26j & 0.35-0.73j \\ 0.35-0.73j & -0.27-0.26j \end{bmatrix}$. The scattering matrices of the four background structures mentioned in the main text are as follows:

$$\mathbf{S}^{Ab1}(\omega = \Omega_A) = \begin{bmatrix} -0.35-0.19j & 0.44-0.80j \\ 0.44-0.80j & -0.35-0.19j \end{bmatrix}, \quad \mathbf{S}^{Ab2}(\omega = \Omega_A) = \begin{bmatrix} -0.25-0.17j & 0.53-0.79j \\ 0.53-0.79j & -0.25-0.17j \end{bmatrix}$$

$$\mathbf{S}^{Ab3}(\omega = \Omega_A) = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}, \quad \mathbf{S}^{Ab4}(\omega = \Omega_A) = \begin{bmatrix} 0 & e^{-jkd_A} \\ e^{-jkd_A} & 0 \end{bmatrix},$$

where $d_A = 80$ nm is the distance between the reference planes of the resonator. We have obtained the scattering matrices of the background structures 1 and 2 from FDTD simulations. In contrast, we have calculated the scattering matrices of the background structures 3 and 4 analytically.

As the next step, we use Eq. (B58) to get the non-radiative decay rate and the output coupling coefficients for each background structure:

$$\text{Background 1: } \begin{bmatrix} |f_1^{A(0)}|^2 & f_1^{A(0)} (f_2^{A(0)})^* \\ f_2^{A(0)} (f_1^{A(0)})^* & |f_2^{A(0)}|^2 \end{bmatrix} \approx 10^{12} \times \begin{bmatrix} 5.4-0.05j & -5.36+0.41j \\ -5.36+0.41j & 5.4-0.05j \end{bmatrix}$$

And then, $f_1^{A(0)} = f_2^{A(0)} = 2.33 \times 10^6$, $\Gamma_A^{nr} = 4.51 \times 10^{13} 1/s$.

$$\text{Background 2: } \begin{bmatrix} |f_1^{A(0)}|^2 & f_1^{A(0)} (f_2^{A(0)})^* \\ f_2^{A(0)} (f_1^{A(0)})^* & |f_2^{A(0)}|^2 \end{bmatrix} \approx 10^{12} \times \begin{bmatrix} 6.03+4.77j & -4.76+5.44j \\ -4.76+5.44j & 6.03+4.77j \end{bmatrix}$$

And then, $f_1^{A(0)} = f_2^{A(0)} = 2.46 \times 10^6$, $\Gamma_A^{nr} = 4.45 \times 10^{13}$ 1/s.

$$\text{Background 3: } \begin{bmatrix} |f_1^{A(0)}|^2 & f_1^{A(0)} (f_2^{A(0)})^* \\ f_2^{A(0)} (f_1^{A(0)})^* & |f_2^{A(0)}|^2 \end{bmatrix} \approx 10^{13} \times \begin{bmatrix} 3.67-1.31j & 1.79-3.70j \\ 1.79-3.70j & 3.67-1.31j \end{bmatrix}$$

And then, $f_1^{A(0)} = f_2^{A(0)} = 6.06 \times 10^6$, $\Gamma_A^{nr} = 1.38 \times 10^{13}$ 1/s.

$$\text{Background 4: } \begin{bmatrix} |f_1^{A(0)}|^2 & f_1^{A(0)} (f_2^{A(0)})^* \\ f_2^{A(0)} (f_1^{A(0)})^* & |f_2^{A(0)}|^2 \end{bmatrix} \approx 10^{13} \times \begin{bmatrix} 1.52+2.10j & 0.43+1.85j \\ 0.43+1.85j & 1.52+2.10j \end{bmatrix}$$

And then, $f_1^{A(0)} = f_2^{A(0)} = 3.90 \times 10^6$, $\Gamma_A^{nr} = 3.53 \times 10^{13}$ 1/s.

In the above results, we have put $\angle(f_1^{A(0)}) = 0$ as the phase reference in each case. Also, we have deduced $\angle(f_2^{A(0)}) = 0$ from the symmetry observed in the resonator near-field distributions (Figure B2). We can estimate the frequency-dependent input-coupling coefficients from Eq. (B42b) and by considering $\mathbf{H}_A \approx \mathbf{I}$ as the resonator modes are orthogonal and the materials are low-loss.

B.5.2. Nanolaminate plasmonic crystal

The spatial period of the crystal and its nanodome and nanohole sub-arrays is $P=400$ nm. We have considered the metals to be Palik silver and the dielectrics to be SiO_2 with $n=1.5$. The substrate is also a polymer pillar array with $n=1.5$. We have chosen the thickness of 30 nm for all the metal layers. Also, from the bottom to the top, the thicknesses of the dielectric layers are 5 nm, 10 nm, and 15 nm, respectively. In what follows, we use the Kappa-estimation lemma to find the parameters of the BBCMT models for the nanodome and nanohole arrays in the uncoupled state. Then, we compare the BBCMT-calculated and FDTD-simulated reflectance and transmittance spectra for $d=0$ up to $d=2000$ nm. Finally, we show the results for a CMT model without the non-resonant loading effect.

Parameters of the nanodome array

From the FDTD-simulated absorbance spectra of the nanodome array for top and bottom illuminations (Figure 3.6(a-b)), we can find $\Omega_A = 1.83 \times 10^{15}$ rad/s, $\Delta\omega_A = 1.62 \times 10^{14}$ rad/s, $A_{A1}^{\max} = 0.31$ and $A_{A2}^{\max} = 0.59$. Inserting these values into Eqs. (B59) and (B60) with the minus sign gives us $\Gamma_A^{nr} = 2.77 \times 10^{13}$ 1/s, $\kappa_{A1}^{A(0)} = 6.06 \times 10^6$ 1/s, and $\kappa_{A2}^{A(0)} = -8.36 \times 10^6$ 1/s. We have chosen the minus sign by fitting the reflectance and transmittance data (not shown in the paper). Also, we have set $\text{angle}(\kappa_{A1}^{A(0)}) = 0$ as the reference and approximated $\text{angle}(\kappa_{A2}^{A(0)}) \approx \pi$ since the mode we are considering has a dominant magnetic dipole nature. This choice of the phase angle matches the near-field distribution of the mode as well.

Parameters of the nanohole array

From the FDTD-simulated absorbance spectra of the nanohole array for top and bottom illuminations (Figure 3.6(c-d)), we would find $\Omega_B = 2.03 \times 10^{15}$ rad/s, $\Delta\omega_B = 6.61 \times 10^{13}$ rad/s, $A_{B1}^{\max} = 0.15$ and $A_{B2}^{\max} = 0.04$. Inserting these values into Eqs. (B54) and (B55) with the plus sign gives us $\Gamma_B^{nr} = 3.15 \times 10^{13}$ 1/s, $\kappa_{B1}^{B(0)} = 1.60 \times 10^6$ 1/s, $\kappa_{B2}^{B(0)} = -8.19 \times 10^5$ 1/s. We have chosen the plus sign by fitting the reflectance and transmittance data (not shown in the paper). Also, we have set $\text{angle}(\kappa_{B1}^{B(0)}) = 0$ as the reference, and approximated $\text{angle}(\kappa_{B2}^{B(0)}) \approx \pi$ based on the near-field distributions of the mode, though as both resonator A and the incident wave are located in the region B1, $\kappa_{B2}^{B(0)}$ is not important for our analysis of the MIM system.

Extra colormaps related to section 3.4.2 of the main text

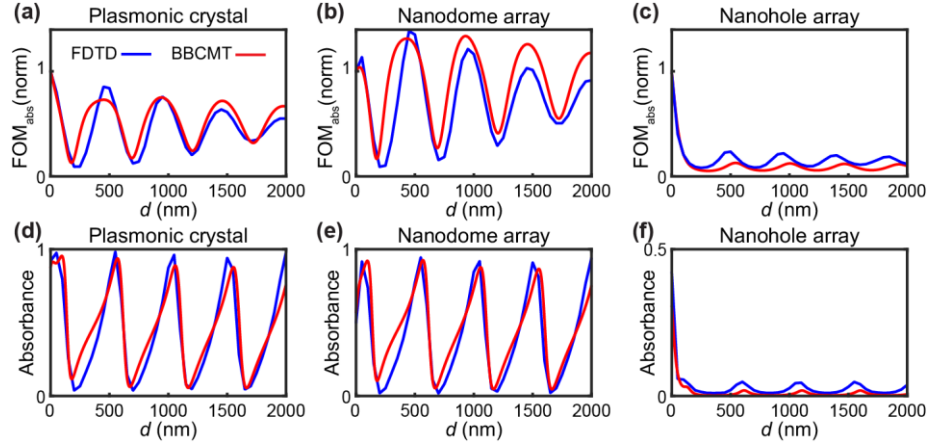


Figure B3. (a-c) Normalized FOM_{abs} from BBCMT calculations and FDTD simulations for the nanolaminate plasmonic crystal (a), the coupled nanodome array (b), and the coupled nanohole array (c). For each value of d , we have defined the figure of merit (FOM) as the area under the absorbance curve. Also, we have normalized the FOM for all values of d to that of $d=0$. (d-f) BBCMT-calculated and FDTD-simulated absorbance of the nanolaminate plasmonic crystal (d), the coupled nanodome array (b), and the coupled nanohole array (f) at the frequency of $\omega = 1.9 \times 10^{15}$ rad/s. All the data in this figure are acquired from the colormaps in Figure 7 of the main text.

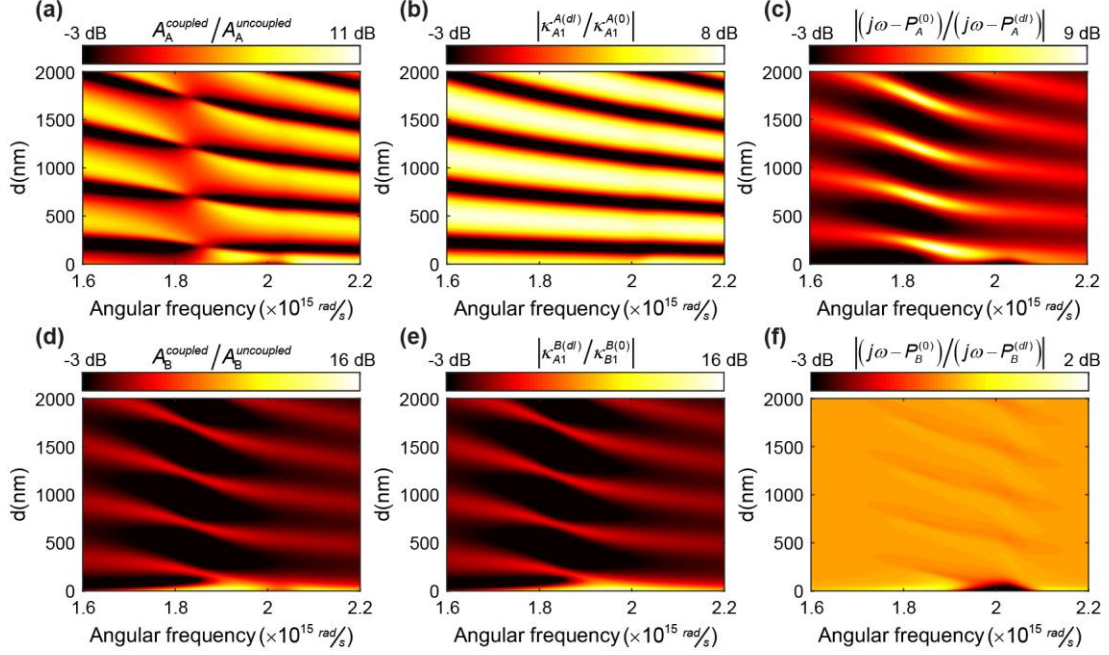


Figure B4. (a, d) Absorption enhancement of the nanodome (a) and nanohole (d) arrays in the coupled state with respect to those for the uncoupled state. (b, e) Enhancement ratio of the input-coupling coefficients for the nanodome (b) and nanohole (e) arrays in the coupled state with respect to those for the uncoupled state. (c, f) Enhancement ratio of the resonance factors for the nanodome (b) and nanohole (e) arrays in the coupled state with respect to those for the uncoupled state. All the colormaps are obtained from the BBCMT analysis for the excitation from the top side and are plotted in the $d - \omega$ plane.

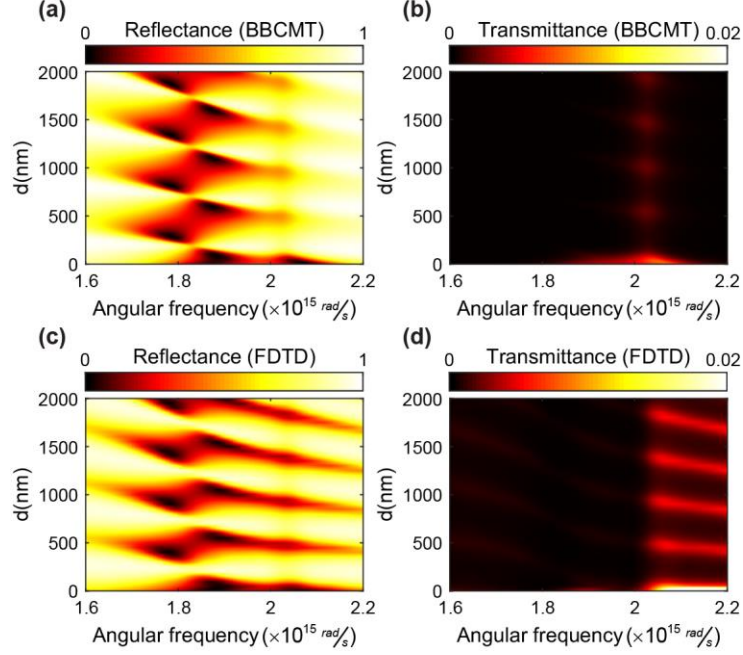


Figure B5. Comparison of the reflectance and transmittance spectra of the nanolaminate plasmonic crystal calculated by BBCMT versus those simulated by FDTD for $d=0$ up to $d=2000$ nm. The resulting spectra are shown as colormaps in the $d - \omega$ plane. The colormaps calculated from BBCMT and FDTD share several features, such as: 1) When d gets large, reflectance and transmittance asymptotically become periodic functions of d ; 2) The maximum transmittance is attained for $d \sim 0$; 3) The transmittance is pretty small for both cases such that the reflectance colormaps of the nanolaminate plasmonic crystal look almost like its absorbance colormaps in Figure 7(a, d) of the main text.

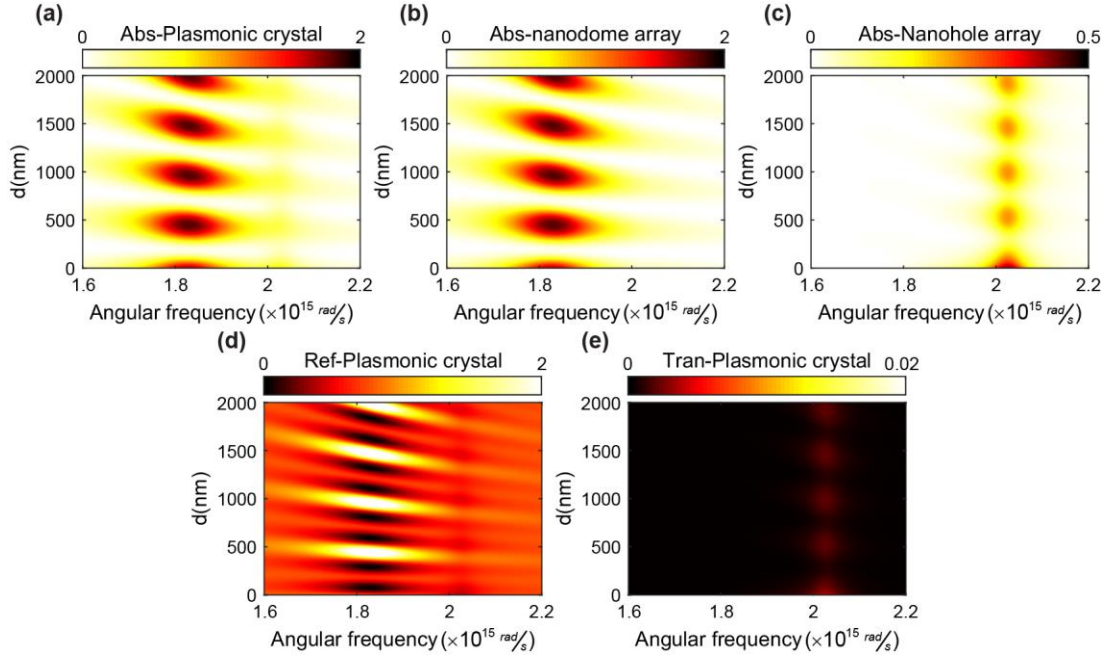


Figure B6. CMT calculations of reflectance, transmittance, and absorbance spectra for $d=0$ up to $d=2000$ nm when the non-resonant loading effect is not considered. The resulting spectra are shown as colormaps in the $d - \omega$ plane. As observed, the quality of fitting considerably degrades when we do not consider the non-resonant loading effect.

Table B1. Big picture overview of TCMT, common QNM theories, and BBCMT (this work)

Framework	Derivation	Main features
TCMT	- Mainly phenomenological. - Based on energy considerations.	- Intuitive pictures of the resonators' electromagnetic interactions. - Oversimplified assumptions.
Common QNM theories	- Derived from Maxwell's equations. - Based on un-conjugated field products.	- Accurate. - Poor connection to Poynting's theorem. - Complex formulation. - Not compatible with TCMT.
BBCMT	- Derived from Maxwell's equations. - Based on conjugated field products.	- Accurate. - Well-connected to Poynting's theorem. - Intuitive pictures of the resonators' electromagnetic interactions. - Reduces to TCMT under certain constraints and assumptions.

Chapter 4: Two-tier Nanolaminate Plasmonic Crystals for Broadband Multiresonant Light Concentration with Spatial Mode Overlap

(This chapter is a slightly modified version of “Two-tier Nanolaminate Plasmonic Crystals for Broadband Multiresonant Light Concentration with Spatial Mode Overlap” by Seied Ali Safiabadi Tali, Junyeob Song, Wonil Nam, and Wei Zhou, published in journal of Advanced Optical Materials 9.10 (2021): 2001908 and has been reproduced here with the permission of the copyright holder.)

Abstract

Effective trapping and nano-localization of different colored photons simultaneously at the same position remain a challenge in nanophotonics research but can boost applications based on nonlinear multiphoton processes. For achieving broadband nanoscale light concentration, a promising strategy is to employ multiresonant plasmonic devices that support multiple hybridized surface plasmon modes with spatial overlap at several different resonance wavelengths. However, high-order plasmonic modes from hybridization tend to have a dark multipolar nature and are less useful due to weak interactions with free-space light. Here, we report that nanolaminate plasmonic crystals in a two-tier configuration can support many (~ 10) spatially overlapped and highly-excitabile hybridized plasmonic modes under free-space light illumination between 400 – 1400 nm. Combination of nanoimprinting lithography and multilayered physical vapor deposition techniques enables wafer-scale fabrication of nanolaminate plasmonic crystals consisting of nanolaminate nanodome and nanohole arrays as the two closely-separated subsystems, and measurements demonstrate their multiresonant plasmonic responses in good agreement with numerical calculations. Coupled-mode theory analysis reveals that the unique broadband multiresonant responses of the two-tier nanolaminate plasmonic crystals are due to the synergistic effects of the strong near-field interactions between the modes in the nanodome and nanohole subsystems and the ground-plane-like loading effect from the nanohole subsystem.

4.1. Introduction

Plasmonic nanostructures can serve as resonant optical nanoantennas to trap and concentrate light at the deep subwavelength scale and thus can enable nanolocalized enhancement of light-matter interactions for various applications in energy conversion, information technology, biochemical sensing, and spectroscopy.^{1, 2, 4, 8, 10, 91} Conventional designs of plasmonic devices optimize single-resonant near-field characteristics within one wavelength band, which is sufficient for applications based on single-photon excitation/emission processes, including photothermal conversion, hot carrier generation, elastic/inelastic scattering, photoluminescence, and electroluminescence.^{8, 10, 91, 284, 285} Nevertheless, for many nonlinear nanophotonics applications, it is highly desirable to use multiresonant plasmonic devices that can simultaneously enhance multiphoton excitation/emission processes in several different wavelength bands at the same hotspot locations.^{5, 7, 25, 32, 37, 92-94, 190, 286, 287}

For constructing multiresonant plasmonic devices, a general approach is to assemble multiple building-block plasmonic resonators within a very close distance; and the optical coupling between spectrally matched non-orthogonal elementary modes of building blocks can result in multiple hybrid plasmonic modes of different resonance wavelengths that spatially overlap⁹⁵⁻⁹⁷. Based on the geometrical configuration of building-block resonators, multiresonant plasmonic devices can be classified into three types: 1) in-plane arrangement,^{7, 25, 26, 31, 146, 184, 190, 286-288} 2) core-shell arrangement,^{32, 289-293} and 3) out-of-plane arrangement.^{209, 211, 294-296} Since it is straightforward to create plasmonic systems with accurate nanoscale control of planar geometries by top-down nanolithography, most previous studies have focused on developing in-plane multiresonant plasmonic devices.^{7, 25, 26, 31, 146, 184, 190, 286-288} Despite the simplicity in design and fabrication, in-plane multiresonant plasmonic devices face two severe limitations due to the planar layout of multiple building-block resonators. 1) The device footprint tends to be large, and accordingly, the surface density of multiresonant hotspots is typically low; 2) Since the nearest-neighbor coupling of elementary modes dominates between in-plane arranged building-block resonators, the planar multiresonant systems usually support a limited number (<4) of hybridized plasmonic modes with spatial overlaps. Recently, Reshef et al. demonstrated that using in-plane plasmonic metasurfaces with a finite out-of-plane dielectric cladding can increase the number of modes by creating several Fabry-Perot-like (FP-like) resonances²⁹⁷. However, such a method primarily depends on the broad electric dipolar plasmonic modes, limiting the maximum attainable absorption to 50%²⁹⁸ and

keeping the field enhancement factor relatively small compared to gap plasmonic modes.⁹⁷ As the second type of multiresonant plasmonic devices, chemically synthesized core-shell metal-insulator-metal (MIM) multilayered nanoparticles can support multiple hybrid modes by mixing the elementary modes at different metal-dielectric interfaces,^{32, 289-293} but have difficulties in accurate nanoscale control of core-shell geometries for scalable fabrication. Moreover, in both the in-plane metasurfaces with dielectric cladding and the MIM core-shell architectures, lack of the environment access to the hotspots restricts the capability for sensing applications. The third type of multiresonant plasmonic devices, i.e., out-of-plane MIM multilayered nanostructures, has recently drawn increasing attention.^{209, 211, 294-296} By allowing for vertical stacking of many MIM resonator building blocks with shared metal layers between the neighboring blocks, out-of-plane multiresonant plasmonic devices can have appealing features,²⁹⁵ including 1) increased surface density of multiresonant hotspots in plasmonic nanogaps, and 2) scalable fabrication by well-controlled thin-film deposition and nanolithography processes. Despite the substantial development of different multiresonant plasmonic devices, a crucial but challenging issue remains that high-order modes from plasmon hybridization tend to have a dark multipolar nature and interact poorly with free-space light.^{96, 97}

Here, we report a new type of two-tier multiresonant plasmonic system -- nanolaminate plasmonic crystals (Figure 4.1(a)) -- that can support many (~ 10) hybridized plasmonic modes with spatial overlap and can allow for multiresonant nanoscale light concentration across a wide wavelength range between 400 and 1400 nm. Uniquely, nanolaminate plasmonic crystals have a two-tier configuration and consist of two closely-separated multiresonant plasmonic subsystems, respectively, (1) a MIM nanolaminate nanodome array that supports multiple localized plasmonic modes M_n^L (Figure 4.1(b)), and (2) a MIM nanolaminate nanohole array that supports multiple delocalized plasmonic modes M_n^D (Figure 4.1(c)).

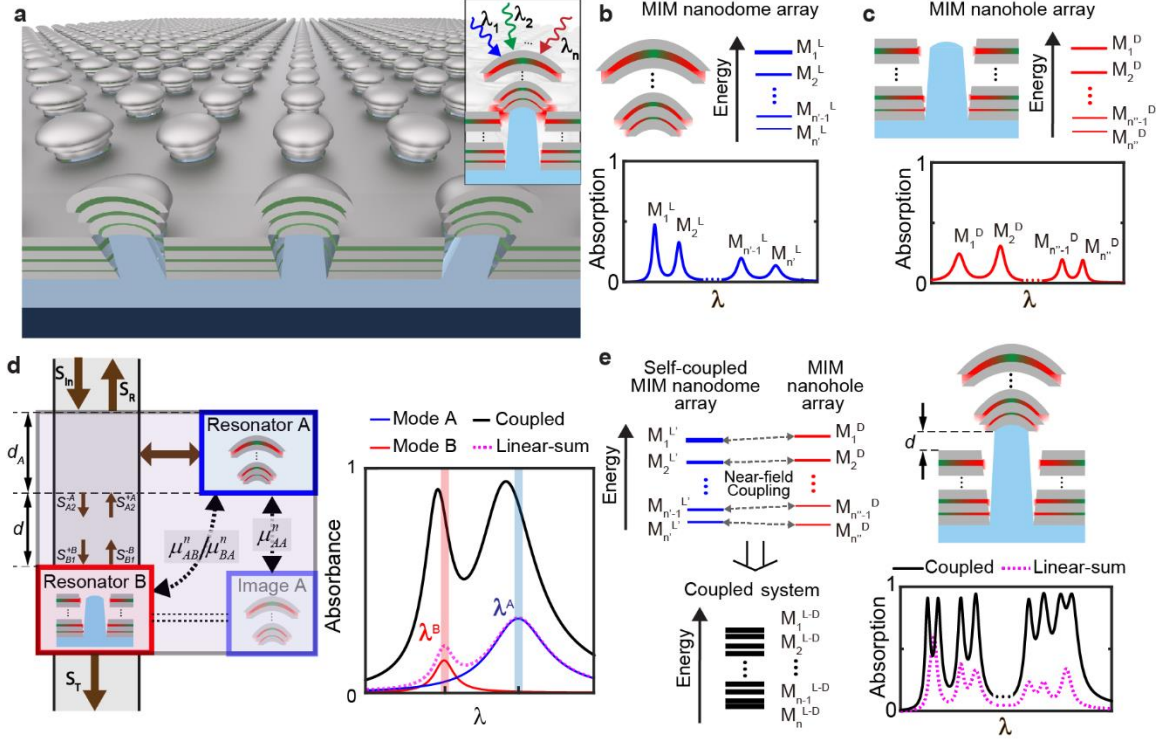


Figure 4.1. Nanolaminate plasmonic crystals in the two-tier configuration for broadband multiresonant nanolocalized light concentration. (a) Scheme of nanolaminate plasmonic crystals consisting of nanolaminate nanodomains and nanohole arrays as the two multiresonant subsystems. (b) Nanolaminate nanodomains support multiple localized plasmonic modes M_n^L by hybridization. (c) Nanolaminate nanohole arrays support multiple delocalized plasmonic modes M_n^D by hybridization. However, the high-order modes from hybridization in multiresonant subsystems tend to have a dark multipolar nature. (d) Coupled-mode theory (CMT) modeling and analysis of optical interactions between the representative Mode A and Mode B in the two subsystems, showing that the coupled system can have a higher light absorption than the summation of those from the two uncoupled subsystems. (e) Schematic energy diagram and absorption spectra for the two-tier multiresonant systems that can support multiple hybrid plasmonic modes M_n^{L-D} with spatial overlaps and with stronger interactions with free-space light.

As illustrated in Figure 4.1(d), the coupled-mode theory (CMT) analysis reveals that the optical interactions between Mode A in the nanolaminate nanodome array (modeled as a side-coupled Resonator A) and Mode B in the nanolaminate nanohole array (modeled as a directly-coupled Resonator B) can significantly increase the total light absorption in the coupled system, much over the summed light absorption from the two subsystems. From the CMT analysis (details in SI), we find that the absorption increase for the coupled system has two primary microscopic origins, including (1) the near-field mutual coupling between Mode A and Mode B, and (2) the ground plane-like loading effect of Resonator B, which enhances the coupling of Mode A to the incident light. Thus, through optical interactions between the two uncoupled multiresonant subsystems, nanolaminate plasmonic crystals as the coupled two-tier multiresonant systems can support a series

of hybrid M_n^{L-D} modes, which have stronger interactions with free-space light compared to the uncoupled M_n^L and M_n^D modes (Figure 4.1(e)). Furthermore, compared to conventional in-plane multiresonant plasmonic systems, out-of-plane nanolaminate plasmonic crystals can possess a much higher surface density of hotspots for broadband multiresonant light concentration by a tight vertical stacking of many MIM nanocavities.

4.2. Results and Discussion

To validate the predictions from CMT analysis, we fabricated samples of nanolaminate plasmonic crystals in the two-tier configuration with different geometric designs and experimentally investigated their optical properties. Briefly, wafer-scale nanolaminate plasmonic crystals were created by line-of-sight electron beam evaporation of alternating Ag and SiO₂ layers on a nanoimprinted polymer nanopillar array.²⁹⁵ Such fabrication strategy guarantees the nanodomains to be self-aligned above the nanoholes. Nanolaminate plasmonic crystals can show a very dark appearance in the top-view (Figure 4.2(a)), manifesting a broadband absorption in the visible range. Nevertheless, as viewed in an oblique angle (Figure 4.2(b)), we can observe a vivid rainbow-color due to the optical diffraction from periodic nanostructures on the sample. While the top-view scanning electron microscopy (SEM) image (Figure 4.2(c)) shows a uniform periodicity for the nanostructures, the cross-sectional SEM image (Figure 4.2(d)) reveals irregular roughnesses and geometries at the surface of sidewalls for MIM nanodomains and nanoholes. Also, the diameters of MIM nanodomains and nanoholes vary between individual units due to the geometry nonuniformity of nanowells in the PDMS template used for nanoimprinting the polymer nanopillar arrays. Notably, MIM nanodomains have an inversely tapered shape because of the shadowing effect in the line-of-sight electron-beam deposition.

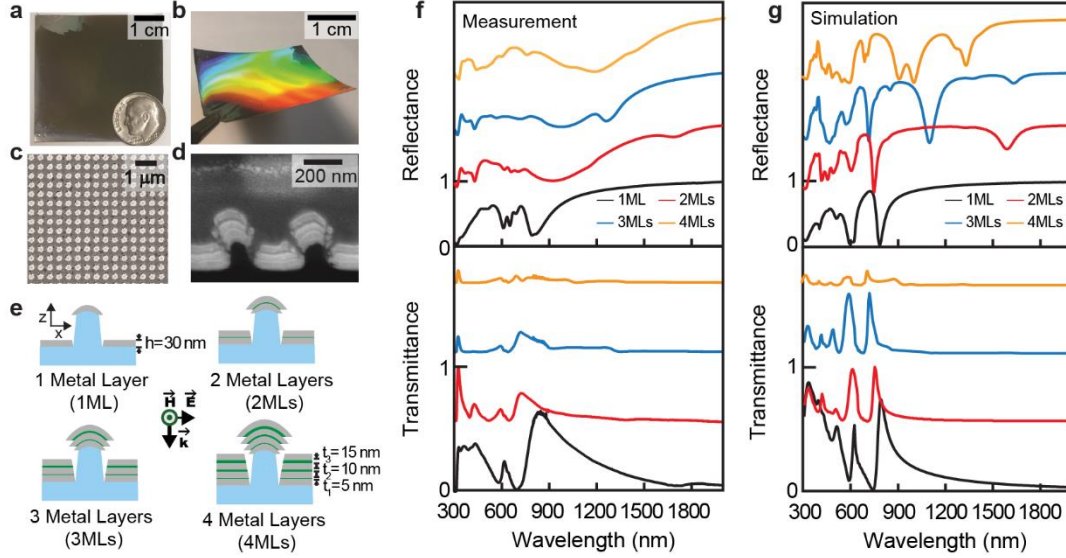


Figure 4.2. Multiresonant optical responses of fabricated nanolaminate plasmonic crystals with different numbers of metal-dielectric layers. (a) Top-view and (b) tilted-view optical camera images of a wafer-scale sample of the four-metal-layer nanolaminate plasmonic crystal. (c) Top-view, and (d) cross-sectional scanning electron microscope (SEM) images of the 4MLs nanolaminate plasmonic crystal. (e) Scheme of four different types of fabricated nanolaminate plasmonic crystals with 1 metal layer (1ML), 2 metal layers (2MLs), 3 metal layers (3MLs), and 4 metal layers (4MLs). The thicknesses of dielectric nanogap layers for nanolaminate plasmonic crystals increase from 8 nm in the bottom to 10 nm in the middle and 15 nm in the top, respectively. (f) Measured, and (g) FDTD-calculated reflection and transmission spectra for the different samples of nanolaminate plasmonic crystals in (e).

As depicted in Figure 4.2(e), we first investigated four different types of fabricated nanolaminate plasmonic crystals with 1 metal layer (1ML), 2 metal layers (2MLs), 3 metal layers (3MLs), and 4 metal layers (4MLs) by reflection and transmission spectroscopy (Figure 4.2(f)). Limited by the height of nanopillar arrays and the chosen thicknesses of individual metal/dielectric layers, the maximum total number of metal layers is four for our fabricated nanolaminate plasmonic crystals. The tapered shape of the nanodomes causes enlarged diameters of individual MIM nanocavities from the bottom to the top in the vertical stack, which leads to spectrally detuned elementary nanogap modes in MIM nanocavities of equal dielectric nanogap thicknesses.²⁰⁹ All the Ag layers have a fixed thickness of 30 nm. However, to allow spectral matching of elementary nanogap modes for effective hybridization, we have chosen increasing dielectric nanogap thicknesses from 5 nm in the bottom to 10 nm in the middle and 15 nm in the top for different individual MIM nanocavities. Notably, the symmetry breaking in the inversely tapered shape of MIM nanodomes can lead to a bianisotropic magneto-electric nature for the supported plasmonic nanogap modes.²⁹⁹ From reflection measurements (Figure 4.2(f)), 2MLs/3MLs/4MLs nanolaminate plasmonic crystals can support multiple resonant modes over a broad spectral range between 400 and 1700

nm. Furthermore, by stacking more metal-dielectric layers, the overall optical response of nanolaminate plasmonic crystals can be changed significantly due to the introduction of some new modes and the spectral detuning of some existing modes. For example, the change from 1ML to 2MLs can cause a new mode emerging at ~ 1650 nm, and a further change from 2MLs to 3MLs can spectrally shift this mode to ~ 1300 nm. Transmittance measurements in Figure 4.2(f) reveal that only a subset of modes in reflection spectra can induce high optical transmission peaks, and the resonant wavelengths of these high-transmission modes (e.g., at 600-615 nm, and 750-850 nm) show relatively weak dependence on the geometric changes by adding more metal-dielectric layers in the system. To study the observed resonant features in measurements, we used the finite-difference time-domain (FDTD) simulations to calculate far-field and near-field optical properties of nanolaminated plasmonic crystals (see Methods). In Figure 4.2(g), the FDTD-calculated reflection and transmission spectra show different multiresonant optical responses among 1ML/2MLs/3MLs/4MLs samples, in agreement with experimental results. By comparing FDTD-calculated near-field profiles of modes in different samples (Figure C1), it is revealed that the added metal-dielectric interfaces in MIM nanodomains and nanohole arrays can introduce new localized and delocalized plasmonic modes into the system, which can also spectrally detune the existing plasmonic modes through near-field interactions. Furthermore, the transmission peaks are associated with Bloch SPP modes at the metal-substrate interface of MIM nanohole arrays.³⁰⁰ Compared to calculations, resonant features in the measurements show much broader linewidths, which can come from homogeneous broadening due to interface roughness and material defects/impurity and inhomogeneous broadening due to geometric variations between unit cells (Figure 4.2(d)). There also exist slight differences between the measured and simulated resonance wavelengths (Figure 4.2(f-g)), that can stem from the dissimilarities between the fabricated and the simulated structures in terms of geometry and materials' dielectric functions.

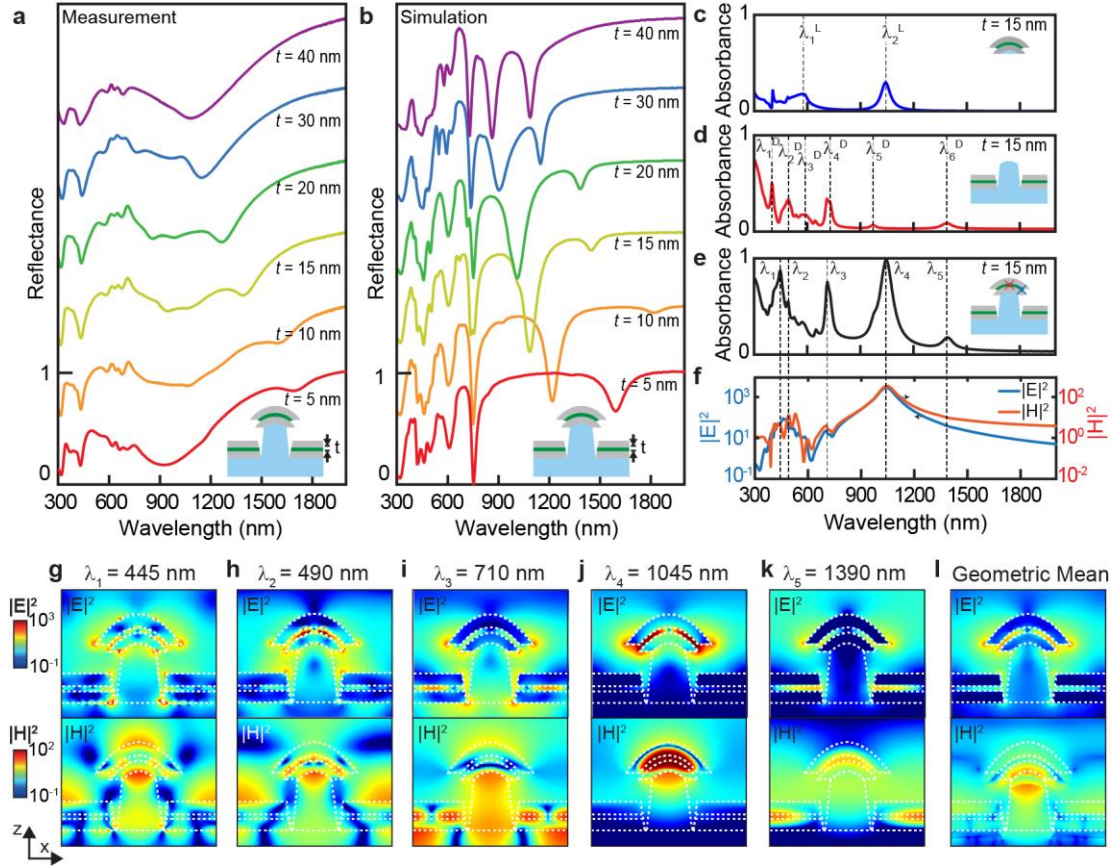


Figure 4.3. The strong dependence of multiresonant optical responses on the dielectric nanogap thickness (t). (a) Measured and (b) FDTD-calculated reflection spectra for 2MLs nanolaminate plasmonic crystals with different t from 5 to 40 nm. (c-d) FDTD-calculated absorption spectra for the 2MLs nanolaminate nanodome (c) and the 2MLs nanolaminate nanohole (d) arrays as the two multiresonant plasmonic subsystems ($t = 15$ nm). (e-f) FDTD-calculated spectra of (e) absorption and (f) near-field $|E|^2/|H|^2$ intensities for 2MLs nanolaminate plasmonic crystals with $t = 15$ nm. (g-k) The FDTD-calculated x-z distribution maps of $|E|^2$ and $|H|^2$ for the modes λ_1 - λ_5 marked in Figure 4.3(e). l, Geometrically-averaged x-z distribution maps of $|E|^2$ and $|H|^2$ among λ_1 - λ_5 modes.

Unlike conventional in-plane engineered plasmonic systems, the multiresonant optical properties of nanolaminate plasmonic crystals also strongly depend on out-of-plane geometries, such as the thicknesses of individual dielectric nanogap layers. To investigate the effects of nanogap thickness t on the supported plasmonic modes, we fabricated 2MLs nanolaminate plasmonic crystals with different t ranging from 5 to 40 nm and measured their reflection (Figure 4.3(a)) and transmission spectra (Figure C1(a)). As t increases from 5 to 40 nm, the resonant feature at 1600 nm blueshifts towards ~ 900 nm. As t increases from 5 to 10 nm, a new resonant feature emerges at 1650 nm, which continuously blueshifts towards ~ 1150 nm with t increasing from 10 nm to 40 nm. Furthermore, the modes associated with transmission peaks only negligibly shift. The FDTD calculations in Figure 4.3(b) and Figure C1(b) show similar t -dependence trends for different

plasmonic modes supported in 2MLs plasmonic crystals in a decent match with the measurements in Figure 4.3(a) and Figure C1(a).

To understand the microscopic natures of different plasmonic modes in 2MLs nanolaminate plasmonic crystals as well as the origins behind their different t -dependent behaviors, we calculated the optical responses of the 2MLs nanolaminate nanodome (Figure 4.3(c)) and nanohole arrays (Figure 4.3(d)) as the two uncoupled subsystems to compare with those of the coupled system (Figure 4.3(e)). As shown in Figure 4.3(c), MIM nanodomains support two prominent absorption peaks associated with the superradiant electric dipole (ED) mode at $\lambda_1^L=575$ nm,^{97, 209} and the darker magnetic dipole (MD) gap mode at $\lambda_2^L=1045$ nm^{97, 209, 301} (Figure C2). Interestingly, the non-symmetric shape of the tapered nanodomains makes the ED mode at λ_1^L non-orthogonal to the gap plasmonic modes. Consequently, the dark high-order gap plasmonic modes^{97, 299} can indirectly get excited through coupling to the ED mode, as exhibited by the several small peaks around $\lambda_1^L=575$ nm in Figure 4.3(c). Furthermore, the MD mode at λ_2^L becomes bianisotropic²⁹⁹ to achieve a larger optical absorption under the upward illumination than the downward illumination (Figure C2). Figure 4.3(d) shows that the MIM nanohole array can induce multiple absorbance peaks by exciting the band-edge Bloch SPP modes of different lattice orders (details in Figure C3). By two-dimensional (2D) Fourier analysis of E_z field patterns for different gaps or interfaces, we can determine the dominant Bloch SPP modes responsible for a specific absorbance peak: (1) $\lambda_1^D=400$ and $\lambda_2^D=495$ are dominated by $(\pm 1, \pm 1)$ and $(\pm 1, 0)$ Bloch SPP modes at the metal-medium interface, respectively; (2) $\lambda_3^D=585$, $\lambda_4^D=730$, $\lambda_5^D=970$, and $\lambda_6^D=1385$ are associated with $(\pm 2, \pm 1)$, $(\pm 2, 0)$, $(\pm 1, \pm 1)$, and $(\pm 1, 0)$ Bloch SPP modes inside the dielectric layer of MIM nanohole array, respectively; (3) The supported resonant features at λ_1^D , λ_2^D , λ_3^D , and λ_4^D can also induce high transmission peaks due to the excitation of Bloch SPP modes at the metal-substrate interface (Figure C3).

As shown in Figure 4.3(e), 2MLs nanolaminate plasmonic crystals support multiple absorption peaks, and their peak wavelengths are close to but not the same as the modes in the uncoupled subsystems of MIM nanodomains (Figure 4.3(c)) and MIM nanohole arrays (Figure 4.3(d)). Indeed, the near-field interactions of elementary modes in uncoupled subsystems cause the observed spectral shifts of the hybrid modes in the coupled system of nanolaminate plasmonic crystals. FDTD-calculations of near-field mode profiles confirm that the modes in 2MLs nanolaminate plasmonic crystals (Figure 4.3(g-k)) share spatially correlated patterns with their associated

dominant elementary modes in the uncoupled subsystems (more details in Figure C4). For example, the hybrid modes at $\lambda_1, \lambda_2, \lambda_3$ in the 2MLs nanolaminate plasmonic crystal carry the near-field distribution features of both localized elementary modes at λ_1^L in the MIM nanodome array and delocalized elementary modes at λ_1^D, λ_2^D , and λ_4^D in the MIM nanohole array. Moreover, the hybrid modes at λ_4 and λ_5 in the 2MLs nanolaminate plasmonic crystal directly originate from the optical coupling between λ_2^L mode in the MIM nanodome array and λ_5^D and λ_6^D in the MIM nanohole array. As revealed by the FDTD-calculated absorption spectra in Figure 4.3(c-d), the coupling between the subarrays can significantly increase the absorption of the modes at λ_1, λ_3 , and λ_4 in the 2MLs nanolaminate plasmonic crystal. According to the CMT analysis, the increased absorption of these hybrid modes is due to the near-field interactions between spectrally overlapped modes in the uncoupled arrays as well as the ground plane-like loading effect from the nanohole array (details in SI). FDTD-calculated near-field spectra (Figure 4.3(f)) and mode profiles (Figure 4.3(g-l)) demonstrate that 2MLs nanolaminate plasmonic crystals can induce $\sim 2/\sim 1$ order of magnitude enhancement of electric/magnetic field intensities widely between 400 and 1100 nm by supporting multiple plasmonic modes with spatial overlaps. Despite their promising multiresonant properties with spatial mode overlaps, the 2MLs nanolaminate plasmonic crystal still faces limitations of relatively low absorption in the wavelength range above 1100 nm. As shown in Figure 4.2, the multiresonant optical responses of nanolaminate plasmonic crystals can be further improved by stacking more metal-dielectric layers as they introduce more elementary modes in the subsystems of MIM nanodomains and nanohole arrays.

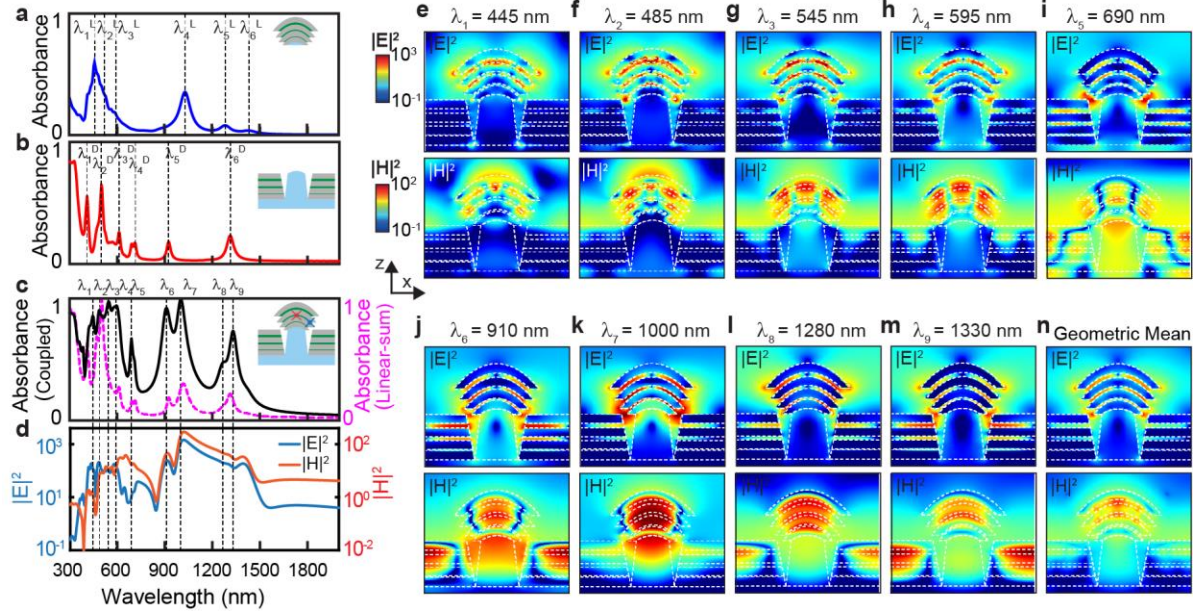


Figure 4.4. Broadband multiresonant light concentration in dense arrays of nanogap hotspots. FDTD-calculated absorption spectra for (a) 4MLs nanolaminate nanodome and (b) 4MLs nanolaminate nanohole arrays as the two multiresonant plasmonic subsystems. (c-d) FDTD-calculated spectra of (c) absorption and (d) near-field $|E|^2/|H|^2$ intensities for the 4MLs nanolaminate plasmonic crystal. (e-m) FDTD-calculated x-z distribution maps of $|E|^2$ and $|H|^2$ for the modes λ_1 - λ_9 marked in part (c). (n) Geometrically averaged x-z distribution maps of $|E|^2$ and $|H|^2$ among λ_1 - λ_9 modes.

Figure 4.4 provides a systematic analysis of the FDTD-calculated far-field and near-field optical properties for the different plasmonic modes supported in 4MLs nanolaminate plasmonic crystal. By comparing the absorbance spectra of the two uncoupled subsystems, 4MLs nanolaminate nanodome and nanohole arrays (Figure 4.4(a-b)), with the coupled 4MLs system (Figure 4.4(c)), shows a spectral correspondence between resonance wavelengths of the modes in the coupled system and those in the uncoupled subsystems. Compared to the 2MLs MIM nanodome array (Figure 4.3(c)), the 4MLs nanolaminate nanodome array (Figure 4.4(a)) can support more plasmonic modes due to an increased number of metal-dielectric interfaces and accordingly supported localized plasmonic modes (Figure C5), which contributes to the improved and broader multiresonant optical properties of the coupled 4MLs nanolaminate plasmonic crystal. Notably, in 4MLs nanolaminate nanodomains, $\lambda_1^L=470$ nm, $\lambda_2^L=495$ nm, and $\lambda_3^L=595$ nm correspond to high-order nanogap modes, $\lambda_4^L=1015$ nm is for the MD mode, and $\lambda_5^L=1265$ nm and $\lambda_6^L=1410$ nm correspond to subradiant magnetic modes of quadrupolar and octupolar natures, respectively. Similar to 2MLs nanodomains, the nanogap modes in 4MLs nanodomains are coupled to the ED mode, making them bianisotropic (Figure C5). Furthermore, just as the 2MLs nanolaminate nanohole

array, 4MLs nanolaminate nanohole array can support multiple Bloch SPP modes at different gaps and interfaces (Figure C6).

Figure 4.4(c) shows that 4MLs nanolaminate plasmonic crystals can achieve much higher absorption than the summation of light absorption from the two uncoupled subsystems, i.e., 4MLs nanolaminate nanodome and nanohole arrays. From the FDTD-calculated near-field profiles of $|E|^2/|H|^2$ (Figure 4.4(e-m)), each mode in the 4MLs nanolaminate plasmonic crystal can be traced back to one or two elementary modes in the uncoupled 4MLs subsystems, and their near-field features are closer to the elementary mode with the higher spectral overlap (More details in Figure C7 and Table C1). For example, the modes at $\lambda_1=445$ nm, $\lambda_2=485$ nm, and $\lambda_3=545$ nm mostly derive from the multiple high-order nanogap modes in the 4MLs nanodome array. The modes at $\lambda_4=595$ nm and $\lambda_5=690$ nm mainly originate from the delocalized Bloch SPP modes in the 4MLs nanohole array. Nevertheless, the modes at $\lambda_6=910$ nm, $\lambda_7=1000$ nm, $\lambda_8=1280$ nm, and $\lambda_9=1330$ nm have a mixed nature from the hybridization of both LSP modes in the 4MLs nanodome array and delocalized Bloch SPP modes in the 4MLs nanohole array. In addition to improved far-field broadband absorption, the 4MLs nanolaminate plasmonic crystal also shows an enhanced broadband near-field performance for subwavelength light concentration. As shown in Figure 4.4(e-m), highly intense electric and magnetic fields can be concentrated in nanogap hotspots at nine different resonant wavelengths ranging from 400 nm to 1330 nm. The near-field distribution maps of geometrically-averaged field intensities at the nine different resonant wavelengths ($l_1 - l_9$) confirm the spatial overlap among all the modes with ~ 3 and ~ 2 orders of average magnitude enhancements for $|E|^2$ and $|H|^2$, respectively (Figure 4.4(n)), which agrees with the calculated spectra of enhancement factors for $|E|^2$ and $|H|^2$ at nanogap regions (Figure 4.4(d)).

To investigate the effects of near-field interactions on multiresonant optical properties, we calculated the absorption spectra of 4MLs nanolaminate plasmonic crystals at varying distances (d : 0 - 160 nm) between the top of the nanolaminate nanohole array and the bottom of the nanolaminate nanodome array (Figure 4.5(a)). As expected, all the modes in the 4MLs nanolaminate plasmonic crystal reach their highest absorbance levels at $d=0$ nm, which from the CMT analysis (details in SI) is due to the two synergistic effects: (1) Strong near-field interactions between elementary modes in the two subsystems; (2) Magnetic dipole natures of the gap LSP modes in tapered nanolaminate nanodomains can allow for enhanced absorption of light due to the constructive interference between the directly incident light and the back-reflected light from the

ground-plane-like nanohole array subsystem. As d increases continuously from 0 nm to 160 nm, the overall absorption of different modes is reduced but with very different trends. The different d -dependence for different modes indicates that (1) there are different pathways for optical interactions between the subsystems, and (2) the relative contributions of different pathways depend on d and can be different for different modes. As shown in Figure 4.5(b), the CMT-modeled d -dependent absorption curves (dashed curves) for the two representative modes λ^A and λ^B , are in good agreement with FDTD calculations (solid dots). As a mode dominated by the elementary delocalized plasmonic Bloch modes in the nanolaminate nanohole array, λ^A mode shows a slightly increased absorption as d increases from 0 to 20 nm. As d further increases from 20 to 160 nm, the absorption gradually decreases to a value slightly less than that of the uncoupled nanohole array. By comparison, as a mode dominated by the elementary localized mode in the nanolaminated nanodomains, λ^B mode shows reduced absorption as d increases from 0 to 20 nm. As d further increases from 20 to 80 and 160 nm, the absorption of λ^B mode first slightly increases and then reduces to a value slightly above that of the uncoupled nanodome array.

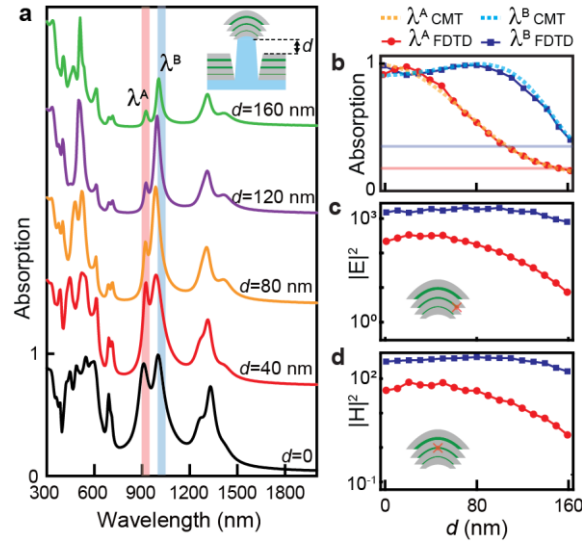


Figure 4.5. The strong dependence of multiresonant optical responses on the separation distance (d) between the two multiresonant subsystems. (a) FDTD-calculated absorption spectra for the 4MLs nanolaminate plasmonic crystal with different d between 0 and 160 nm. (b) Peak absorption values for λ^A and λ^B modes (also labeled in part (a)) by FDTD calculations (solid curves & dots) and CMT modeling (dashed lines) as a function of d . Horizontal lines represent the absorption values for the corresponding modes in the uncoupled multiresonant subsystems. (c-d) FDTD-calculated near-field intensities of (c) $|E|^2$ and (d) $|H|^2$ at resonant wavelengths for λ^A and λ^B modes as a function of d .

According to the CMT analysis (details in SI), the decline of absorption for λ^A mode is due to the exponential weakening of its near-field coupling to λ^B mode. This weakening leads to an initial increase in λ^B absorbance as the energy transfer rate to the dark λ^A mode goes down. However, the increase of d also reduces the effective coupling of λ^B mode to the incident light due to the decreased degree of constructive interference between the direct and back-scattering coupling pathways, leading to the reduction of absorbance for λ^B mode. As shown in Figure 4.5(c-d), the d -dependence curves of near-field $|E|^2/|H|^2$ intensities for λ^A and λ^B modes at nanogap hotspots have similar trends as their corresponding d -dependence far-field absorption curves, manifesting the correlated microscopic physics between the absorption from hot-carrier generation and the near-field enhancement from plasmonic charge/current accumulations in metal nanostructures. Overall, both FDTD simulations and CMT analysis indicate that a small distance between multiresonant subsystems is crucial to enhance the levels of absorption and local field concentration for all the modes in the two-tier multiresonant systems.

4.3. Conclusion

In conclusion, the nanolaminate plasmonic crystals in a two-tier configuration can support many spatially overlapped and highly excitable hybridized plasmonic modes to enable multiresonant nanoscale light concentration across a wide wavelength range of 400 to 1400 nm. From coupled-mode theory analysis and numerical simulations, the microscopic origin of highly excitable spatially overlapped multiresonant behaviors for the two-tier nanolaminate plasmonic crystals is due to the near-field coupling between the modes of the less excitable multiresonant subsystems as well as the ground-plane-like loading effect from the nanohole array subsystem. We envision that nanolaminate plasmonic crystals can serve as a high-performance multiresonant nano-optics platform to enhance multiple excitation/emission transitions of multiphoton nonlinear optical processes across a wide wavelength range simultaneously. By incorporating different functional materials (e.g., nonlinear materials, emissive gain medium, and strongly-correlated electronic materials) within different dielectric layers of nanolaminate plasmonic crystals, multifunctional active plasmonic devices can potentially be created with wavelength-multiplexed multiresonant capability.

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Appendix C

C.1. Methods

Sample fabrication and characterization. Nanolaminate plasmonic crystals were fabricated in cm^2 areas on flexible and heat-stabilized polyester (PET) films using nanoimprint lithography and directional electron beam deposition techniques. First, pre-patterned silicon (Si) wafer was used to create polydimethylsiloxane (PDMS) stamps with a periodic nanohole array with a height of 150 nm, a radius of 120 nm, and a periodicity of 400 nm, respectively. We then used the as-prepared PDMS stamp to squeeze one or two droplets of NOA83H optical adhesive (from Norland, USA) onto PET films. Next, the samples were cured by ultra-violet exposure (365 nm, 100 W) for 1 minute, detaching the PDMS stamp, and baking in a convection oven with 80°C overnight. Finally, alternating layers of Ag and SiO_2 layers were deposited using an electron beam evaporator. A thin Cr adhesion layer (0.5 nm thickness) was deposited between alternating Ag and SiO_2 layers.

Far-field optical measurements. Reflection and transmission far-field optical measurements were conducted using Cary 5000 UV-Vis-NIR spectrophotometer (Agilent Inc.).

Numerical calculations. We performed three-dimensional Finite Difference Time Domain simulations using commercial software (FDTD solutions, Lumerical Inc.) to numerically calculate the far-field spectra and the near-field distributions of the plasmonic crystal systems and their building block arrays. A uniform mesh size of 3 nm (in x, y, and z directions) was used. The silver dielectric function was obtained from the Palik handbook of optical constants for solids.²⁸³ Also, the constant refractive index of 1.5 was used for SiO_2 .

Theoretical modeling. Coupled-mode theory modeling and analysis were carried out to understand optical behaviors of nanolaminate plasmonic crystals. In this model, the two building-blocks of nanodome and nanohole arrays were treated as a side-coupled resonator and a directly-coupled resonator, respectively. The parameters of the uncoupled resonators in this model were obtained from FDTD simulations of the uncoupled nanodome and nanohole arrays. Furthermore, the near-field coupling parameters between the building-block arrays were obtained from the FDTD simulations of the plasmonic crystal system for distances of $d=0$ and $d=80$ nm between the building-block arrays. More details can be found in the supporting information.

C.2. Temporal coupled mode theory analysis of the two-tier nanolaminate plasmonic crystals

We employ temporal coupled-mode theory (CMT) to model and analyze the optical response of the 4MLs nanolaminate plasmonic crystal as a function of the distance between the two subsystems of nanodome arrays and nanohole arrays in the wavelength range from 800 nm to 1200 nm. For this purpose, we first used the CMT to model the optical response of the two uncoupled subsystems of nanodome and nanohole arrays and then investigate the optical response of the coupled system by introducing the optical interaction pathways between the two subsystems.

C.2.1. CMT model for the subsystem of nanolaminate nanodome array

Rather than considering each nanodome structure as a separate resonator, we treat the collective nanodome array as a single resonator (resonator A). Due to the subwavelength size, nanodome array can allow light transmission at nonresonant wavelength conditions, confirmed by FDTD calculations showing the spectral matching of the absorption peaks with transmission dips for the nanodome array (Figure C5). Figure C5 also reveals that the mode at λ_4^L dominates the optical response for resonator A between 800 nm and 1200 nm. Moreover, as the periodicity of the array is smaller than the light wavelength in our spectral range of interest ($P = 400 \text{ nm} < \lambda$), the phase-matching condition only allows for the 0th order backscattering (or reflection) and forward-scattering (or transmission) at the normal incidence angle with a preserved polarization. Therefore, we can treat resonator A as a single-mode side-coupled resonator²³⁵ with a top port and a bottom port, as shown in Figure 4.1(d) of the main text. The coupled-mode, output-coupling, and absorption equations for resonator A in the uncoupled state are expressed as follows²³⁵:

$$j\omega\alpha = \left(j\Omega_A - \Gamma_A^{nr} - \Gamma_A^{r,1} - \Gamma_A^{r,2} \right) \alpha + \kappa_1^A S_1^{+A} + \kappa_2^A S_2^{+A}, \quad (\text{B.1a})$$

$$\begin{bmatrix} S_1^{-A} \\ S_2^{-A} \end{bmatrix} = \begin{bmatrix} 0 & e^{-jkd_A} \\ e^{-jkd_A} & 0 \end{bmatrix} \begin{bmatrix} S_1^{+A} \\ S_2^{+A} \end{bmatrix} - \begin{bmatrix} 0 & e^{-jkd_A} \\ e^{-jkd_A} & 0 \end{bmatrix} \begin{bmatrix} \left(\kappa_1^A \right)^* \\ \left(\kappa_2^A \right)^* \end{bmatrix} \alpha, \quad (\text{B.1b})$$

$$A_A = 2\Gamma_A^{nr} |\alpha|^2, \quad (\text{B.1c})$$

where ω and k represent the angular frequency and the wavenumber of the incident plane wave in free space, respectively. d_A is the physical length of the resonator in the direction of propagation

for the incident plane wave and A_A is the absorption of the resonator. α , Ω_A , and Γ_A^{nr} denote the amplitude, resonance angular frequency, and non-radiative decay rate of the mode, respectively. Also, $\Gamma_A^{r,1}(\Gamma_A^{r,2})$, $\kappa_1^A(\kappa_2^A)$, $S_1^{+A}(S_2^{+A})$, and $S_1^{-A}(S_2^{-A})$ are the radiative decay rate, input-coupling coefficient, input power wave, and output power wave for the top (bottom) port, respectively. $\kappa_1^A(\kappa_2^A)$ can be expressed in terms of $\Gamma_A^{r,1}(\Gamma_A^{r,2})$ as follows:

$$\kappa_1^A = \sqrt{2\Gamma_A^{r,2}} e^{j\theta_1^A}, \quad (\text{B.2a})$$

$$\kappa_2^A = \sqrt{2\Gamma_A^{r,1}} e^{j\theta_2^A}, \quad (\text{B.2b})$$

where $\theta_1^A(\theta_2^A)$ is the phase angle of $\kappa_1^A(\kappa_2^A)$. Without loss of generality, we put $\theta_1^A = 0$ as the reference phase angle. Furthermore, we put $\theta_2^A = \pi$ from the phase angles of the λ_4^L mode near-field patterns in both sides of the nanodome array (Figure C5). This choice matches the dominant magnetic dipole nature of λ_4^L mode. By fitting the background-subtracted absorption curves of the nanodome array for the illuminations from top-side ($S_1^{+A} = 1$ and $S_2^{+A} = 0$) and bottom-side ($S_1^{+A} = 0$ and $S_2^{+A} = 1$), we find the following values for the parameters in the resonator CMT model (Figure C8(a)):

$$\Omega_A = 1.83 \times 10^{15} \text{ rad/s},$$

$$\Gamma_A^{nr} = 2.77 \times 10^{13} \text{ 1/s},$$

$$\Gamma_A^{r,1} = 3.50 \times 10^{13} \text{ 1/s},$$

$$\Gamma_A^{r,2} = 1.84 \times 10^{13} \text{ 1/s},$$

$$\kappa_1^A = 6.06 \times 10^6 \text{ 1/s},$$

$$\text{and } \kappa_2^A = -8.36 \times 10^6 \text{ 1/s}.$$

C.2.2. CMT model for the subsystem of nanolaminate nanohole array

Due to the subwavelength size of the nanoholes, the nonresonant transmission of the incident plane wave through the nanohole array is negligible²⁷⁹. Thus, the incident light is mostly reflected from the nanohole array surface unless it gets coupled to its Bloch SPP modes, as confirmed by the

spectral matching between absorption peaks and reflection dips in FDTD calculations (Figure C6). Figure C6 also reveals that the mode at λ_5^D dominates the optical response of the nanohole array between 800 nm and 1200 nm. Moreover, just as the nanodome array, the nanohole array only induces the 0th order backscattering and forward-scattering with a preserved polarization. In this regard, we can treat the nanohole array as a single-mode directly-coupled resonator²³⁵(resonator B) with top and bottom ports, as shown in Figure 4.1(d) of the main text. The coupled-mode, output-coupling, and absorption equations for resonator B in the uncoupled state are expressed as follows:

$$j\omega\beta = \left(j\Omega_B - \Gamma_B^{nr} - \Gamma_B^{r,1} - \Gamma_B^{r,2} \right) \beta + \kappa_1^B S_1^{+B} + \kappa_2^B S_2^{+B}, \quad (\text{B.3a})$$

$$\begin{bmatrix} S_1^{-B} \\ S_2^{-B} \end{bmatrix} = \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} S_1^{+B} \\ S_2^{+B} \end{bmatrix} - \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} (\kappa_1^B)^* \\ (\kappa_2^B)^* \end{bmatrix} \beta, \quad (\text{B.3b})$$

$$A_B = 2\Gamma_B^{nr} |\beta|^2, \quad (\text{B.3c})$$

where A_B is the absorption of the resonator, and β , Ω_B , and Γ_B^{nr} denote the amplitude, resonance angular frequency, and non-radiative decay rate of the mode, respectively. Also, $\Gamma_B^{r,1}$ ($\Gamma_B^{r,2}$), κ_1^B (κ_2^B), S_1^{+B} (S_2^{+B}), and S_1^{-B} (S_2^{-B}) are the radiative decay rate, input-coupling coefficient, input power wave, and output power wave for the top (bottom) port, respectively. κ_1^B (κ_2^B) can be expressed in terms of $\Gamma_B^{r,1}$ ($\Gamma_B^{r,2}$) as follows:

$$\kappa_1^B = \sqrt{2\Gamma_B^{r,1}} e^{j\theta_1^B}, \quad (\text{B.4a})$$

$$\kappa_2^B = \sqrt{2\Gamma_B^{r,2}} e^{j\theta_2^B}, \quad (\text{B.4b})$$

where θ_1^B (θ_2^B) is the phase angle of κ_1^B (κ_2^B). Without loss of generality, we set $\theta_1^B = 0$ as the reference phase angle. Furthermore, we set $\theta_2^B = \pi$ from the phase angles of the λ_5^D mode near-field patterns in both sides of the nanohole array. By fitting the background-subtracted absorption curves of the nanodome array for the illuminations from top-side ($S_1^{+B} = 1$ and $S_2^{+B} = 0$) and bottom-side ($S_1^{+B} = 0$ and $S_2^{+B} = 1$), we find the following values for the parameters in the resonator CMT model (Figure C8(b)):

$$\Omega_B = 2.03 \times 10^{15} \text{ rad/s},$$

$$\Gamma_B^{nr} = 3.14 \times 10^{13} \text{ 1/s},$$

$$\Gamma_B^{r,1} = 1.27 \times 10^{12} \text{ 1/s},$$

$$\Gamma_B^{r,2} = 3.35 \times 10^{11} \text{ 1/s},$$

$$\kappa_1^B = 1.60 \times 10^6 \text{ 1/s},$$

$$\text{and } \kappa_2^B = -8.19 \times 10^5 \text{ 1/s}.$$

C.2.3. CMT model for the two-tier nanolaminate plasmonic crystal

The two-tier nanolaminate plasmonic crystals consist of the two closely stacked subsystems of nanodome (resonators A) and nanohole (resonators B) arrays that transfer energy through both near-field and (propagating) radiative interactions (Figure 4.1(d) of the main text). In the CMT modeling, the radiative interactions between the nanodome and nanohole arrays are mediated by x-polarized plane waves that propagate between the two arrays, as expressed in the following equations:

$$S_2^{+A} = e^{-jkd} S_1^{-B}, \quad (\text{B.5a})$$

$$S_1^{+B} = e^{-jkd} S_2^{-A}. \quad (\text{B.5b})$$

Moreover, coupled-mode equations for the coupled resonators A and B can be expressed as:

$$j\omega\alpha = \left[(j\Omega_A - \Gamma_A^{nr} - \Gamma_A^{r,1} - \Gamma_A^{r,2}) + \mu_{AA}^n \right] \alpha + \kappa_1^A S_{inc} + \kappa_2^A S_2^{+A} + \mu_{AB}^n \beta, \quad (\text{B.6a})$$

$$j\omega\beta = \left(j\Omega_B - \Gamma_B^{nr} - \Gamma_B^{r,1} - \Gamma_B^{r,2} \right) \beta + \kappa_1^B S_1^{+B} + \mu_{BA}^n \alpha, \quad (\text{B.6b})$$

where $S_2^{+B} = 0$ and $S_1^{+A} = S_{inc} = 1$ considering that the incident wave is illuminated from the top side. The self-coupling term μ_{AA}^n represents the near-field interaction of resonator A with its image due to the ground plane-like loading effect from resonator B. Moreover, the coefficients μ_{AB}^n and μ_{BA}^n denote the near-field coupling between the modes of the two resonators. Due to the subwavelength size of the nanodomains, the self-coupling coefficient for the nanohole array due to

the loading effect from nanodomains is small, and we can neglect it for simplicity. By inserting Eqs. (B.5) into Eqs. (B.6) we would get:

$$j\omega\alpha = \left[(j\Omega_A - \Gamma_A^{nr} - \Gamma_A^{r,1} - \Gamma_A^{r,2}) + \mu_{AA}^n + \mu_{AA}^r \right] \alpha + \left(\kappa_1^A - \kappa_2^A e^{-jk(d_A+2d)} \right) S_{inc} + \left(\mu_{AB}^n + \mu_{AB}^r \right) \beta, \quad (\text{B.7a})$$

$$j\omega\beta = \left(j\Omega_B - \Gamma_B^{nr} - \Gamma_B^{r,1} - \Gamma_B^{r,2} \right) \beta + e^{-jk(d_A+d)} \kappa_1^B S_{inc} + \left(\mu_{BA}^n + \mu_{BA}^r \right) \alpha, \quad (\text{B.7b})$$

with the radiative coupling terms μ_{AA}^r , μ_{AB}^r and μ_{BA}^r defined as:

$$\mu_{AA}^r = \kappa_2^A e^{-jk(d_A+2d)} \left(\kappa_1^A \right)^*, \quad (\text{B.8a})$$

$$\mu_{AB}^r = \kappa_2^A e^{-jkd} \left(\kappa_1^B \right)^*, \quad (\text{B.8b})$$

$$\mu_{BA}^r = -\kappa_1^B e^{-jk(d_A+d)} \left(\kappa_1^A \right)^*. \quad (\text{B.8c})$$

Since the near-field components of a resonator decay exponentially with the distance away from the resonator, the near-field coupling terms in Eqs. (B.7a) can be expressed as:

$$\mu_{AA}^n = \mu_{AA}^{n0} e^{-\alpha_{AA}kd}, \quad (\text{B.9a})$$

$$\mu_{AB}^n = \mu_{AB}^{n0} e^{-\alpha_{AB}kd}, \quad (\text{B.9b})$$

$$\mu_{BA}^n = \mu_{BA}^{n0} e^{-\alpha_{BA}kd}, \quad (\text{B.9c})$$

where d is the distance between the two resonators, and μ_{AA}^{n0} , μ_{AB}^{n0} and μ_{BA}^{n0} are the near-field coupling parameters at $d=0$, and α_{AA} , α_{AB} and α_{BA} are the spatial decay rates of the near-field coupling terms.

By setting $\mu_{BA}^{n0} = -\left(\mu_{AB}^{n0} \right)^*$ and $\alpha_{AB} = \alpha_{BA}$ ²³⁴, and then fitting the FDTD-simulated absorption spectra of the nanolaminate plasmonic crystals for $d=80$ and $d=120$ nm (Figure C8(c)), we find the following values for the parameters of coupling between the resonators A and B:

$$\mu_{AA}^{n0} = 5.7 \times 10^{13} e^{j\pi/2} \text{ 1/s},$$

$$\mu_{AB}^{n0} = -\left(\mu_{BA}^{n0} \right)^* = 8.7 \times 10^{13} e^{j\pi/2} \text{ 1/s},$$

$$\alpha_{AA} = 0.5,$$

and $\alpha_{AB} = \alpha_{BA} = 2.9$.

Next, by inserting the extracted coupling parameters back into Eqs. (B.7), we find the mode amplitudes for the coupled resonators. Then, considering $A_{total} = A_A + A_B$ together with Eqs. (B.1c) and (B.3c), we calculate the absorption spectra of the nanolaminate plasmonic crystals for different d values. A side-by-side comparison between the CMT-calculated spectra and those calculated by FDTD for some selected values of d reveals a decent match between the two (Figure C8(c)). Notably, the CMT modeling results can match well the FDTD calculations for the d -dependency of resonance wavelengths and resonant absorption values of λ^A and λ^B modes (Figure 4.5 in the main text).

From CMT modeling and analysis based on Eqs. (B.7), the highly excitable multiresonant optical responses of the nanolaminate plasmonic crystals at small d can be attributed to the following origins:

- The near-field coupling terms, μ_{AB}^n and μ_{BA}^n , between the modes of the nanodome and nanohole arrays at small d can boost the absorption of light in the nanohole array modes while only cause a slight reduction in the absorption of the modes from the nanodome array. The radiative coupling terms, μ_{AB}^r and μ_{BA}^r , also contribute to further enhance the interaction between the resonators, however this effect is negligible compared to the near-field coupling effect.
- The self-coupling terms, μ_{AA}^n and μ_{AA}^r , represent the radiative and near-field self-induced back-actions⁵⁸ of the nanodome array due to the ground-plane-like loading effect from the nanohole array. Such back-action leads to the modification of the resonance wavelengths and radiative decay rates for the modes of the nanodome array, which can thus improve the impedance-matching with the incident wave for higher excitability.
- The term $-\kappa_2^A e^{-jk(d_A+2d)}$ induces an extra channel for coupling of the nanodome array to the incident light through its nonresonant backscattering from the ground-plane like nanohole array. For the magnetic dipole mode and some other high order modes, this term constructively adds to the direct coupling channel to the incident wave when d is small. Such constructive interference can effectively double the optical absorption of the modes under free-space light excitation. The backscattering coupling channel becomes even more

prominent considering that the nanodome array is a bianisotropic resonator and better absorbs the light incident from the bottom-side ($|\kappa_2^A| > |\kappa_1^A|$), leading to a 3-fold increase in the effective absorption of λ^B mode in the coupled system.

Finally, the slight mismatches between the spectra calculated from the CMT model and the FDTD-calculated spectra are neglecting the effects from off-resonant modes in two subsystems of nanodome and nanohole arrays.

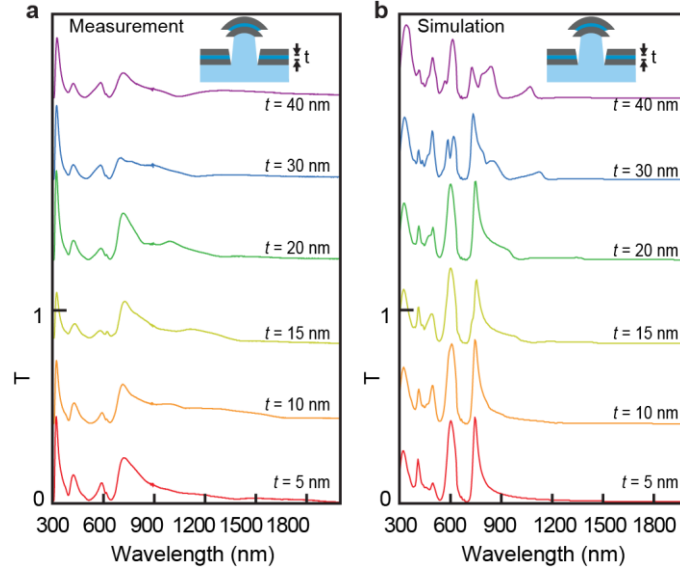


Figure C1. (a) Measured and (b) FDTD-calculated transmission spectra for the 2MLs nanolaminate plasmonic crystals with different t from 5 to 40 nm.

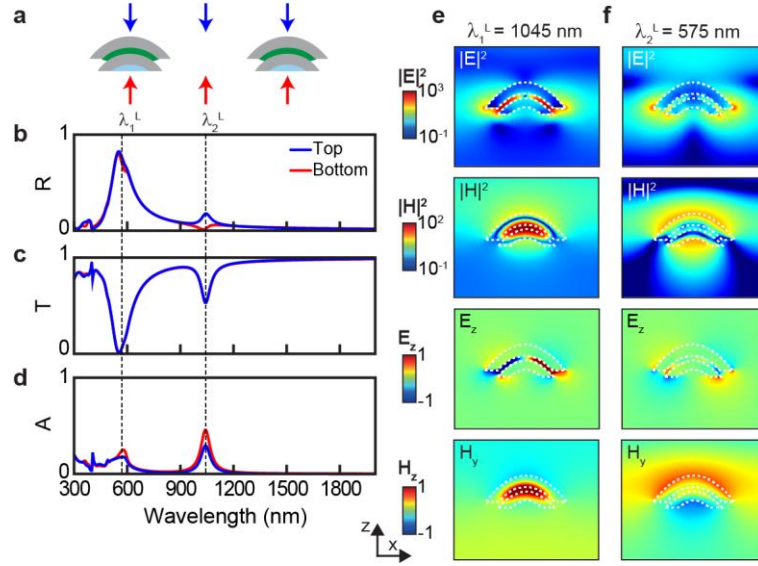


Figure C2. (a) The 2MLs nanolaminate nanodome array with $t = 15$ nm illuminated from the top and bottom ports. (b-d) FDTD-calculated far-field spectra for top-port (downward) and bottom-port (upward) illuminations. (e-f) The FDTD-calculated x-z distribution maps of $|E|^2$, $|H|^2$, E_z , and H_y for the modes λ_1^L and λ_2^L marked in b-d.

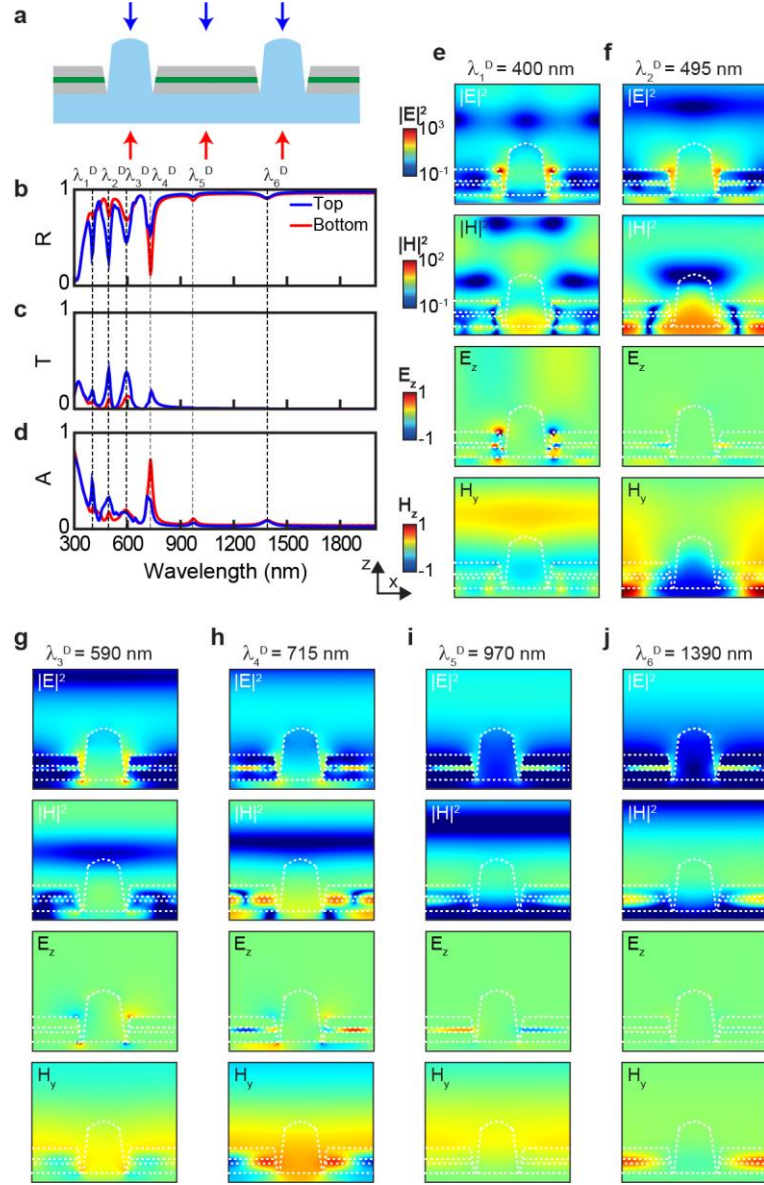


Figure C3. (a) The 2MLs nanolaminate nanohole array with $t = 15$ nm illuminated from the top and bottom ports. (b-d) FDTD-calculated far-field spectra for top-port and bottom-port illuminations. (e-j) The FDTD-calculated x-z distribution maps of $|E|^2$, $|H|^2$, E_z , and H_y for the modes $\lambda_1^D - \lambda_6^D$ marked in b-d.

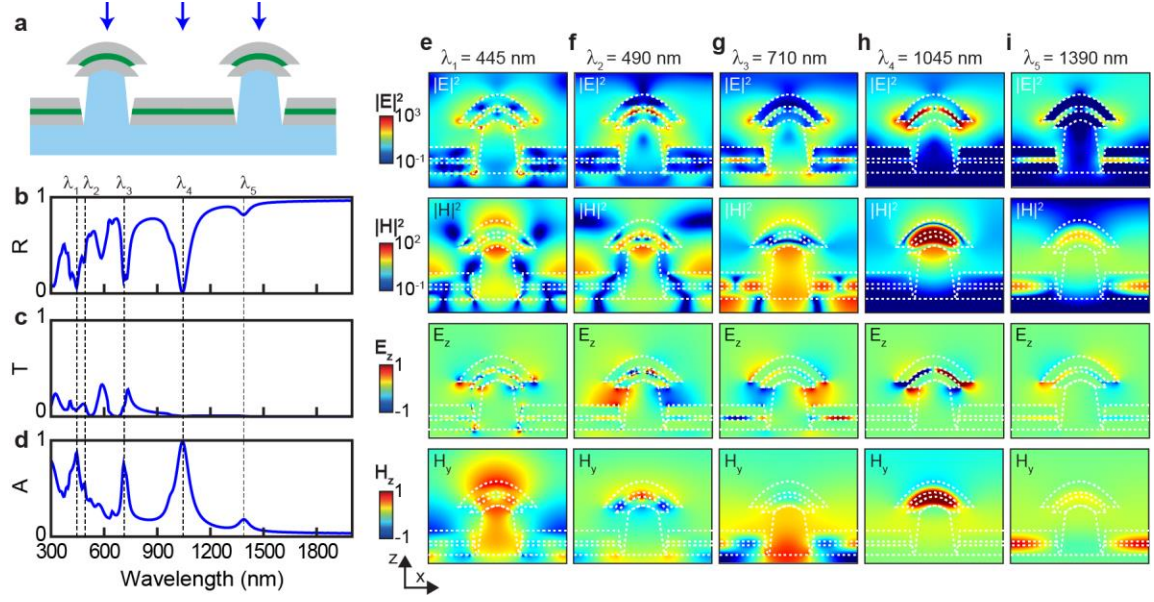


Figure C4. (a) The 2MLs nanolaminate plasmonic crystal with $t = 15$ nm illuminated from the top port. (b-d) FDTD-calculated far-field spectra for the top-port illumination. (e-i) The FDTD-calculated x - z distribution maps of $|E|^2$, $|H|^2$, E_z , and H_y for the modes $\lambda_1 - \lambda_5$ marked in b-d.

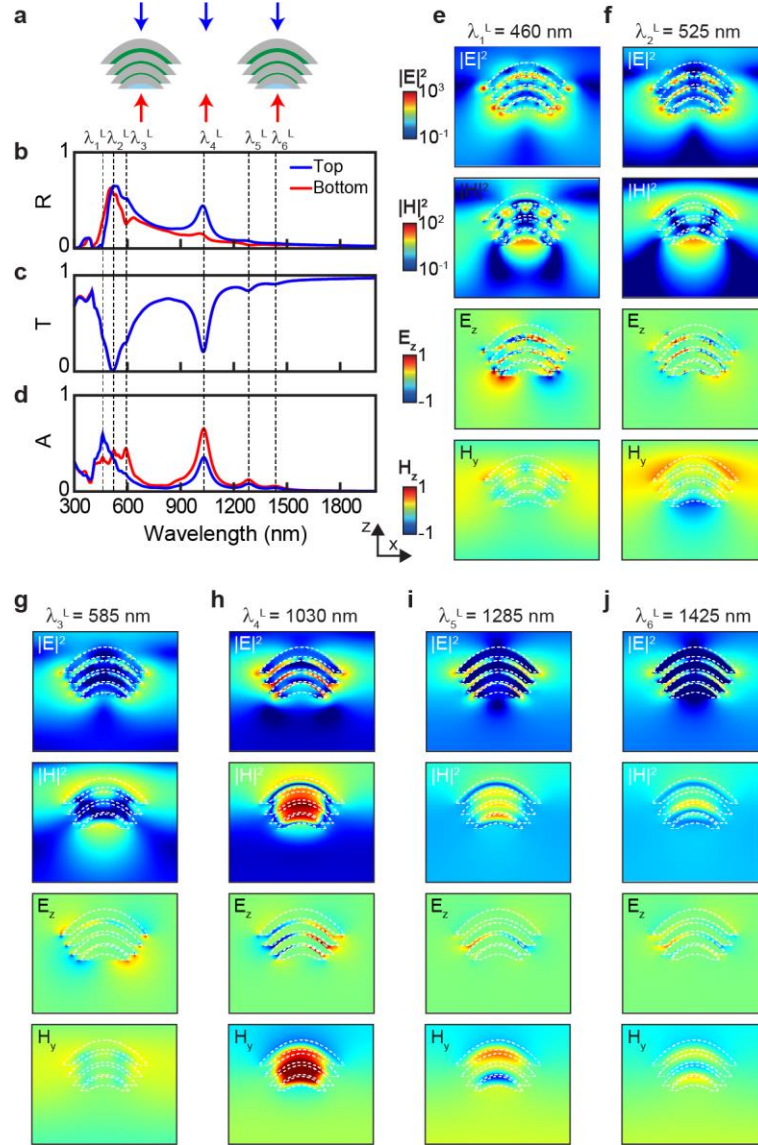


Figure C5. (a) The 4MLs nanolaminate nanodome array illuminated from the top and bottom ports. (b-d) FDTD-calculated far-field spectra for top-port and bottom-port illuminations. (e-j) The FDTD-calculated x-z distribution maps of $|E|^2$, $|H|^2$, E_z , and H_y for the modes $\lambda_1^L - \lambda_6^L$ marked in b-d.

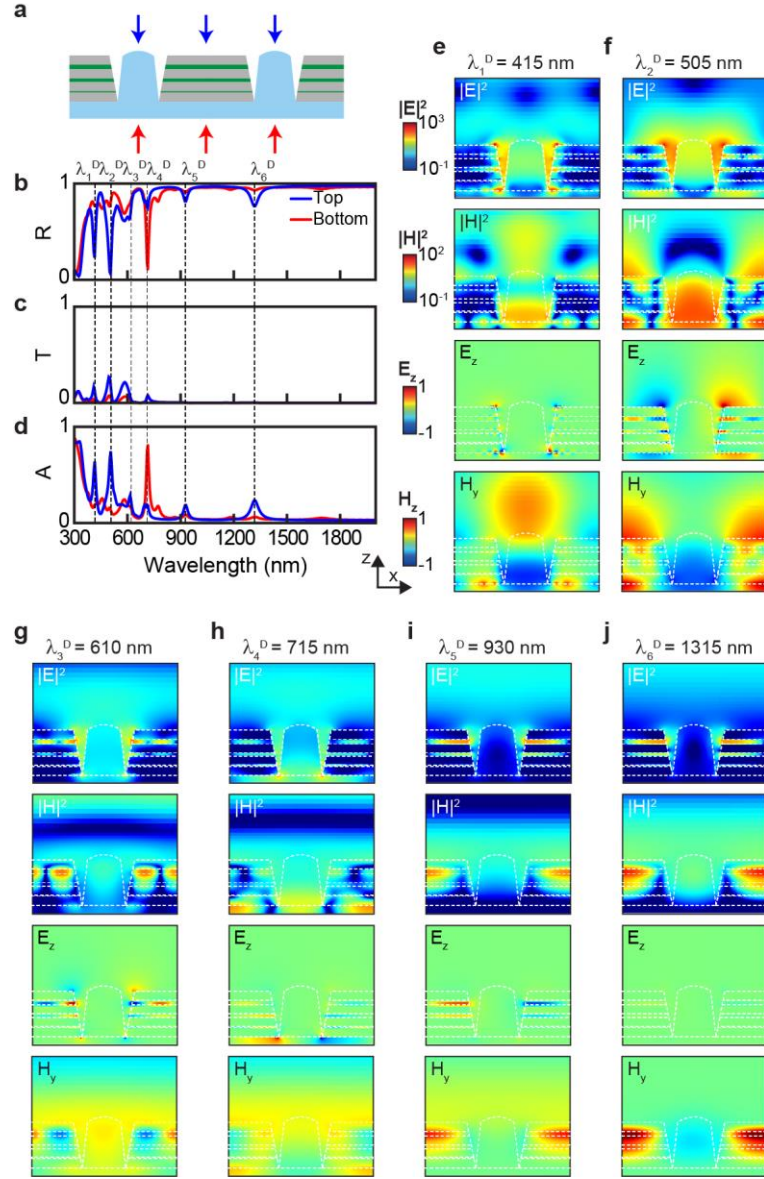


Figure C6. (a) The 4MLs nanolaminate nanohole array illuminated from the top and bottom ports. (b-d) FDTD-calculated far-field spectra for top-port and bottom-port illuminations. (e-j) The FDTD-calculated x-z distribution maps of $|E|^2$, $|H|^2$, E_z , and H_y for the modes $\lambda_1^D - \lambda_6^D$ marked in b-d.

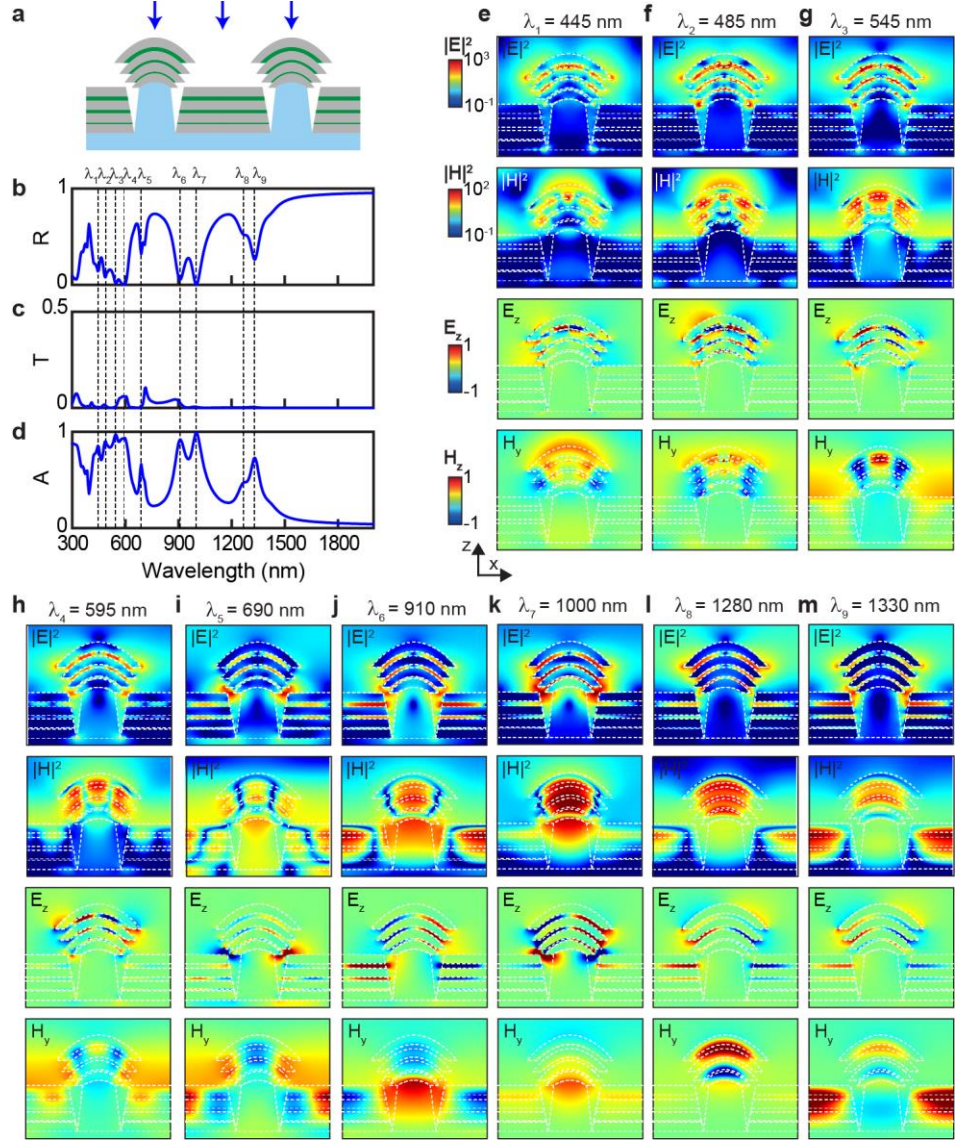


Figure C7. (a) The 4MLs nanolaminate plasmonic crystal illuminated from the top port. (b-d) FDTD-calculated far-field spectra for the top-port illumination. (e-m) The FDTD-calculated x - z distribution maps of $|E|^2$, $|H|^2$, E_z , and H_y for the modes $\lambda_1 - \lambda_9$ marked in b-d.

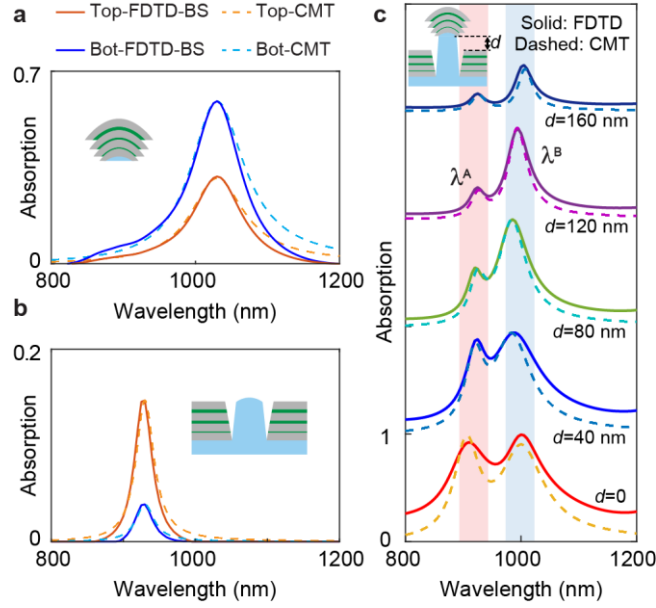


Figure C8. (a-b) CMT fitting of the background-subtracted FDTD-calculated absorption spectra of the 4MLs nanolaminate nanodome (a) and nanohole (b) arrays for top-port and bottom-port illuminations in the wavelength range 800-1200 nm. (c) The parameters in the CMT equations are set to fit the FDTD-calculated absorption spectra of the nanolaminate plasmonic crystal for $d=80$ nm and $d=120$ nm cases. Then, the CMT predicts the absorption spectra for the rest of d values. Side-by-side comparison between the CMT-calculated and the FDTD-calculated spectra reveals a decent match between the two in terms of resonance wavelengths and resonant absorption values for λ_A and λ_B modes.

Table C1. Quality factors (Q-factors) and dominant natures of the resonances in the 4ML nanolaminate plasmonic crystal structure. For each resonance, the quality factor is estimated from the corresponding resonance in the dominant array. We estimate the Q-factors of the fabricated 4ML system to be about half of their corresponding simulated results. Compared to other multiresonant plasmonic systems^{297, 302}, the plasmonic crystal modes' Q-factors are in the medium range.

$\lambda_1=445$ nm	Nanodome array	>40
$\lambda_2=485$ nm	Nanodome array	>40
$\lambda_3=545$ nm	Nanodome array	>40
$\lambda_4=595$ nm	Nanohole array	>40
$\lambda_5=690$ nm	Nanohole array	34.5
$\lambda_6=910$ nm	Nanohole array	31
	Nanodome array	
$\lambda_7=1000$ nm	Nanodome array	12.8
	Nanohole array	
$\lambda_8=1280$ nm	Nanodome array	19.8
	Nanohole array	
$\lambda_9=1330$ nm	Nanohole array	21.9
	Nanodome array	

Chapter 5: Anti-Stokes Emission from Plasmonic Structures: Mechanisms and Correlation with Second Harmonic Generation

(This is the draft of a paper by Safiabadi Tali SA, Mudiyansele Rathsara R. H. H., Qian Y, Smith N, Zhao Y, Morral A, Song J, Nie M, Magill B. A., Khodaparast G. A., and Zhou W that is under submission.)

Abstract

Motivated by its applications in sensing and spectroscopy, photoluminescence (PL) emission from noble metals has gained much attention in recent years. However, despite the consensus that plasmon enhancement plays a critical role, PL emission origins are still debated and its correlations to other non-linear modalities, such as the second harmonic generation (SHG), is underexplored. This work comprehensively studies the mechanisms and properties of the anti-Stokes photoluminescence (ASPL) and SHG emissions from plasmonic structures under ultrafast near-infrared (NIR) illumination. The study is primarily enabled by designing multiresonant nanolaminate plasmonic crystals (NPCs) with spatially overlapped modes across the whole Vis-NIR spectral range. We then investigate the effects of the incident laser power, wavelength, and polarization on the intensity, spectral shape, and polarization of the NPCs' non-linear emission. To interpret the experimental results, we use a combination of the coupled-mode theory, quantum optics, and statistical mechanics analyses to model the plasmonic-enhanced PL and SHG emissions in the time domain. Our PL model generally includes both intraband recombination (IBR) and electronic Raman scattering (ERS) processes and we find that an IBR-dominant picture can best fit the experimental power-laws and spectral features of ASPL and SHG. Correlations observed between the excitation and emission polarizations show that rather than radiative electronic transitions, ASPL and SHG photons stem from the decay of the surface plasmon modes providing the Purcell enhancement at the emission wavelengths. The amount of energy coupled into each plasmonic mode for emission depends on the energy and spatial distributions of the microscopic non-linear sources, which is highly impacted by the excitation conditions.

5.1. Introduction

In nanophotonics, frequency conversion has received considerable attention due to various applications in characterization and spectroscopy³⁰³⁻³⁰⁵, bioimaging and sensing^{50, 306-311}, and optoelectronics^{40, 312-320}. Given the poor optical nonlinearity of natural materials, nonlinear signals at macroscale are typically achieved by complex phase-matching techniques and optically large samples^{320, 321}, both of which are not feasible at the nanoscale. A proven solution is utilizing the surface plasmons supported at metal-dielectric interfaces^{5, 321, 322} to enhance the deep-subwavelength nonlinear processes through field concentration at the excitation wavelength(s)^{58, 323-329} and/or increasing the local density of photonic states at the emission wavelength(s) (Purcell effect)^{58, 311, 329-331}. Plasmonic systems can directly serve as nonlinear sources as well. Although plasmonic structures typically possess centrosymmetric materials without intrinsic second-order nonlinearity, they can sustain strong second-harmonic responses at their surface where centrosymmetry is broken³²⁵. Efficient third-harmonic responses have also been reported from Plasmonic structures, arising from both metal and dielectric bulks^{310, 332}. Starting with Mooradian's pioneering work in 1969³³³, it was noticed that plasmonic structures can generate broadband and non-parametric photoluminescence (PL) signals as well, in both Stokes³³³⁻³⁴⁷ and anti-Stokes³⁴²⁻³⁵¹ regimes. Following this discovery, several scientists investigated the origin of plasmonic PL signals. Visible PL emission from gold nanostructures was attributed to the interband transitions between the metals' sp band electrons and d band holes^{333, 340-342, 350, 351}. However, this mechanism could not account for the infrared PL emission of gold-based systems and PL emission of silver-based systems, as the emission photon energies in both scenarios are far below the d band and Fermi level separation. It was instead suggested that intraband recombination (IBR) of hot carriers across the sp band^{334, 335, 338, 339, 342, 344, 346, 348, 349} or electronic Raman scattering (ERS) of sp band electrons through intermediate virtual levels^{336, 343, 345} must be responsible. Yet, as of today, there is no consensus on the dominant mechanism. Furthermore, very few works have investigated how the plasmonic PL emission is correlated with the parametric nonlinear emissions such as the second harmonic generation (SHG)^{348, 352}. Finally, despite the general acceptance on the enhancement effects of the plasmonic modes, more investigation is still needed to fully discern the roles they play in the PL process, especially when multiple modes are involved.

This work thoroughly investigates the mechanisms and correlations of the anti-Stokes photoluminescence (ASPL) and SHG emissions from plasmonic structures under ultrafast near-infrared (NIR) illumination (Figure 5.1(a)). The primary enabling factor in our study is taking advantage of two-tier nanolaminate plasmonic crystals (NPCs)^{276, 353}, shown in Figure 5.1(a-b), that can support spatially overlapped plasmonic modes across the whole Vis-NIR spectral range and offer independent control over the plasmonic modes at the excitation and emission wavelengths. We study the effects of the incident laser power, wavelength, and polarization on the intensity, spectral shape, and polarization of the ASPL and SHG emissions from NPCs.

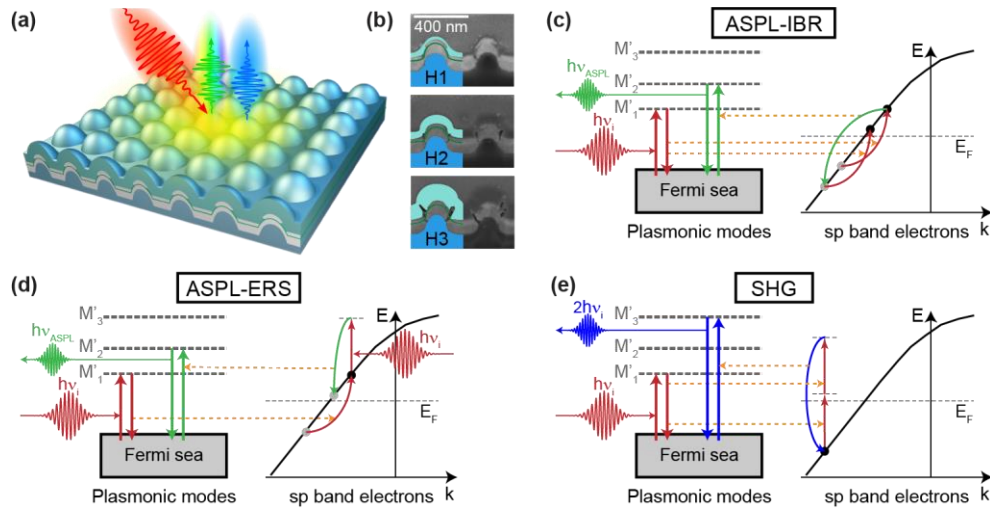


Figure 5.1. (a) Simultaneous second harmonic and up-conversion photoluminescence emissions from nanolaminate plasmonic crystals upon excitation by a near infrared (NIR) ultrafast laser pulse. (b) Cross-sectional view SEM pictures of H1, H2, and H3 samples. The samples are only different in terms their TiO₂ thickness. (c-d) Anti-Stokes Photoluminescence (ASPL) process based on the intraband recombination (IBR) and electronic Raman scattering (ERS) pictures, respectively. (e) The second harmonic generation (SHG) process.

To interpret the experimental results (Table D1), we model the PL and SHG emissions in the time domain by a novel combination of the coupled-mode theory³⁵⁴, quantum optics, and statistical mechanics analyses. Our models consider the time-evolution of the hot carrier distributions due to electron-photon, electron-electron, and electron-phonon interactions and plasmonic enhancement of the non-linear emissions through incident light concentration, Purcell effect and providing extra momentum for intraband electronic transitions. Our PL model generally includes both the IBR

(Figure 5.1(c)) and ERS (Figure 5.1(d)) pictures and our SHG model (Figure 5.1(e)) accounts for the modification of the second-order response due to perturbed electron distribution.

We find that an IBR-dominant PL process (Figure 5.1(c)) can best explain the trends and correlations of the ASPL and SHG power-laws and spectral features. Our model further suggests that the relative contribution levels of the native (pre-excitation), non-thermalized, thermalized hot carriers is the factor that decides the ASPL power-law, cut-off wavelength, and lifetime. Correlations observed between the excitation and emission polarizations show that ASPL and SHG photons are a result of surface plasmon decay rather than radiative electronic transitions³³⁴ (Figure 5.1(c-e)). Furthermore, by controlling the energy, momentum, and spatial distributions of the hot carriers, the excitation conditions highly influence the portion of the non-linear energy coupled into each plasmonic mode for emission. Structural imperfections could also impact the ASPL emission properties by scattering and trapping the hot carriers and SHG emission properties by breaking the geometrical centrosymmetry. By comprehensively analyzing the fundamentals of the plasmonic ASPL and SHG emissions, this work paves the way in designing plasmonic devices with desired non-linear emission properties for sensing and spectroscopy applications.

5.2. Results and discussion

Two sets of NPCs are used in this work (Table 1): H1-H3 consist of a corrugated Ag-SiO₂-Ag nanolaminate array coated by 25 nm, 60 nm, and 130 nm TiO₂ cladding layers, respectively (Figure 5.1(b) and Figure D1(a)). G1-G3 are similar except not possessing the top SiO₂ and Ag layers. The nonlinear optical measurements were carried out in a free-space setup where ultrafast laser pulses with tunable power, wavelength, and polarization are incident at 30° (Figure D1(b)). The laser pulses have a *sech*² temporal shape with $\Delta t_{inc} = 140 \text{ fs}$ full width at half maximum and $f_{inc} = 80 \text{ MHz}$ repetition rate. The nonlinear emission was collected using a CCD spectrometer in the normal direction and 490 – 890 nm spectral range.

Table 5.1. Description of the samples used in this work (PPA: polymer pillar array). H3 is the main sample and the other samples are used to analyze the effects of the system geometry on the non-linear emission. Our sample designs offer independent control over the plasmonic modes at the excitation ($> 950\text{ nm}$) and emission wavelengths ($490 - 890\text{ nm}$).

Sample	Description
H1	Si/PPA/Ag (80 nm)/SiO ₂ (6 nm)/Ag (30 nm) /TiO ₂ (25 nm)
H2	Si/PPA/Ag (80 nm)/SiO ₂ (6 nm)/Ag (30 nm) /TiO ₂ (60 nm)
H3	Si/PPA/Ag (80 nm)/SiO₂ (6 nm)/Ag (30 nm) /TiO₂ (130 nm)
G1	Si/PPA/Ag (80 nm)/TiO ₂ (25 nm)
G2	Si/PPA/Ag (80 nm)/TiO ₂ (60 nm)
G3	Si/PPA/Ag (80 nm)/TiO ₂ (130 nm)

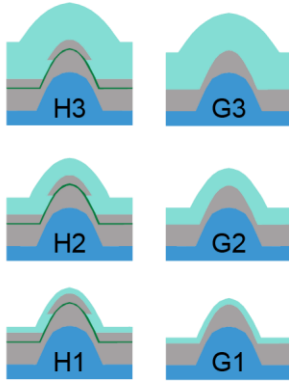


Figure 5.2(a-c) show the absorption spectra of the samples under normal white-light illumination. G samples show a multitude of absorption resonances below 950 nm that redshift upon increasing the TiO₂ cladding thickness. However, they show a relatively weak optical absorption after 950 nm. FDTD simulations of the G samples' far-field and near-field optical responses (Figure D2) reveal that the observed absorption resonances belong to the delocalized Bloch SPP modes on the Ag-TiO₂ interface. When the cladding thickness goes up, the effective index above the metal layer increases and as a result, the Bloch SPP resonances (and thus absorption peaks) redshift.

Compared to the G samples, H samples possess an extra SiO₂-Ag layer which introduces localized gap modes, residing in the NPCs dome part, and delocalized gap modes, sandwiched between the two Ag nanohole arrays (Figure D2). By ~ 3 order enhancement of the incident field (Figure D2), these gap modes significantly augment the absorption after 950 nm and dominate the optical response in this spectral range (Figure 5.2(a-c)). Interestingly, the three H samples have comparable absorption spectra after 950 nm, indicating that the gap modes are only slightly affected by the cladding thickness. In contrast, as evidenced by the similarity between the H2 and G2 (H3 and G3) absorption spectra, the optical response below 950 nm is less affected by the gap modes, except for very thin ($< 30\text{ nm}$) cladding thicknesses. In accordance with this observation, FDTD simulations (Figure D2) reveal that the H samples' plasmonic modes below 950 nm are a hybrid of the gap modes and the Bloch SPP modes on the Ag-TiO₂ interface.

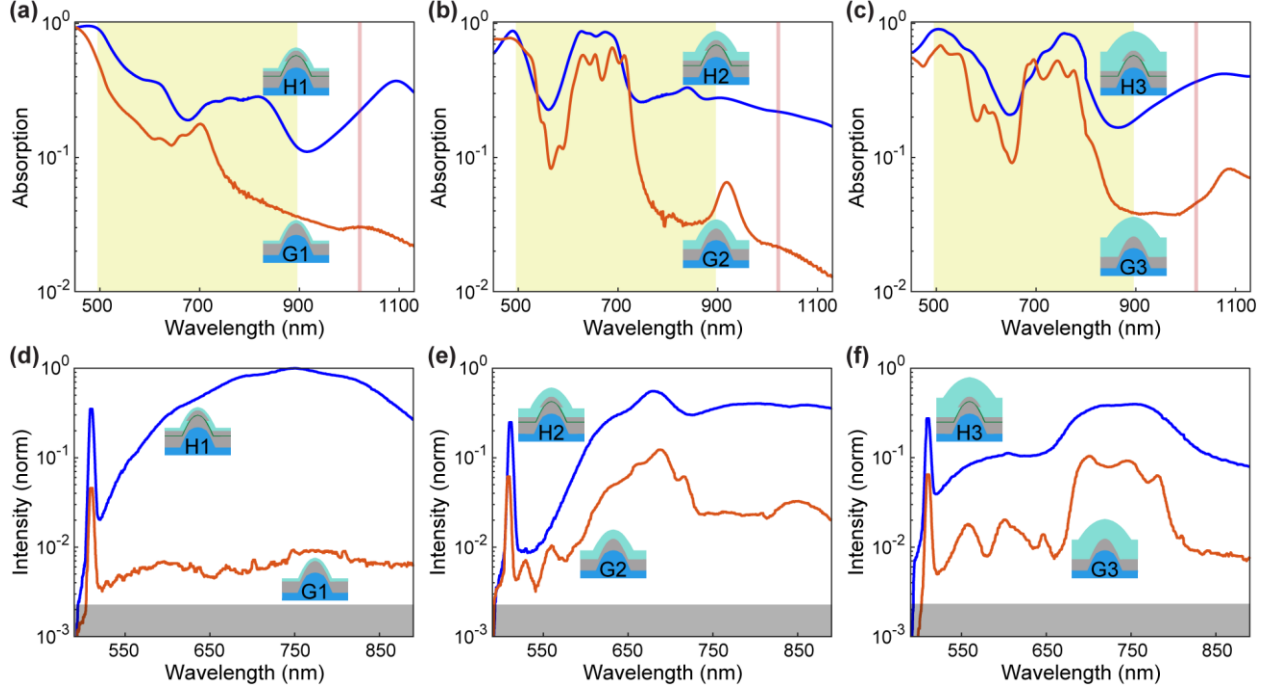


Figure 5.2. (a-c) Absorption spectra of the samples under normal white light excitation. (d-f) Nonlinear emission spectra of the samples under P-polarized, 1020 nm , and 128 mW excitation. The H and G samples in each graph have the same TiO_2 cladding thickness.

Figure 5.2(d-f) show the nonlinear emission spectra of the samples under P-polarized pulsed-laser excitation with the incident wavelength and power of $\lambda_{inc} = 1020\text{ nm}$ and $P_{inc} = 128\text{ mW}$, respectively. For all the samples, the nonlinear emission spectrum features a sharp SHG peak coinciding with a broad ASPL emission that quickly drops below the SHG wavelength. Both SHG and ASPL intensities are ~ 1 order (or more) larger for the H samples compared to the G samples, owing to the enhanced electric field and absorption that the gap modes of the H samples provide at the excitation wavelength. Except for G1 that has an ASPL emission close to the noise floor and its resonances cannot be discerned, we find a high resemblance between the ASPL and absorption resonances for both H and G samples. This observation suggests that the plasmonic modes active at the emission wavelength define the resonance features in the ASPL lineshape through the Purcell effect. Conversely, despite enhancing the ASPL intensity, the plasmonic modes active at the excitation wavelength do not directly influence the ASPL lineshape features.

Figure 5.3(a) shows the H3 nonlinear emission spectra for different incident powers from $P_{inc} = 48\text{ mW}$ up to $P_{inc} = 128\text{ mW}$ but fixed incident wavelength ($\lambda_{inc} = 1020\text{ nm}$) and polarization (P). The figure clearly shows that both SHG and ASPL grow non-linearly with the incident power. Exponential fitting of the integrated SHG (505-515 nm) and ASPL (530-890 nm) intensities as a

function of P_{inc} reveals that they are roughly two-photon processes with the average power laws of ~ 2.36 and ~ 2.22 , respectively (Figure D3(b)). Nevertheless, the non-integer power-laws and the observation that power-laws generally increase as P_{inc} goes up (Figure 5.3(b)) manifest that the SHG and ASPL underlying mechanisms are more complex than simple two-photon excitation and emission.

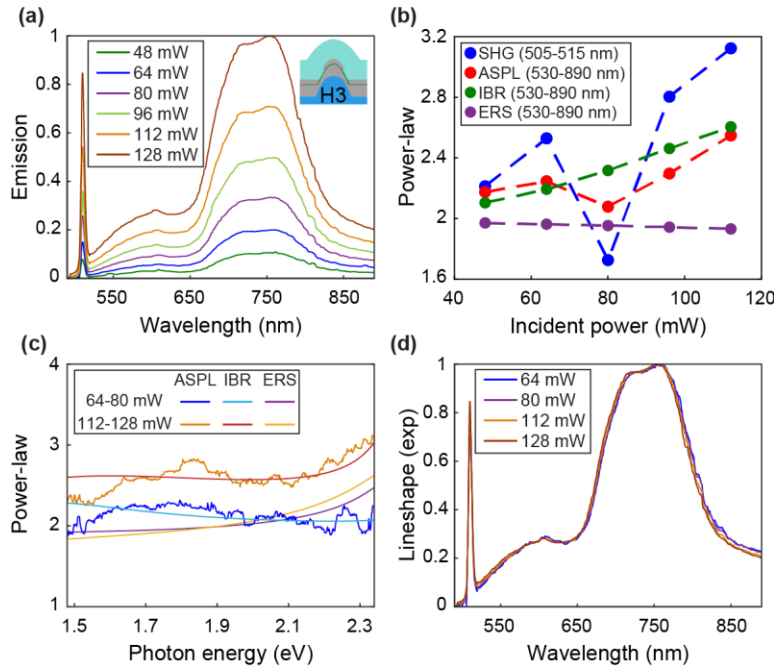


Figure 5.3. (a) H3 nonlinear emission spectra for fixed incident wavelength (1020 nm) and polarization (P) but different incident powers ranging from 48 mW up to 128 mW. (b) SHG (experimental), ASPL (experimental), IBR (model), and ERS (model) power-laws as a function of the incident power (P_{inc}). (c) Experimental and modeled spectral power-laws at two different power levels. (d) Comparison of the emission lineshapes for 64, 80, 112, and 128 mW incident powers.

The observed SHG power-laws indicate that the second-order susceptibility ($\chi^{(2)}$) depends on the incident power. This dependence arises because $\chi^{(2)}$ is a function of the electrons' energy distribution inside the metal³²⁰, which can be perturbed by pulsed laser excitation³⁵². Further investigation is required to understand the anomalous decrease in SHG power-law at 80 mW.

To analyze the ASPL non-linear behavior, it is more proper to calculate the power-law as a function of the emission photon energy ($h\nu$) besides P_{inc} ³⁴⁶ (Figure 5.3(c) and Figure D3). We see that although the power-law fluctuates with $h\nu$, it remains about ~ 2 up to $P_{inc} \sim 80$ mW. As P_{inc} further goes up, the power-law grows above 2 and becomes a generally increasing function of $h\nu$. In accordance with the observed power-law behaviors, Figure 5.3(d) shows that the ASPL

spectral shape is almost independent of the incident power up to $\sim P_{inc} = 80 \text{ mW}$ but starts to blueshift as P_{inc} increases above $\sim 80 \text{ mW}$. Figure D4 further manifests that the ASPL level below the SHG wavelength is negligibly small and insensitive to P_{inc} at all the incident power levels, except when $P_{inc} = 128 \text{ mW}$. We show below that the observed ASPL features match an IBR-dominant photoluminescence picture.

Absorption of the incident laser photons promotes the silver electrons from the occupied states below the Fermi level to the unoccupied states above the Fermi level, thus generating a distribution of hot electrons and holes. An incident laser pulse also induces surface plasmons (collective free electron oscillations) which can highly enhance the light absorption through the Landau damping process. Interband transitions have a negligible contribution to the absorption since the pump photon energy (1.22 eV) is much lower than the energy required for the transition from d band to the Fermi-surface in silver ($\sim 4 \text{ eV}$). Therefore, the absorption primarily occurs through the intra-sp-band electronic transitions. The initial and final electronic states in the intraband transitions have a momentum mismatch that is bridged by electron-phonon and electron-electron scattering processes or surface confinement of the plasmonic modes³⁵⁵.

Before the excitation ($t = 0$ in Figure 5.4(a)), the electrons are at thermal equilibrium with the lattice and follow the Fermi-Dirac distribution $f(\epsilon, T_0) = 1 / \left[\exp \left(\frac{\epsilon - E_F}{K_B T_0} \right) + 1 \right]$, where ϵ is the electron energy, $E_F = 5.49 \text{ eV}$ is the silver Fermi energy, K_B denotes the Boltzmann constant, and $T_0 = 300 \text{ K}$ is the medium temperature. Generation of hot carriers perturbs the equilibrium electron distribution in the energy range from $\sim E_F - h\nu_{inc}$ up to $\sim E_F + h\nu_{inc}$, where h and ν_{inc} represent the Planck's constant and the incident frequency, respectively. Perturbation of the electron distribution (occupation probability) due to a pulsed excitation can be approximated as follows^{356, 357}:

$$G(\epsilon, t) = \frac{M I_{inc}(t)}{\sqrt{\epsilon}} \left\{ \sqrt{\epsilon - h\nu_{inc}} f(\epsilon - h\nu_{inc}, T_0) [1 - f(\epsilon, T_0)] - \sqrt{\epsilon + h\nu_{inc}} f(\epsilon, T_0) [1 - f(\epsilon + h\nu_{inc}, T_0)] \right\}, \quad (1)$$

where $I_{inc}(t)$ is the incident power flux and the constant M characterizes the excitation strength, including the effects of plasmonic field confinement and all the excitation conditions (angle,

polarization, etc.) except the incident power. The laser pulses in this work have the normalized intensity of $I_{inc}(t) = \frac{0.88P_{inc}}{f_{inc}\Delta t_{inc}} \left[\text{sech} \left(\frac{1.76t}{\Delta t_{inc}} \right) \right]^2$ with $f_{inc} = 80 \text{ MHz}$ and $\Delta t_{inc} = 140 \text{ fs}$.

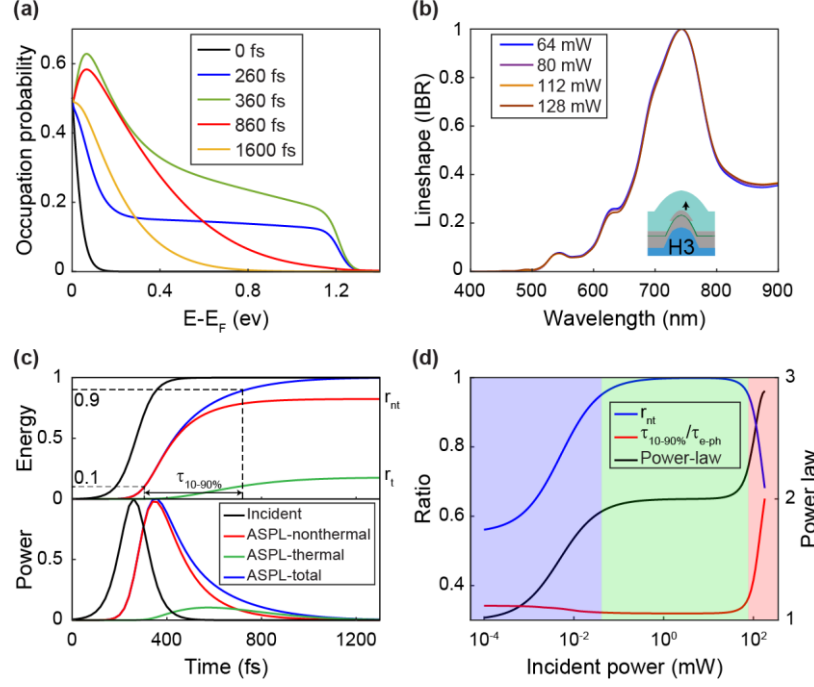


Figure 5.4. PL model for a system with $M = 0.26$ and $\beta = 1$ (IBR-dominant picture) excited by a laser pulse ($\lambda_{inc} = 1020 \text{ nm}$) peaking at $t = 260 \text{ fs}$. (a) Electron energy distributions at different times before, during, and after the excitation for $P_{inc} = 128 \text{ mW}$. (b) Comparison of the emission lineshapes for 64, 80, 112, and 128 mW incident powers. (c) Incident and ASPL (530-890 nm) power and energy versus time for $P_{inc} = 128 \text{ mW}$. Energy curves are acquired by integration of the power curves. The total ASPL power and energy can be divided into two components contributed by the non-thermal (ρ_{nt}) and thermal (ρ_t) hot carriers, respectively. $\tau_{10-90\%}$, r_{nt} , and r_t represent the ASPL emission time, and non-thermalized and thermalized contribution levels to ASPL, respectively. (d) Dependency of r_{nt} , $\tau_{10-90\%}$ (normalized to $\tau_{e-ph} = 850 \text{ fs}$), and power-law on the incident power. The ASPL process could fall into weak (blue), moderate (green), or strong (red) excitation regimes.

A common perturbative approach is to divide the total electron distribution as $\rho(\epsilon, t) = \rho_t(\epsilon, t) + \rho_{nt}(\epsilon, t)$, where the thermalized component ρ_t has a Fermi-Dirac distribution with the electronic temperature $T_e(t) \geq T_0$ and the non-thermalized component ρ_{nt} has a non-Fermi distribution³⁵⁸. In the equilibrium situation before the excitation, $T_e = T_0$ and $\rho_{nt} = 0$. The excitation process (Eq. (1)) initially generates non-thermalized carriers ($G = \left. \frac{d\rho_{nt}}{dt} \right|_{gen}$) but as soon as the generation occurs, electron-electron (e-e) collisions transfer the energy from the non-thermalized carriers to the thermalized ones, leading to a rise in T_e . The lifetime of a non-thermalized hot electron due to

e-e collisions is given by the Fermi-liquid theory as $\tau_{e-e}(\epsilon) \propto 1/(\epsilon - E_F)^2$ and the proportionality constant is chosen to acquire the silver thermalization time of 350 fs ³⁵⁶. Eventually, due to electron-phonon (e-ph) collisions, the hot carriers lose their energy to the lattice, and both the non-thermalized and thermalized electron populations decay to their equilibrium conditions. The lifetime of this decay is assumed similar ($\tau_{e-ph} = 850 \text{ ps}$ in silver) for both the thermalized and non-thermalized electrons ^{356, 358}. The above-explained picture culminates in two master equations (section D.2) that govern the time evolution of ρ_t and ρ_{nt} . Although the photoluminescence process also consumes the hot carriers, it has a very low quantum yield ($< 10^{-5}$) ³³⁵ and thus was not included in the master equations. For certain M , λ_{inc} , and P_{inc} , the master equations allow us to calculate the electron distribution ($\rho = \rho_t + \rho_{nt}$) at different times before, during, and after the pulsed excitation. As an example, Figure 5.4(a) shows $\rho(\epsilon, t)$ curves for a system with $M = 0.26$ and excited by a $\lambda_{inc} = 1020 \text{ nm}$ and $P_{inc} = 128 \text{ mW}$ pulse. More details are also given in Figure D5. We next use the obtained electron distributions to calculate the PL emission.

Generally, PL occurs when electromagnetic fields perturb the intrinsic Hamiltonian inside the metal ($H_0 \rightarrow H_0 + H_{int}$), and thereby, transition the electrons across the different electronic states. Here, H_{int} is the interaction Hamiltonian and in a fully quantum mechanical picture, can be contributed by the incident field and all the optical modes, excited or unexcited. By expanding H_{int} using the Coulomb gauge in Maxwell's equations, and then using the Fermi's golden rule, PL's spectral power density can be expressed as (section D.3):

$$S(\nu) \propto f_{inc} \left(\frac{4h\nu^3}{c^3} \right) L_{eff}(\nu) [\beta \psi_{IBR}(\nu) + (1 - \beta) \psi_{ERS}(\nu)], \quad (2)$$

where $(4h\nu^3)/c^3$ is the product of the local density of photonic states in vacuum ($4\nu^2/c^3$) and the photon energy $h\nu$. $L_{eff}(\nu)$ is the effective emission enhancement factor which defines the resonance features in the spectral shape and accounts for both the Purcell effect and quantum efficiency of the plasmonic modes. Since the metallic PL process has a low intrinsic yield, $L_{eff}(\nu)$ has the same value as the effective quantum yield enhancement ²⁸⁵. $0 \leq \beta \leq 1$ is a ratio that determines the dominance level of the IBR and ERS processes in the PL emission. $\psi_{IBR}(\nu)$ and $\psi_{ERS}(\nu)$ respectively represent the number of electron-hole pairs available for photoluminescence at frequency ν from the IBR and ERS processes, and are defined as (section D.3):

$$\psi_{IBR}(\nu) = \int_{-\infty}^{+\infty} \int_{h\nu}^{+\infty} \xi_{IBR}(\epsilon, \nu) \rho(\epsilon, t) [1 - \rho(\epsilon - h\nu, t)] \epsilon^{3/2} d\epsilon dt, \quad (3)$$

$$\psi_{ERS}(\nu) = \int_{-\infty}^{+\infty} \left(\frac{I_{inc}(t)}{\nu_{inc}} \right) \int_{h\nu}^{+\infty} \xi_{ERS}(\epsilon, \nu) \rho(\epsilon, t) [1 - \rho(\epsilon + h\nu_{inc} - h\nu, t)] \sqrt{\epsilon} d\epsilon dt, \quad (4)$$

where $\xi_{IBR}(\epsilon, \nu) = a(\epsilon) e^{\frac{-h\nu}{b(\epsilon)KT}}$ and $\xi_{ERS}(\epsilon, \nu) = a'(\epsilon) e^{\frac{-h(\nu - \nu_{inc})}{b'(\epsilon)KT}}$ account for the momentum provided by the plasmonic modes in electronic transitions. $a \sim 32.2$, $b \sim 11.6$, $a' \sim 23.4$, and $b' \sim 23$ are good approximations considering the electron energy levels in this work. In the IBR process (Figure 5.1(c)), emission of a photon with the energy $h\nu$ requires the recombination of an electron in the state ϵ with the hole in the state $\epsilon - h\nu$ (inverse Landau damping). However, to generate a similar photon in the ERS process (Figure 5.1(d)), an incident photon first excites the electron in the state ϵ to the virtual state $\epsilon + h\nu_{inc}$ and then, the electron in the virtual state recombines with the hole in the state $\epsilon + h\nu_{inc} - h\nu$. In both IBR and ERS processes, the initial state must be occupied while the final state must be unoccupied. As evident from Eqs. (3), emission at the frequency ν through the IBR process can continue as long as electron and hole pairs with $h\nu$ energy difference are available, even after the excitation pulse has vanished. However, as Eq. (4) indicates, emission via the ERS process vanishes with the excitation pulse.

We estimated $L_{eff}(\nu)$ in Eq. (2) from FDTD simulations with electric dipole source (section D.4) and found that for a z-polarized dipole above the silver dome, the FDTD-calculated spectrum decently mimics the resonances in the experimental lineshapes (Figure D6 and 4(b)). This result reveals that the ASPL emission is prevailed by the z-polarized hot carriers inside the metallic dome, which could be due to combined effects of higher generation rate and higher Purcell factor. Hence, the only unknowns in Eqs. (1)-(4) and the master equations are M and β .

By fitting the experimental power-laws, we found $M = 0.26$ and $r = 1$, revealing that the ASPL emission is dominated by the IBR process (IBR curves in Figure 5.3(b-c) and Figure D3). Our model resulted in ASPL lineshapes that have a weak dependency on the incident power and sharply drop below the SHG wavelength (Figure 5.4(b)). In addition, the model predicted that above $P_{inc} \sim 80 \text{ mW}$, the ASPL lineshape starts to blueshift and rise below the SHG wavelength (IBR curves in Figure D4). Matching of these results with the experimental observations (Figure D4) indicates that the IBR-dominant model correctly captures the ASPL dynamics.

The model suggests that the excitation power level can affect the ASPL's power-law, spectral features, and emission time through influencing the contribution level of the native (pre-excitation), non-thermalized and thermalized carriers to the emission. Figure 5.4(c) bottom panel displays the instantaneous powers of an incident laser pulse ($\lambda_{inc} = 1020 \text{ nm}$ and $P_{inc} = 128 \text{ mW}$) and the resulting ASPL pulse (for $M = 0.26$ and $\beta = 1$) as a function of time. By integrating the power curves, we can calculate the total energy delivered/emitted by the incident/emitted pulse by time t (Figure 5.4(c) top panel). Furthermore, by inserting $\rho = \rho_{th} + \rho_{nt}$ into Eq. (3), we can find the instantaneous contribution levels of the non-thermalized (ρ_{nt}) and thermalized (ρ_t) hot carriers to the total ASPL power and energy. Then, we define the ASPL emission time ($\tau_{10-90\%}$), and the levels of the non-thermalized and thermalized carriers' contribution to the ASPL (r_{nt} and $r_t = 1 - r_{nt}$) as illustrated in Figure 5.4(c) top panel, respectively. Native carriers' contribution level is also included in r_t .

Depending on the incident power, the ASPL process could fall into weak (blue), moderate (green), or strong (red) excitation regimes with distinct r_{nt} , $\tau_{10-90\%}$, and power-law features (Figure 5.4(d)). In the weak-excitation regime, $\tau_{10-90\%} \sim \tau_{e-e} = 350 \text{ fs}$, $r_{nt} < 0.95$, and ASPL is co-contributed by the native and non-thermalized hot carriers. Reaching the weak-excitation regime for H3 sample requires $P_{inc} < 70 \text{ }\mu\text{W}$, which could not be tested experimentally due to low signal-to-noise ratio. Yet, the model predicts that ASPL power-laws (integrated and spectral) are between 1 and 2, spectral power-law increases with $h\nu$, and the ASPL cut-off occurs above the SHG wavelength in this regime. These predictions are consistent with the experimental observations for continuous-wave excitation³⁴⁹. The moderate-excitation regime ($70 \text{ }\mu\text{W} < P_{inc} < 80 \text{ mW}$ for H3) features $\tau_{10-90\%} \sim 320 \text{ fs} < \tau_{e-e}$ and $r_{nt} > 0.95$. The power-laws are ~ 2 in this regime as the non-thermalized carriers dominantly contribute to the ASPL emission, and two intraband transitions by the excitation wave are required to generate a non-thermalized electron-hole pair with $> h\nu_{inc}$ energy difference. Furthermore, the ASPL cut-off occurs around the SHG wavelength. In both the weak and moderate excitation regimes, ASPL decay (over time) results from electron-electron interactions.

In the strong-excitation regime ($P_{inc} > 80 \text{ mW}$ for H3), T_e reaches $\sim 2000 \text{ K}$, which increases the contribution of the thermalized hot carriers to the ASPL emission non-negligible ($r_{nt} < 0.95$). Therefore, the ASPL emission decays due to electron-phonon interactions in this excitation regime, making τ increase with P_{inc} and $\tau_{e-e} < \tau_{10-90\%} < \tau_{e-ph}$ (Figure 5.4(d)). Furthermore,

ASPL emission below the SHG wavelength grows and the ASPL power-laws go above 2 (IBR curves in Figure D3 and Figure D4). ASPL's spectral power-law increases with $h\nu$ as well, which leads to a blueshift in its spectral shape³⁴⁴ (IBR curves in Figure 5.3(c), Figure 5.4(b), Figure D3, and Figure D4). Please note that the exact shape of the curves in Figure 5.4(d) are specific to our experimental conditions and while the relationship between r_{nt} , power-laws and cut-off wavelength remain similar for other experimental conditions, the emission times and the incident power range in excitation regime might be very different.

Despite the good agreement between the IBR model and the experimental results, the experimental spectral power-laws are lower than the modeled results below ~ 1.6 eV emission photon energies. Yet, our model could still fit the experimental power-laws in this spectral range when lower M values were utilized. In this regard, the mismatch between the modeled and experimental power-laws could stem from our implicit assumption of uniform excitation level across the whole structure by considering a single deterministic M value. However, structural imperfections (such as surface roughness) and the gaussian laser profile makes the excitation non-uniform in practice. Furthermore, our model could not explain the anomalous decrease in the experimental ASPL power-laws around 80 mW. We believe that this anomaly could originate in some non-linear resonant processes not included in our mode, although further investigation is required.

To further understand why an IBR-dominant picture ($\beta = 1$) works better than a mixed IBR-ERS picture ($\beta < 1$), we modeled the ASPL emission using the ERS-dominant picture ($\beta = 0$) as well. We observed that several predictions of the ERS-dominant model contradict the experimental results (ERS curves in Figure 5.3(b-c), Figure D3, and Figure D4). For example, the integrated power-law has little sensitivity to the incident power and cannot go above 2 (Figure 5.3(b)). Also, the spectral power-law below ~ 1.9 eV goes down as the incident power increases (Figure 5.3(c)). Moreover, ERS model predicts a non-negligible level of ASPL emission below the SHG wavelength (Figure D4(d)), unless M is unrealistically low such that T_e remains below 600 K. However, such a low M value contradicts the observation that SHG power-law is larger than 2, which requires large perturbations of the electron distribution to make $\chi^{(2)}$ power-dependent.

Figure 5.5(a) shows the H3 nonlinear emission spectra for different incident wavelengths from $\lambda_{inc} = 960$ nm up to 1040 nm. The incident power ($P_{inc} = 128$ mW) and polarization (P) are fixed. We see that changing λ_{inc} not only impacts both ASPL and SHG intensities but also modifies their ratio, such that I_{SHG} (integrated in $\lambda_{inc}/2 \pm 5$ nm) gets maximized for $\lambda_{inc} =$

1040 nm while I_{ASPL} (integrated in 530-890 nm) is the highest for $\lambda_{inc} = 1020$ nm (Figure 5(b)). Moreover, I_{SHG} is ~ 2 times more sensitive to λ_{inc} than I_{ASPL} . SHG's high sensitivity to λ_{inc} is partly due to $\chi^{(2)}$'s dispersive behavior. Another major reason is SHG's coherent nature, which causes a $\Delta\lambda_{inc}/2$ - shift in its emission band as the incident wavelength shifts for $\Delta\lambda_{inc}$ (Figure 5.5(a)); This property leads to λ_{inc} -dependent modification of both the excitation and emission enhancement for SHG, as the optical response of plasmonic modes is wavelength-dependent.

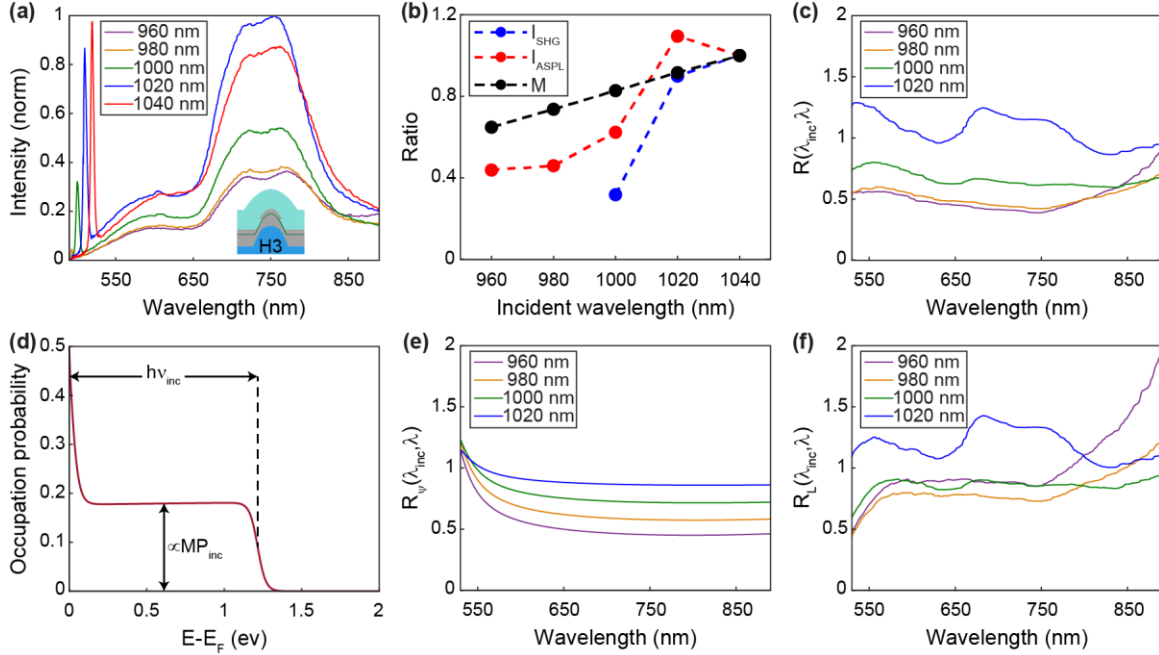


Figure 5.5. (a) H3 nonlinear emission spectra ($S(\lambda_{inc}, \lambda)$) for fixed incident power (128 mW) and polarization (P) but different incident wavelengths ranging from 960 nm up to 1040 nm. (b) M (in Eq. (1)), I_{SHG} (505 – 515 nm), and I_{ASPL} (530 – 890 nm) as a function of the incident wavelength. (c) ASPL spectral intensity ratios ($R(\lambda_{inc}, \lambda) = S(\lambda_{inc}, \lambda)/S(1040 \text{ nm}, \lambda)$) acquired from the spectra in part (a). (d) laser-induced perturbation of the electron distribution when the electron-electron and electron-phonon scattering effects are neglected. (e, f) $R_\psi(\lambda_{inc}, \lambda)$ and $R_L(\lambda_{inc}, \lambda)$ represent the $R(\lambda_{inc}, \lambda)$ components due to modification of the available hot electron-hole pairs ($\psi(\nu)$) and the effective emission enhancement factor (L_{eff}), respectively.

The situation is more complicated for ASPL as changing λ_{inc} does not affect its intensity uniformly across the emission band, as shown by the spectral intensity ratios ($R(\lambda_{inc}, \lambda) = S(\lambda_{inc}, \lambda)/S(1040 \text{ nm}, \lambda)$) in Figure 5.5(c). Furthermore, each λ_{inc} value (960, 980, 1000 and 1020 nm) causes distinct resonance features in the $R(\lambda_{inc}, \lambda)$ spectra. Hence, changing λ_{inc} not only alters the ASPL intensity but also modifies its lineshape (Figure D7). A primary reason for the modification of the ASPL intensity and lineshape is λ_{inc} -dependency of $\psi_{IBR}(\nu)$ in Eq. (3).

$\psi_{IBR}(\nu)$ is a function of the electron distribution $\rho(\epsilon, t)$ and from Eq. (1), changing λ_{inc} can modify $\rho(\epsilon, t)$ by alteration of the incident photon energy ($h\nu_{inc}$) and the excitation strength factor M . λ_{inc} -dependency of M roots in the wavelength-dependent response of the plasmonic modes. These effects can be discerned in Figure 5.5(d), which simply illustrates how the electron distribution would be after the excitation when electron-electron and electron-phonon scattering effects are neglected.

To calculate $M(\lambda_{inc})$, we notice that due to low ASPL quantum yield ($< 10^{-5}$)³³⁵, most of the generated hot carriers get absorbed due to electron-phonon interactions, thus $A(\lambda_{inc}) \sim \int_{-\infty}^{+\infty} G(\epsilon, t) \epsilon^{3/2} dt \sim M(\lambda_{inc})$, where $A(\lambda_{inc})$ is the linear absorption spectrum. By fitting the power-laws in Figure 5.3(b-c), it was previously found that $M(1020 \text{ nm}) = 0.26$. We estimate the M values for the other incident wavelengths (Figure 5.5(b)) by fitting the H3 sample's absorption spectrum in Figure 5.2(c).

In the next step, we use the master equations to find the time-evolution of the carrier distributions for each λ_{inc} , and then, use Eqs. (2) and (3) with $L(\nu) = 1$ to find $R_\psi(\lambda_{inc}, \lambda)$, i.e., the spectral intensity ratios due to λ_{inc} -dependency of ψ_{IBR} (Figure 5.5(e)). $R_\psi(\lambda_{inc}, \lambda)$ rising at low wavelengths is caused by the ASPL dropping below the SHG ($\lambda_{inc}/2$), as evident in Figure 5.5(a) and Figure D7. $R_\psi(\lambda_{inc}, \lambda)$ spectra in Figure 5.5(e) also capture the general trend that $R(\lambda_{inc}, \lambda)$ goes up with λ_{inc} . However, R_ψ spectra do not show the resonant features in $R(\lambda_{inc}, \lambda)$ curves, indicating they are not coming from $\psi_{IBR}(\nu)$ modification. We argue that $R(\lambda_{inc}, \lambda)$ resonant features are instead caused by λ_{inc} -dependency of the effective emission enhancement factor $L_{eff}(\nu)$. Considering the incoherent nature of the photoluminescence process, $L_{eff}(\nu)$ can be expressed as (section D.4):

$$L_{eff}(\nu) = \sum_{\hat{l}=\hat{x},\hat{y},\hat{z}} \iiint_{V_m} \phi_{eff}^l(r, \nu) F_l(r, \nu) d^3r, \quad (5)$$

where V_m denotes the metallic parts of the system. $F_l(r, \nu)$ represents the radiative decay enhancement of an $\hat{l}$ -polarized dipole at position r and frequency ν versus a similar dipole in free space⁵⁸. FDTD simulations show that $F_l(r, \nu)$ spectrum is very sensitive to r and l (Figure D6). ϕ_{eff}^l describes the effective spatial distribution of the $\hat{l}$ -polarized electron-hole pairs (dipole

approximation) with the energy $h\nu$ over the course of emission and is normalized as $\sum_{l=\hat{x},\hat{y},\hat{z}} \iiint_{V_m} \phi_{eff}^l d^3r = 1$. $\phi_{eff}^l(r, \nu)$ is a function of the hot carriers' energy, spatial and momentum distributions, and in fact acts like a weighting function that determines which dipole positions and directions dominantly contribute to $L_{eff}(\nu)$.

Carrier distributions are dynamic since after the generation, the hot carriers quasi-ballistically transport and scatter through the system metallic parts with $\sim v_f = 1.4 \text{ nm/fs}$ and inelastic mean free paths of tens of nanometers^{359, 360}. Nevertheless, the initial distributions of the hot carriers, right after the generation, are determined by the excitation conditions. In this regard, $L_{eff}(\nu)$ is a function of the excitation conditions. In specific, by modifying the energy distribution of the hot carriers, changing λ_{inc} modifies the hot carriers' momentum distribution too. Also, as the hot carriers' lifetime depends on their energy, their effective spatial distribution also gets affected by changing λ_{inc} . Finally, as plasmonic modes have a wavelength-dependent response, changing λ_{inc} can modify the excitation field profile and by that, the initial spatial distribution of the hot carriers³⁶⁰. From Eq. (2), we can get the L_{eff} ratios for different incident wavelengths (Figure 5.5(f)) as $R_L(\lambda_{inc}, \lambda) = L_{eff}(\lambda_{inc}, \lambda) / L_{eff}(1040 \text{ nm}, \lambda) = R(\lambda_{inc}, \lambda) / R_\psi(\lambda_{inc}, \lambda)$.

To further understand how the hot carriers' spatial distribution influences the non-linear emission, we study the effects of incident polarization. Figure 5.6(a) displays the H3 nonlinear emission spectra for P and S incident polarizations when the incident wavelength and power are fixed at $\lambda_{inc} = 1020 \text{ nm}$ and $P_{inc} = 64 \text{ mW}$, respectively. We see that SHG and ASPL emissions are both larger for the S-polarized excitation. Nevertheless, the ASPL intensity ratio $D(\lambda) = S(pol_{inc} = S, \lambda) / S(pol_{inc} = P, \lambda)$, is not uniform and exhibits multiple resonances across the emission band (Figure 5.6(b)). Just as $R(\lambda_{inc}, \lambda)$ spectra in Figure 5.5(c), we can break $D(\lambda)$ into D_ψ and D_L components that account for the ASPL alteration due to pol_{inc} -dependency of $\psi_{IBR}(\nu)$ and $L_{eff}(\nu)$ terms in Eq. (2), respectively. D_L stems from the modification of the hot carriers' spatial distribution and like R_L in Figure 5.5(f), determines the resonant features in $D(\lambda)$ spectra. However, unlike R_ψ in Figure 5.5(e), D_ψ is almost independent of the emission wavelength as changing pol_{inc} only affects the excitation level but not the incident photon energy (Figure 5.5(d)). FDTD simulations and angled reflectance measurements indicate that S and P incident polarizations have comparable absorption levels (Figure D8), making $D_\psi \sim 1$ and $D(\lambda) \approx D_L(\lambda)$ (Figure 5.6(b)).

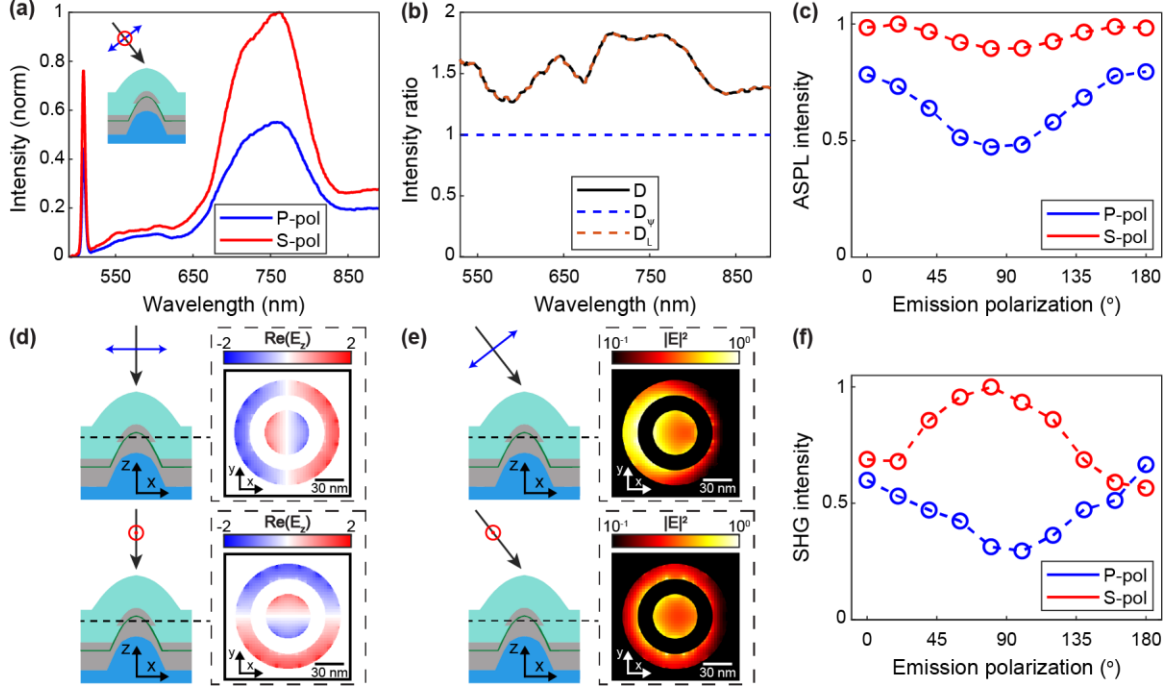


Figure 5.6. (a) H3 nonlinear emission spectra ($S(pol_{inc}, \lambda)$) for fixed incident power (128 mW) and wavelength (1020 nm) but different incident polarizations (P and S). (b) $D(\lambda) = S(pol_{inc} = S, \lambda)/S(pol_{inc} = P, \lambda)$ is the spectral intensity ratio between the S and P incident polarizations acquired from part (a) spectra. $D_\psi(\lambda)$ and $D_L(\lambda)$ represent the $D(\lambda)$ components due to modification of the available electron-hole pairs energy ($\psi(v)$) and the effective emission enhancement factor (L_{eff}), respectively. (c) I_{ASPL} (530 – 890 nm) dependency on the emission polarization (pol_{em}) for each of P and S incident polarizations. (d) FDTD-simulated $Re(E_z)$ distributions in the H3 dome part for two cases of normal excitation with perpendicular polarizations (at 761 nm). NPCs possess degenerate plasmonic modes with perpendicular polarizations. (e) FDTD-simulated $|E|^2$ distributions in the H3 dome part for 30°-angled excitation with P and S polarizations (at 1020 nm). $|E|^2$ profiles at the excitation wavelength (denoted by $|E_{ex}|^2$ in the text) estimate the hot carriers' spatial distributions right after the generation. (f) I_{SHG} (505 – 515 nm) dependency on pol_{em} for P and S incident polarizations.

Our experiments so far affirm that the ASPL emission results from plasmonic-enhanced hot carrier generation and recombination. However, a critical question remains that do the ASPL photons come from radiative carrier recombination, or does carrier recombination first generates surface plasmons, and the far-field emission later occurs due to surface plasmon decay? This dilemma can be resolved by studying the pol_{inc} effect on the ASPL's emission polarization (pol_{em}). Figure 5.6(c) shows the integrated ASPL intensity I_{ASPL} as a function of pol_{inc} and pol_{em} . We see that I_{ASPL} distribution is ~ 5 times more uniform for $pol_{inc} = S$ than $pol_{inc} = P$ (based on relative standard deviations), even though ASPL lineshapes are comparable over the different excitation and emission polarizations (Figure 5.6(a) and Figure D9).

If ASPL emission were due to radiative carrier recombination, the emission would have been equally split among all the emission polarizations. This scenario can explain why different excitation and emission polarizations give similar lineshapes. However, ASPL emission due to radiative carrier recombination cannot account for the $I_{ASPL}(pol_{em})$ non-uniformity and its dependency on pol_{inc} . Hence, ASPL emission should mainly originate from the surface plasmon decay. In this scenario, electron-hole pairs act like microscopic sources (with ϕ_l^{eff} distribution in Eq. (5)) that excite the plasmonic modes active at the emission wavelengths. The excited modes then convert part of their received energy to the PL photons travelling to the far-field and the rest of their energy gets re-absorbed by the metal electrons.

To explicitly include this picture into Eq. (5), we can use the black-box coupled-mode theory³⁵⁴ to express F_l as a summation of the contributions from different plasmonic modes (section D.4):

$$F_l(r, \nu) = \frac{\gamma_r}{\gamma_r^0} = \sum_p \mathcal{P}_p \eta_p, \quad (6)$$

where γ_r and $\gamma_r^0 = \omega^2/\pi^2 c^3$ are the radiative decay rates of the dipole in the presence of the plasmonic system and in the free-space, respectively. $\mathcal{P}_p(l, r, \nu) = [3\epsilon_0 c^3/(8\pi^2 \nu^2)] \sigma_p(\nu) |E_p(r) \cdot \hat{l}|^2$ represents the Purcell effect of the p^{th} mode, where $E_p(r)$ and $\sigma_p(\nu) = \frac{\Gamma_p/\pi}{(2\pi\nu - 2\pi\nu_p)^2 + \Gamma_p^2}$ are the mode's normalized electric field and spectral shape, respectively. ν_p is the mode oscillation frequency and $\Gamma_p = \Gamma_p^r + \Gamma_p^{nr}$ is the mode decay rate, with Γ_p^r and Γ_p^{nr} being its radiative and non-radiative components. Also, $\eta_p = \Gamma_p^r/\Gamma_p$ is the quantum efficiency of the p^{th} plasmonic mode that characterizes its coupling to the far-field. By combining Eqs. (2), (3), (5), and (6), we can rewrite the PL formula as:

$$S(\nu) \propto f_{inc} \sum_p \gamma_p \eta_p, \quad (7)$$

where $\gamma_p \propto (h\nu) \psi_{IBR}(\nu) \sigma_p(\nu) \sum_{\hat{l}=\hat{x},\hat{y},\hat{z}} \iiint_{V_m} \phi_{eff}^l(r, \nu) |E_p(r) \cdot \hat{l}|^2 d^3r$ represents the rate of energy transfer from the hot carriers to the p^{th} plasmonic mode at the frequency ν . Based on Eq. (7), contribution level of a plasmonic mode to the PL emission depends on: 1- Spectral overlap between the hot electron-hole pairs and the plasmonic mode ($\sigma_p(\nu) \psi_{IBR}(\nu)$); 2- Spatial overlap

between the hot electron-hole pairs and the plasmonic field ($\iiint_{V_m} \phi_{eff}^l(r, \nu) |E_p(r) \cdot \hat{l}|^2 d^3r$); 3- Mode quantum efficiency η_p .

Due to structural symmetry, NPCs support two sets of degenerate plasmonic modes with perpendicular polarizations (Figure 5.6(d)). Since the degenerate modes have similar lineshape and quantum efficiency, it is ultimately the directional and spatial distributions of the hot electron-hole pairs that determine the contribution of each degenerate mode to the ASPL emission. In this regard, by affecting the hot carriers' spatial and momentum distribution, changing pol_{inc} can alter the $I_{ASPL}(pol_{em})$ distribution with little modification in the ASPL lineshape, consistent with the results of polarization measurements. We further check our hypothesis by a rough comparison of $I_{ASPL}(pol_{em})$ and ϕ_{eff}^l distributions for the two incident polarizations. Initial spatial distribution of the hot carriers right after the generation follows the $|E_{ex}|^2$ profile inside the metallic parts, where E_{ex} is the excitation electric field³⁶⁰. FDTD-simulations (Figure 5.6(e)) show that $pol_{inc} = S$ creates a more uniform $|E_{ex}|^2$ profile than $pol_{inc} = P$, which leads to a more uniform electron-hole pair distribution (ϕ_{eff}^l). Accordingly, based on Eq. (7), degenerate plasmonic modes of perpendicular polarizations would have a more balanced contribution to the ASPL emission for $pol_{inc} = S$. Matching of this result with the experimental observations in Figure 5.6(c) further validates Eq. (7) and our hypothesis on the correlation between the excitation and emission polarizations for ASPL.

As shown in section D.4, the more uniform $|E_{ex}|^2$ profile for $pol_{inc} = S$ could also be a cause of its higher ASPL emission than $pol_{inc} = P$ (Figure 5.6(a)). Nonetheless, our analysis based on the FDTD simulations cannot explain why $I_{ASPL}(pol_{em} = 0/180^\circ)$ is higher for $pol_{inc} = S$ than $pol_{inc} = P$ (Figure 5.6(c)). This result could partially be due to the incident polarization effects on the hot carriers' scattering and momentum distribution, which are beyond our FDTD-based analysis. Capturing the full effects of the incident polarization requires consideration of the microscopic structural imperfections such as bulk defects and surface roughness, which are excluded from the FDTD simulations. By changing the plasmonic field distributions and acting as scatter and trap centers for the hot carriers, the structural imperfections can uniquely modify γ_p for each plasmonic mode active at the emission wavelengths. Hence, the symmetry between the degenerate plasmonic modes breaks and $I_{ASPL}(pol_{em})$ distribution could deviate from the ideal situation.

Figure 5.6(f) shows the SHG intensity for different excitation and emission polarizations. We observe that for both $pol_{inc} = S$ and $pol_{inc} = P$, SHG polarization is distributed among all the possible angles from $pol_{em} = 0$ up to $pol_{em} = 180$, but the SHG intensity ($I_{SHG}(pol_{em})$) is largest when pol_{em} and pol_{inc} are aligned. pol_{inc} -dependency of $I_{SHG}(pol_{em})$ reveals that the far-field SHG photons do not come from the radiative electron transitions, just as ASPL. The far-field SHG photons instead come from the radiative decay of the surface plasmons excited by relaxation of the two-photon-excited electrons (Figure 5.1(e)).

Since NPCs' materials are centro-symmetric, we can assume that bulk second-order susceptibility ($\chi^{(2)}$) is negligible and ideally, SHG arises from the metallic interfaces where centrosymmetry is broken and the electric field is larger³²¹. Then, using the black-box coupled-mode theory³⁵⁴, the SHG emission rate can be expressed as a summation of emission rates from individual plasmonic modes (section D.5) as follows:

$$I_{SHG} \propto f_{inc} \left(\frac{16v_{inc}^2}{c^3} \right) \sum_p \gamma_p^{SHG} \eta_p, \quad (8)$$

where $\gamma_p^{SHG} \propto \sigma_p(2v_{inc}) \int_{-\infty}^{+\infty} \left| \iint_{\partial_m} \chi^{(2)}(t) (E_{ex}(t) \cdot \hat{n})^2 \cdot (E_p \cdot \hat{n})^* dS \right|^2 dt$, with ∂_m and $\hat{n}$ representing the metallic surfaces and their normal vector, respectively. In accordance with SHG's coherent nature (unlike ASPL), phase information of E_{ex} and E_p must also be considered in the γ_p^{SHG} integral. Since $|E_{ex}(t)|^2 \propto I_{inc}(t)$, Eq. (8) implies that $I_{SHG} \propto |I_{inc}(t)|^2$, giving the SHG process the power-law of 2. When the incident field is intense enough to affect $\chi^{(2)}$ through perturbing the electron distribution, SHG power-law could become larger than 2 as well. This scenario is compatible with the experimental results in Figure 5.3(b) and is reflected in the time-dependency of $\chi^{(2)}$ in the γ_p^{SHG} formula.

In our experiments, the angled incident beam only breaks the symmetry in the x direction (Figure 5.6(e)). Hence, Eq. (8) indicates that SHG should be ideally x-polarized ($pol_{em} = 0$) regardless of the incident polarization (section D.5). Contradiction of this theoretical result to the experimental observations in Figure 5.6(f) evidences the existence of random structural imperfections that by breaking the geometrical symmetry, prevent the destructive interference between the microscopic SHG sources. These imperfections might cause some bulk contribution to the SHG as well.

5.3. Summary and Outlook

In summary, this work comprehensively analyzed the mechanisms and properties of ASPL and SHG emissions from plasmonic structures under NIR illumination. Our study was based on multiresonant NPCs offering spatially overlapped modes across the whole Vis-NIR spectral range as well as independent control over the plasmonic modes active at excitation and emission wavelengths. In specific, we studied the effects of the incident laser power, wavelength, and polarization on the intensity, spectral shape, and polarization of the NPCs' non-linear emission. To analyze the experimental results, we modeled the plasmonic-enhanced PL and SHG emissions in the time domain through a unique combination of the coupled-mode theory, quantum optics, and statistical mechanics. The PL model generally includes both the IBR and ERS pictures and considers the time-evolution of the hot carriers due to electron-photon, electron-electron, and electron-phonon interactions. The models also consider the momentum conservation in electronic transitions and can explicitly express how different plasmonic modes contribute to enhancing the transition rates at the excitation and emission wavelengths.

We found that only an IBR-dominant picture can explain the power-laws and spectral shapes of the ASPL and their correlation with SHG's power-laws at different incident power levels. The modeling further suggested that contribution level of the non-thermalized carriers to the ASPL emission is the factor that determines the emission time, spectral shape, and power-laws. For a certain system, the non-thermalized carriers' contribution is determined by the excitation conditions (pulse width, wavelength, polarization, power, etc.) and generally, the system could fall into weak, moderate, or strong excitation regimes with distinct emission time, spectral shape and power-laws. Interestingly, we observed that in the moderate and strong excitation regimes, second-order susceptibility could itself become power-dependent, leading to larger than 2 SHG power-laws.

We observed a strong correlation between the excitation and emission polarizations for both ASPL and SHG, revealing that rather than radiative electronic transitions, non-linear emission photons stem from the decay of the plasmonic modes providing the Purcell enhancement at the emission wavelengths. Measuring the non-linear emission from different samples showed that the Purcell effect of these plasmonic modes also primarily determines the resonance features in the ASPL lineshape. Nevertheless, by controlling the energy, momentum, and spatial distributions of the hot

carriers, excitation conditions such as wavelength and polarization determine how much energy couples into each plasmonic mode for emission. Hence, ASPL lineshape is impacted by the excitation conditions as well. Our polarization measurements further hinted that microscopic structural imperfections could influence the ASPL emission properties by trapping or scattering the hot carriers and affect the SHG emission properties by breaking the centrosymmetry. By casting light upon the fundamentals of ASPL and SHG emission from plasmonic structures, this work paves the way in designing more efficient non-linear plasmonic devices for sensing and spectroscopy applications.

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Appendix D

D.1. Experimental methods

Absorption. Cary 5000 spectrophotometer was used to measure the diffuse and specular reflectance (R) spectra of the samples using a monochromator and integrating sphere setup. As the samples' silver ground plane and the silicon substrate made the transmission zero ($T=0$), we could obtain the absorption (A) spectra from $A=1-R$.

Nonlinear measurement setup (Figure D1(b)). Laser pulses are generated using a wavelength-tunable Ti: Sapphire laser module (Chameleon Ultra II) with $f_{inc} = 80 \text{ MHz}$ repetition rate and $\Delta t_{inc} = 140 \text{ fs}$ full width at half maximum. The light exiting the laser module has $\sim 1 \text{ W}$ power but an acousto-optic modulator attenuates the laser pulses to control the incident power. Polarization of the pulses is also controlled by a half-wave plate. After passing through the beam-shaping lenses, the laser pulse is about 1 mm over the sample. The nonlinear emission is collected in the normal direction by a $NA=0.1$ collimating lens. The collimated beam then goes to a nitrogen-cooled CCD spectrometer (Horiba iHR550) through a short-pass filter with 490-900 nm passband. In some experiments, an analyzer on the output path is used to select a specific emission polarization.

D.2. Energy distribution of the hot carriers

Perturbation of the electron distribution (occupation probability) distribution due to a pulsed excitation can be approximated to the first order as follows^{356, 357}:

$$G(\epsilon, t) = \frac{MI_{inc}(t)}{\sqrt{\epsilon}} \left\{ \sqrt{\epsilon - \hbar\nu_{inc}} f(\epsilon - \hbar\nu_{inc}, T_0) [1 - f(\epsilon, T_0)] - \sqrt{\epsilon + \hbar\nu_{inc}} f(\epsilon, T_0) [1 - f(\epsilon + \hbar\nu_{inc}, T_0)] \right\}, \quad (D1)$$

where $I_{inc}(t)$ is the incident power flux and the constant M denotes the excitation strength, including the effects of plasmonic field confinement and all the excitation conditions (angle, polarization, etc.) except the incident power. The term $\sqrt{\epsilon}$ in the denominator is added to convert the number of electrons to occupation probability. The laser pulses in our experiments have the normalized

intensity of $I_{inc}(t) = \frac{0.88P_{inc}}{f_{inc}\Delta t_{inc}} \left[\text{sech} \left(\frac{1.76t}{\Delta t_{inc}} \right) \right]^2$. A common perturbative approach is to divide the total electron distribution as $\rho(\epsilon, t) = \rho_t(\epsilon, t) + \rho_{nt}(\epsilon, t)$, where the thermalized component ρ_t has a Fermi-Dirac distribution with the electronic temperature $T_e(t) \geq T_0$ and the non-thermalized component ρ_{nt} has a non-Fermi distribution³⁵⁸. In the equilibrium situation before the excitation ($t = -\infty$), $T_e = T_0$ and $\rho_{nt} = 0$. The excitation process (Eq. (D1)) initially generates non-thermalized carriers ($G = \left. \frac{d\rho_{nt}}{dt} \right|_{gen}$) but as soon as the hot carriers are generated, electron-electron (e-e) collisions start to transfer the energy from the non-thermalized population to the thermalized population, leading to a rise in T_e . Fermi-liquid theory gives the lifetime of a non-thermalized hot electron due to e-e collisions as $\tau_{e-e}(\epsilon) = \tau_0/(\epsilon - E_F)^2$, where we chose $\tau_0 = 7.2 \text{ fs}$ to acquire the silver thermalization time of 350 fs ³⁵⁶. Eventually, due to electron-phonon (e-ph) collisions, the hot carriers lose their energy to the lattice and both the non-thermalized and thermalized electron populations decay to their equilibrium conditions. Lifetime of this decay is assumed similar ($\tau_{e-ph} = 850 \text{ ps}$ in silver) for both the thermalized and non-thermalized electrons^{356, 358}. Following the above discussion, we can write the following two master equations to describe the time evolution of ρ_{nt} and ρ_t above the Fermi level:

$$\begin{aligned} \frac{d\rho_{nt}(\epsilon, t)}{dt} &= \left. \frac{d\rho_{nt}(\epsilon, t)}{dt} \right|_{gen} + \left. \frac{d\rho_{nt}(\epsilon, t)}{dt} \right|_{e-e} + \left. \frac{d\rho_{nt}(\epsilon, t)}{dt} \right|_{e-ph} \\ &= G(\epsilon, t) - \frac{\rho_{nt}(\epsilon, t)}{\tau_{ee}(\epsilon)} - \frac{\rho_{nt}(\epsilon, t)}{\tau_{e-ph}}, \end{aligned} \quad (D2)$$

$$\frac{dE_t(t)}{dt} = - \left. \frac{dE_{nt}(t)}{dt} \right|_{e-e} - \frac{E_t(t) - E_0}{\tau_{e-ph}}, \quad (D3)$$

where $E_{nt}(t) = \frac{\sqrt{2}}{\pi^2 \hbar^3} \left(\frac{m}{|q|} \right)^{3/2} \int_{E_F}^{\infty} \rho_{nt}(\epsilon, t) \epsilon^{3/2} d\epsilon$ and $E_t(t) = \frac{\sqrt{2}}{\pi^2 \hbar^3} \left(\frac{m}{|q|} \right)^{3/2} \int_{E_F}^{\infty} \rho_t(\epsilon, t) \epsilon^{3/2} d\epsilon$ are the energy (in eV) stored in the non-thermalized and thermalized hot electrons (above the Fermi level) at time t , respectively. Here, $\hbar$ is the reduced Planck's constant (in eV.s), $q = -1.602 \times 10^{-19} \text{ C}$ is the electron charge, and $m = 9.109 \times 10^{-31} \text{ kg}$ denotes the free electron mass. $E_0 = E_t(0)$ represents the energy stored in the native (pre-excitation) electrons at $T_0 =$

300 K. Considering that $\rho_t(\epsilon, t) = f(\epsilon, T_e(t)) = 1/\left[\exp\left(\frac{\epsilon - E_F}{K_B T_e(t)}\right) + 1\right]$, knowing $E_t(t)$ allows us to find $T_e(t)$ and $\rho_t(\epsilon, t)$ as well ($E_F = 5.49 \text{ eV}$ is the silver Fermi level and K_B is the Boltzmann constant). Eqs. (D2) and (D3) consider that electron-electron interactions only redistribute the energy between the hot electrons but do not affect their total stored energy. We approximate a symmetric distribution for electrons and holes to conserve the total number of electrons. For certain M , λ_{inc} , and P_{inc} , and considering $\rho_{nt} = 0$ and $T_e = T_0 = 300 \text{ K}$ as the initial conditions, the master equations allow us to calculate the electron distribution ($\rho = \rho_t + \rho_{nt}$) at different times before, during, and after the pulsed excitation.

D.3. Photoluminescence model

By perturbing the intrinsic Hamiltonian inside the metal ($H_0 \rightarrow H_0 + H_{int}$), electromagnetic fields can transition the electrons across the different electronic states inside the metal. In semiclassical transitions, H_{int} can only come from the incident field and the plasmonic modes excited at the fundamental wavelength (λ_{inc}). However, treating the photoluminescence (PL) needs a fully quantum mechanical analysis where all the optical modes, excited or unexcited, can contribute to H_{int} . In this picture, the optical modes cannot be entirely depleted and even at the ground level $|0\rangle$, an optical mode with the resonance frequency of ω holds the zero-point energy of $\hbar\omega/2$ (vacuum fluctuations).

From Fermi's golden rule, the transition rate between the initial state ϕ_i and the final state ϕ_f ($\epsilon_i > \epsilon_f$) can be described as:

$$\Gamma_{i \rightarrow f} = \frac{2\pi}{\hbar^2} |\langle \phi_f | H_{int} | \phi_i \rangle|^2 D(\omega), \quad (\text{D4})$$

where $D(\omega)$ is the density of the photonic states and $\langle \phi_f | H_{int} | \phi_i \rangle = \iiint_{V_m} \phi_f^* H_{int} \phi_i d^3r$ with V_m being the metal volume. Since in our work, both the excitation and emission photon energies are far below the d band and Fermi level separation in silver ($\sim 4 \text{ eV}$), the interband transitions are unlikely and we only consider the intra-sp-band transitions. As the sp band electrons in silver are nearly free, we can approximately write $\phi_i = e^{ik_i \cdot r}$ and $\phi_f = e^{ik_f \cdot r}$. Using the Coulomb gauge in Maxwell's equations, the interaction Hamiltonian H_{int} can be described as:

$$H_{int} = -\frac{q}{m}A \cdot p + \frac{q^2 A^2}{2m}, \quad (D5)$$

where $p = -i\hbar\nabla$ is the momentum operator and A is the vector potential. In the Coulomb gauge, the vector potential A and the electric field E of an optical mode are related as $E = -i\omega A$. For simplicity, we only consider the incident laser and a single plasmonic mode with the following electric fields, respectively:

$$E_{inc} = E_{inc}^0 e^{-ik_{inc} \cdot r}, \quad (D6a)$$

$$E_p = E_p^0 e^{-ik_{px}x} e^{-ik_{py}y} e^{-\alpha_{pz}z}, \quad (D6b)$$

where E_{inc}^0 and E_p^0 are constants, k_{inc} is the incident wavevector, k_{px} and k_{py} are propagation constants of the plasmonic mode parallel to the metal surface, and α_{pz} is the plasmonic mode's spatial decay constant normal to the metal surface. In Eq. (D6), we have considered the positive-frequency components of the fields which correspond to the creation operators (in the second quantization analysis) and are important for photoluminescence. In what follows, we calculate the PL emission rate due to each of the terms involved in Eq. (D5).

D.3.1. Intraband recombination (IBR) process

In the IBR process (Figure 5.1(c) in the main text), photoluminescence of a photon with energy $h\nu$ occurs via, e.g., recombination of an electron in the state ϵ with the hole in the state $\epsilon - h\nu$. Plasmonic modes both enhance the emission by Purcell effect and provide the momentum required for the electronic transition. The emission at frequency ν can continue as long as electron and hole pairs with proper energy difference are available, even after the excitation pulse has vanished. In the IBR model, the initial and final states must satisfy the following energy selection rule:

$$\epsilon_i - \epsilon_f = \hbar(\omega_i - \omega_f) = \hbar\omega = \frac{\hbar^2 k_i^2}{2m} - \frac{\hbar^2 k_f^2}{2m} = h\nu. \quad (D7)$$

Considering the above description, IBR process corresponds to the first term $(-\frac{q}{m}A \cdot p)$ in Eq. (D5). Inserting $H_{int} = -\frac{q}{m}A \cdot p$ into Eq. (D4) gives:

$$\Gamma_{i \rightarrow f} \propto \left| \iiint_{V_m} e^{-i\Delta k \cdot r} E \cdot k_i d^3r \right|^2 D(\omega), \quad (D8)$$

where $\Delta k = k_f - k_i$. Since $|k_{inc}| = \omega_{inc}/c \ll |\Delta k|$ (c is the light speed), putting $E = E_{inc}$ into Eq. (D8) and expanding E_{inc} from Eq. (D6a) gives $\Gamma_{i \rightarrow f} = 0$. In other words, the incident laser field cannot directly induce any (stimulated) PL events as its photons cannot bridge the momentum mismatch between the initial and final states. By putting $E = E_p$ into Eq. (D8) and expanding E_p from Eq. (D6b) we get:

$$\Gamma_{i \rightarrow f} \propto \left| \frac{E_p^0 \cdot k_i}{\alpha_{pz} + i\Delta k_z} \right|^2 \delta(\Delta k_x + k_{px}) \delta(\Delta k_y + k_{py}) D(\omega). \quad (D9)$$

The delta functions are indicative of strict momentum selection rules in x and y directions while the momentum selection rule in z direction is now relaxed. Hence, in contrast to the incident field, the plasmonic modes can provide the momentum required for the transition through their surface confinement and the transition rate can be non-zero in this case.

Typically, $k_{px}, k_{py} \ll |\Delta k|$, and thus we can approximate that $\Delta k_x \approx \Delta k_y \approx 0$. Combining this approximation with Eq. (D7) turns the energy selection rule into:

$$k_{fz} = \pm \sqrt{k_{iz}^2 - 2m\omega/\hbar}. \quad (D10)$$

Another requirement for occurrence of the electronic transition is occupancy of the initial state and emptiness of the final state, which have the probabilities of $\rho(\epsilon_i, t)$ and $1 - \rho(\epsilon_f, t)$, respectively.

By approximating $|E_p^0 \cdot k_i|^2 \sim |E_p^0|^2 |k_i|^2$, including the above-explained considerations into Eq. (D9), and integrating the rate of transition between each two states in the k space, we can calculate the total number of transitions (for a single-pulse excitation) with the energy $\hbar\omega$ as:

$$\begin{aligned} & \Gamma_{\text{tot}} \\ & \propto |E_p^0|^2 D(\omega) \int_{-\infty}^{+\infty} \iiint \frac{|k|^2 \rho\left(\frac{\hbar^2 k^2}{2m}, t\right) \left[1 - \rho\left(\frac{\hbar^2 k^2}{2m} - \hbar\omega, t\right)\right]}{\left|k_z \pm \sqrt{k_z^2 - \frac{2m\omega}{\hbar}}\right|^2 + \alpha_{pz}^2} dk_x dk_y dk_z dt, \end{aligned} \quad (D11)$$

where the results of integrations with + and – signs in the denominator should be added. By converting the Cartesian coordinates to spherical coordinates and considering that $\epsilon = \hbar^2 k^2 / (2m)$, we can rewrite Eq. (D11)'s integration over k space as:

$$\begin{aligned}
& \iiint \frac{|k|^2 \rho\left(\frac{\hbar^2 k^2}{2m}, t\right) \left[1 - \rho\left(\frac{\hbar^2 k^2}{2m} - \hbar\omega, t\right)\right]}{\left|k_z \pm \sqrt{k_z^2 - \frac{2m\omega}{\hbar}}\right|^2 + \alpha_{pz}^2} dk_x dk_y dk_z \\
& \propto \int_{\hbar\omega}^{+\infty} \int_0^{\theta_c(k_r)} \frac{|k_r|^2 \rho(\epsilon, t) [1 - \rho(\epsilon - \hbar\omega, t)]}{\left|k_r \cos \theta \pm \sqrt{k_r^2 \cos^2 \theta - \left(\frac{2m\omega}{\hbar}\right)}\right|^2 + \alpha_{pz}^2} k_r^2 \sin \theta d\theta dk_r \\
& \propto \int_{\hbar\omega}^{+\infty} \int_0^{\theta_c(\epsilon)} \frac{|k_r|^2 \rho(\epsilon, t) [1 - \rho(\epsilon - \hbar\omega, t)]}{\left|\frac{\sqrt{2m\epsilon}}{\hbar} \cos \theta \pm \sqrt{\frac{2m\epsilon}{\hbar^2} \cos^2 \theta - \left(\frac{2m\omega}{\hbar}\right)}\right|^2 + \alpha_{pz}^2} \sqrt{\epsilon} \sin \theta d\theta d\epsilon \\
& \propto \int_{\hbar\omega}^{+\infty} \int_0^{\theta_c(\epsilon)} \frac{\epsilon \rho(\epsilon, t) [1 - \rho(\epsilon - \hbar\omega, t)]}{\left|\sqrt{\epsilon} \cos \theta \pm \sqrt{\epsilon \cos^2 \theta - \hbar\omega}\right|^2 + \frac{\hbar^2 \alpha_{pz}^2}{2m}} \sqrt{\epsilon} \sin \theta d\theta d\epsilon \\
& \propto \int_{\hbar\omega}^{+\infty} \int_{u_c(\epsilon)}^1 \frac{\epsilon \rho(\epsilon, t) [1 - \rho(\epsilon - \hbar\omega, t)]}{\left|u\sqrt{\epsilon} \pm \sqrt{\epsilon u^2 - \hbar\omega}\right|^2 + \frac{\hbar^2 \alpha_{pz}^2}{2m}} \sqrt{\epsilon} du d\epsilon,
\end{aligned}$$

where $u = \cos \theta$ and $u_c(\epsilon) = \cos \theta_c(\epsilon) = \sqrt{\hbar\omega/\epsilon}$. The integration limits are set to keep the final state energy $(\epsilon - \hbar\omega)$ and the term under the radical in the denominator $(\epsilon u^2 - \hbar\omega)$ positive. We assume that $\alpha_{pz} \sim 1 \text{ nm}^{-1}$. By a simple numerical analysis, we can then find that

$$\int_{u_c(\epsilon)}^1 \frac{1}{\left|u\sqrt{\epsilon} - \sqrt{\epsilon u^2 - \hbar\omega}\right|^2 + \frac{\hbar^2 \alpha_{pz}^2}{2m}} du \gg \int_{u_c(\epsilon)}^1 \frac{1}{\left|u\sqrt{\epsilon} + \sqrt{\epsilon u^2 - \hbar\omega}\right|^2 + \frac{\hbar^2 \alpha_{pz}^2}{2m}} du \quad \text{and}$$

$$\int_{u_c(\epsilon)}^1 \frac{1}{\left|u\sqrt{\epsilon} - \sqrt{\epsilon u^2 - \hbar\omega}\right|^2 + \frac{\hbar^2 \alpha_{pz}^2}{2m}} du = \xi_{IBR}(\epsilon, \omega) = a e^{\frac{-\hbar\omega}{bKT}}, \text{ where } a \text{ and } b \text{ are functions of the electron}$$

energy ϵ . However, for the energy levels about 6 eV, which are important for the ASPL process in this work, we approximately have $a \sim 32.2$ and $b \sim 11.6$. Then, we can write:

$$\Gamma_{\text{tot}} \propto |E_p^0|^2 D(\omega) \int_{-\infty}^{+\infty} \int_{\hbar\omega}^{+\infty} \xi_{IBR}(\epsilon, \omega) \rho(\epsilon, t) [1 - \rho(\epsilon - \hbar\omega, t)] \epsilon^{3/2} d\epsilon dt, \text{ where } \xi_{IBR}(\epsilon, \omega) = a e^{\frac{-\hbar\omega}{bKT}} \text{ is the momentum function.}$$

In the main text, we show that the electronic transitions excite the plasmonic modes, rather than directly generating the PL photons. Decay of the excited surface plasmons then generates the far-field PL photons with the quantum efficiency η_p . Hence, to calculate the number of PL photons, we should add the term η_p to Γ_{tot} . Furthermore, we add the term $\hbar\omega$ to convert the number of photons emitted to the energy emitted. In addition, we add the pulsed laser repetition rate f_{inc} to convert the spectral energy emitted per pulse to the spectral power density $S(\omega)$. Considering the above explanations, we can write:

$$S_{IBR}(\omega) \propto f_{\text{inc}} |E_p^0|^2 D(\omega) \eta_p \hbar\omega \int_{-\infty}^{+\infty} \int_{\hbar\omega}^{+\infty} \xi_{IBR}(\epsilon, \omega) \rho(\epsilon, t) [1 - \rho(\epsilon - \hbar\omega, t)] \epsilon^{3/2} d\epsilon dt.$$

The product $|E_p^0|^2 D(\omega)$ in fact characterizes the rate of energy transfer from the electronic transitions to the plasmonic mode. Purcell effect of the p^{th} plasmonic mode on the emission rate is also included in $|E_p^0|^2 D(\omega)$. In the next step, we include the effect of all the plasmonic modes into the equation by replacing $|E_p^0|^2 D(\omega) \eta_p$ with $\sum_p |E_p^0|^2 D(\omega) \eta_p$. Density of photonic states in free space is $\left(\frac{4\nu^2}{c^3}\right)$. If we define the effective emission enhancement factor of the plasmonic system by $L_{\text{eff}}(\nu)$, we can write $\sum_p |E_p^0|^2 D(\omega) \eta_p \propto \left(\frac{4\nu^2}{c^3}\right) L_{\text{eff}}(\nu)$. We also rewrite the formula in terms of the frequency $\nu = \omega/2\pi$. Then, we would finally have:

$$S_{IBR}(\nu) \propto f_{\text{inc}} \left(\frac{4h\nu^3}{c^3}\right) L_{\text{eff}}(\nu) \int_{-\infty}^{+\infty} \int_{h\nu}^{+\infty} \xi_{IBR}(\epsilon, \nu) \rho(\epsilon, t) [1 - \rho(\epsilon - h\nu, t)] \epsilon^{3/2} d\epsilon dt. \quad (\text{D12})$$

D.3.2. Electronic Raman Scattering (ERS) process

In the ERS process (Figure 5.1(d) in the main text), an incident photon first excites the electron in the state ϵ to the virtual state $\epsilon + h\nu_{\text{inc}}$ and then, emission of a PL photon with energy $h\nu$ occurs via recombination of the electron in the virtual state with the hole in the state $\epsilon + h\nu_{\text{inc}} - h\nu$. Just as IBR, plasmonic modes both provide the momentum required for the ERS transitions and enhance their rate by Purcell effect. The initial and final states in an ERS process must satisfy the following energy selection rule:

$$\epsilon_i - \epsilon_f = \frac{\hbar^2 k_i^2}{2m} - \frac{\hbar^2 k_f^2}{2m} = h(\nu - \nu_{inc}). \quad (D13)$$

Considering the above description, ERS can occur through the second term ($q^2 A^2/2m$) in Eq. (D5). Three terms exist in A^2 , which are proportional to E_{inc}^2 , E_p^2 , and $E_{inc} \cdot E_p$, respectively. E_{inc}^2 term cannot bridge the momentum mismatch between the initial and final states and thus gives $\Gamma_{i \rightarrow f} = 0$. E_p^2 also leads to a transition rate less significant than that in Eq. (D9) and can be neglected. However, $E_{inc} \cdot E_p$ term could lead to non-negligible transition rates and in fact corresponds to the ERS process as it simultaneously involves the plasmonic modes and the incident field. Inserting $H_{int} \propto E_{inc} \cdot E_p$ into Eq. (D4) gives:

$$\Gamma_{i \rightarrow f} \propto \left| \iiint_V e^{-i\Delta k \cdot r} E_{inc} \cdot E_p d^3 r \right|^2 D(\omega). \quad (D14)$$

By following Eq. (D12)'s derivation process, we can then obtain the ERS-based PL formula:

$$S_{ERS}(\nu) \propto f_{inc} \left(\frac{I_{inc}(t)}{\nu_{inc}} \right) \left(\frac{4h\nu^3}{c^3} \right) L_{eff}(\nu) \int_{-\infty}^{+\infty} \int_{h\nu}^{+\infty} \xi_{ERS}(\epsilon, \nu) \rho(\epsilon, t) [1 - \rho(\epsilon + h\nu_{inc} - h\nu, t)] \sqrt{\epsilon} d\epsilon dt, \quad (D15)$$

where $I_{inc}(t)$ is the incident intensity and $1/\nu_{inc}$ inclusion is to make Eqs. (D12) and (D15) units compatible and considering that $E_{inc} = -i\omega_{inc} A_{inc}$. Also, $\xi_{ERS}(\epsilon, \nu) = a' e^{\frac{-h(\nu - \nu_{inc})}{b'KT}}$ is the momentum function with $a'(\epsilon) \sim 23.4$ and $b'(\epsilon) \sim 23$ for $\epsilon \sim 6$ eV. We see that $\xi_{ERS} > \xi_{IBR}$, reflecting the fact that the momentum mismatch between the initial and final states is smaller in ERS compared to IBR. Also, we see that the ERS emission rate is proportional to the incident intensity, which is consistent with previous theoretical ERS formulations^{336, 343}. This term causes the ERS emission to decay as soon as the laser pulse vanishes.

D.3.3. Photoluminescence rate

Now, by combining Eqs. (D4) and (D5), and noticing the (D15) derivation from (D14) and (D12) derivation from (D8), we would get the following formula for the PL rate:

$$S(\nu) \propto f_{inc} \left(\frac{4h\nu^3}{c^3} \right) L_{eff}(\nu) [\beta \psi_{IBR}(\nu) + (1 - \beta) \psi_{ERS}(\nu)], \quad (D16)$$

where $0 \leq \beta \leq 1$ is a ratio that determines the dominance level of the IBR and ERS processes in the PL emission. Also, $\psi_{IBR}(\nu)$ and $\psi_{ERS}(\nu)$ respectively represent the number of electron-hole pairs available for photoluminescence at frequency ν from the IBR and ERS processes:

$$\psi_{IBR}(\nu) = \int_{-\infty}^{+\infty} \int_{h\nu}^{+\infty} \xi_{IBR}(\epsilon, \nu) \rho(\epsilon, t) [1 - \rho(\epsilon - h\nu, t)] \epsilon^{3/2} d\epsilon dt, \quad (D17)$$

$$\psi_{ERS}(\nu) = \int_{-\infty}^{+\infty} \left(\frac{I_{inc}(t)}{\nu_{inc}} \right) \int_{h\nu}^{+\infty} \xi_{ERS}(\epsilon, \nu) \rho(\epsilon, t) [1 - \rho(\epsilon + h\nu_{inc} - h\nu, t)] \sqrt{\epsilon} d\epsilon dt. \quad (D18)$$

The reason for adding the factor β to the PL equation (Eq. (D16)) is that the ratio between $\frac{I_{inc}(t)}{\nu_{inc}}$ in ψ_{ERS} integral and the extra ϵ in ψ_{IBR} integral is an experimental parameter that needs to be fitted.

D.4. Emission analysis

D.4.1. Purcell effect and radiative decay enhancement

The analyses in this subsection are based on the black-box coupled-mode theory³⁵⁴. Consider that a dipole emitter P at position r and oscillating at the angular frequency ω lies inside or close to an open and lossy electromagnetic resonator antenna (e.g. a plasmonic system) with orthogonal modes. We can write the following coupled-mode equation for the p^{th} mode in the steady state:

$$j\omega\alpha_p = j\tilde{\omega}_p\alpha_p - \frac{j\omega}{4} P \cdot (E_p)^*, \quad (D19)$$

where $\tilde{\omega}_p$ and α_p are the complex resonance frequency and amplitude of the mode, respectively. $\tilde{\omega}_p$ can be decomposed as $\tilde{\omega}_p = \omega_p + \Gamma_p$, where ω_p is the mode oscillation frequency and $\Gamma_p = \Gamma_p^r + \Gamma_p^{nr}$ is the mode decay rate. Also, E_p is normalized such that $|\alpha_p|^2$ represents the energy stored in the mode.

We assume that the total system emission rate equals the summation of the emission rates from individual modes. Then, after calculating α_p from Eq. (D28), we can calculate the power drawn from the dipole in the steady state as:

$$W = -\frac{\omega}{2} \text{Im} \left[\sum_p \alpha_p E_p \cdot P^* \right] = 2 \sum_p \Gamma_p |\alpha_p|^2 = \frac{\omega^2 |P|^2}{8\pi} \sum_p \sigma_p(\omega) |E_p \cdot \hat{l}|^2, \quad (D20)$$

where $\sigma_p(\omega) = \frac{\Gamma_p/\pi}{(\omega-\omega_p)^2 + \Gamma_p^2}$ is the p^{th} mode's spectral shape and $\hat{l}$ denotes the dipole direction.

The dipole emitted power in free space is $W_{0r} = |P|^2 \omega^4 / (12\pi\epsilon_0 c^3)$. Hence, the Purcell factor would be:

$$\mathcal{P} = \frac{W}{W_{r0}} = \sum_p \mathcal{P}_p = \sum_p \frac{3\epsilon_0 c^3}{2\omega^2} \sigma_p(\omega) |E_p \cdot \hat{l}|^2, \quad (\text{D21})$$

where $\mathcal{P}_p$ represents the Purcell factor of the p^{th} mode. As the resonator is generally lossy, the total emission rate of the system is not the same as the power drawn from the dipole, and the quantum efficiency of the resonator modes should also be taken into account to calculate the emission rate. The emission enhancement of the dipole-resonator coupled system compared to the free-space dipole is:

$$F_l(r, \omega) = \frac{W_r}{W_{r0}} = \frac{\gamma_r}{\gamma_r^0} = \frac{2}{W_0} \sum_p \Gamma_p^r |\alpha_p|^2 = \sum_p \mathcal{P}_p \eta_p, \quad (\text{D22})$$

where W_r and $W_{r0} = W_0$ are the emitted powers of the dipole-resonator coupled system and the free-space dipole, respectively. γ_r and $\gamma_r^0 = \omega^2 / \pi^2 c^3$ are the radiative decay rates of the dipole-resonator coupled system and the free-space dipole, respectively. Also, $\eta_p = \Gamma_p^r / \Gamma_p$ is the quantum efficiency of the p^{th} resonator mode. From a quantum mechanical perspective, Eq. (D22) shows how presence of the resonator modifies the density of photonic states available for the dipole emission.

Eq. (D22) is valid whether the dipole is ideal (no non-radiative decay) or not. We can confirm this by a simple analysis based on the energy conservation principle. Consider that the dipole has a non-zero non-radiative decay rate γ_{nr}^0 , stemming from processes such as vibrational relaxation, etc. Typically, γ_{nr}^0 is an intrinsic property of the emitter which is barely affected by the resonator. In this regard, the dipole non-radiative decay rate is the same for the coupled and free-space systems. If the emitter gets excited with the rate G in the steady state, we can write:

$$\frac{dU}{dt} = G - \mathcal{P} \gamma_r^0 U - \gamma_{nr}^0 U = G - \sum_p \mathcal{P}_p \gamma_r^0 U - \gamma_{nr}^0 U, \quad (\text{D23})$$

where U is the energy stored in the dipole. Also, we can write the following equation for the energy stored in the resonator modes:

$$\frac{d|\alpha_p|^2}{dt} = \mathcal{P}_p \gamma_r^0 U - 2\Gamma_p |\alpha_p|^2. \quad (\text{D24})$$

Since we are in steady state, $dU/dt = d|\alpha_p|^2/dt = 0$. Accordingly, by combining Eqs. (D28) and (D29) we would get:

$$F_l(r, \omega) = \frac{\gamma_r}{\gamma_r^0} = \frac{W_r/U}{\gamma_r^0} = \frac{\sum_p 2\Gamma_p^r |\alpha_p|^2}{\gamma_r^0 U} = \sum_p \mathcal{P}_p \eta_p, \quad (\text{D25})$$

which is similar to Eq. (D22). In our work, the plasmonic system is an optical resonator antenna and the electron-hole pairs inside the metal approximately behave like non-ideal dipoles. The equations in this subsection are consistent with our finding in the main text that the PL emission is resulted from plasmon decay rather than direct radiative recombination of hot carriers.

$F_l(r, \omega)$ can easily be evaluated from FDTD simulations with dipole source. FDTD simulations show that $F_l(r, \omega)$ highly depends on the frequency ω as well as the dipole's position r and direction l (Figure D6). Please note that in deriving the equations in this section, we assumed for simplicity that the plasmonic modes are orthogonal, such that the total emission of the plasmonic system equals the summation of emission from individual modes. However, the mode orthogonality condition is neither a requirement nor considered in the FDTD simulations.

D.4.2. The emission enhancement factor L_{eff}

For the PL emission, the electron-hole pairs are distributed all over the metal. However, due to the incoherent nature of the PL process, we can assume that the emission due to the electron-hole pairs at each position are independent of the emission from the electron-hole pairs in other places. In this regard, the total emission rate would be a summation of the emission rates from different positions and we can write:

$$L_{eff}(\nu) = \sum_{\hat{l}=\hat{x},\hat{y},\hat{z}} \iiint_{V_m} \phi_{eff}^l(r, \nu) F_l(r, \nu) d^3r, \quad (\text{D26})$$

where V_m denotes the metallic parts of the system and ϕ_{eff}^l describes the effective spatial distribution of the $\hat{l}$ -polarized electron-hole pairs (dipole approximation) with the energy $h\nu$ over the course of emission. ϕ_{eff}^l is normalized such that $\sum_{\hat{l}=\hat{x},\hat{y},\hat{z}} \iiint_{metal} \phi_{eff}^l d^3r = 1$. In this regard,

ϕ_{eff}^l in fact acts like a weighting function that determines which dipole positions and directions contribute more to $L_{eff}(\nu)$. $L_{eff}(\nu)$ determines the resonance features in the PL spectrum.

D.4.3. Emission polarization

By combining Eqs. (D12), (D21), (D25), and (D26), we can rewrite the PL emission formula such that the contribution of each plasmonic mode to the PL emission becomes apparent:

$$S_{IBR}(\nu) \propto f_{inc} \sum_p \gamma_p \eta_p, \quad (D27)$$

where $\gamma_p \propto (h\nu)\psi_{IBR}(\nu)\sigma_p(\nu) \sum_{\hat{l}=\hat{x},\hat{y},\hat{z}} \iiint_{V_m} \phi_{eff}^l(r,\nu) |E_p(r) \cdot \hat{l}|^2 d^3r$ with σ_p being the mode lineshape defined in Eq. (D20) and $\psi_{IBR}(\nu) = \int_{-\infty}^{+\infty} \int_{h\nu}^{+\infty} \xi_{IBR}(\epsilon,\nu) \rho(\epsilon,t) [1 - \rho(\epsilon - h\nu,t)] \epsilon^{3/2} d\epsilon dt$. γ_p characterizes the rate of energy transfer from the hot carriers to the p^{th} plasmonic mode at the frequency ν . Due to structural symmetry, each plasmonic mode in NPCs has a degenerate counterpart with perpendicular polarization and according to Eq. (D27), $\phi_{eff}^l(r,\nu)$ decides how much each degenerate mode contributes to the PL emission. Hence, the PL emission polarization highly depends on the directional, spatial, and energy distributions of the hot electron-hole pairs, characterized by $\phi_{eff}^l(r,\nu)$.

D.4.4. Effects of the excitation conditions

$\phi_{eff}^l(r,\nu)$ is a function of the hot carriers' energy, spatial and momentum distributions, all of which highly depend on the excitation conditions. In this regard, the excitation conditions can influence all the PL emission characteristics, including the spectral shape, intensity, and polarization. In the main text, this statement was experimentally demonstrated through measuring the effects of the incident wavelength and polarization on the spectral shape and polarization of the H3 sample's non-linear emission. As an example, polarization measurements revealed that the ASPL emission of the H3 sample is larger for the S-polarized excitation than P-polarized excitation. We show below that this observation could stem from different spatial distributions of the hot carriers for the two incident polarizations.

Figure D8 shows that the two incident polarizations cause comparable levels of absorption, hence $\psi(\nu)|_{S-pol} \approx \psi(\nu)|_{P-pol}$. Also, we found that z-polarized electron-hole pairs have a dominant contribution to the ASPL emission of the H3 sample, which tells that only $l = z$ is important for

both S and P incident polarizations (we only consider ϕ_{eff}^z). However, the electron-hole pairs are differently distributed for the two cases. Initial spatial distribution of the hot carriers, right after the generation, follows the $|E_{ex}|^2$ profile inside the metallic parts, where E_{ex} is the electric field at the excitation wavelength³⁶⁰. Figure 5.6 in the main text shows that the S-polarized excitation leads to a more uniform $|E_{ex}|^2$ profile, which also makes $\phi_{eff}^z(r, \nu)$ more uniform in this case. In NPCs, each plasmonic mode has a degenerate counterpart with similar quantum efficiency η_p and lineshape $\sigma_p(\nu)$ but perpendicular polarization. By assuming that P1 and P2 are the two degenerate plasmonic modes active at the frequency ν , we can approximately write:

$$\frac{S_{IBR}|_{S-pol}}{S_{IBR}|_{P-pol}} \sim \frac{\iiint_{V_m} \phi_{eff}^z|_{S-pol} (|E_{p1} \cdot \hat{z}|^2 + |E_{p2} \cdot \hat{z}|^2) d^3r}{\iiint_{V_m} \phi_{eff}^z|_{P-pol} (|E_{p1} \cdot \hat{z}|^2 + |E_{p2} \cdot \hat{z}|^2) d^3r}$$

Since $|E_{p1} \cdot \hat{z}|^2 + |E_{p2} \cdot \hat{z}|^2$ term gives a symmetric profile across the x and y directions, Cauchy-Schwarz inequality indicates that a more uniform ϕ_{eff}^z must also lead to an equal or larger S_{IBR} . Hence, we can conclude that $S_{IBR}|_{S-pol} \geq S_{IBR}|_{P-pol}$, consistent with the experimental observations in Figure 5.6(a) of the main text.

D.5. Second Harmonic Generation analysis

Although the materials used in our work are centrosymmetric, the centrosymmetry breaks at the material interfaces. As a result, the second order non-linear response is allowed at the metal surfaces where the electron density and plasmonic fields are both high. We assume that the second-order susceptibility, $\chi^{(2)}$, is non-zero only over the metal surfaces (∂_m) and it is zero elsewhere.

We again assume that the plasmonic modes are orthogonal and use the black-box coupled mode theory³⁵⁴ for the SHG analysis. Suppose that the incident laser induces the electric field $E_{ex}(r)$. The incident field creates the second harmonic current sources $j\omega_{SHG}\epsilon_0\chi^{(2)}(E_{ex} \cdot \hat{n})^2\hat{n}$ on the metal surfaces, where $\hat{n}$ is the surface normal. Considering that the SHG sources lie inside the plasmonic system, we can write the following coupled-mode equation for the p^{th} plasmonic mode:

$$j\omega_{SHG}\alpha_p = j\tilde{\omega}_p\alpha_p - \frac{j\epsilon_0\omega_{SHG}}{4} \iint_{\partial_m} \chi^{(2)}(E_{ex} \cdot \hat{n})^2 \cdot (E_p \cdot \hat{n})^* dS, \quad (D28)$$

After calculating α_p from Eq. (D28), we can calculate the emission rate of the p^{th} as:

$$I_{SHG}^p = 2\Gamma_p^r |\alpha_p|^2 = \frac{\pi}{2} |\epsilon_0 v_{inc}|^2 \eta_p \sigma_p(2\omega_{inc}) \left| \iint_{\partial_m} \chi^{(2)}(E_{ex} \cdot \hat{n})^2 \cdot (E_p \cdot \hat{n})^* dS \right|^2. \quad (D29)$$

Eq. (D29) describes the steady state rate of SHG emission for a time-harmonic source. Nevertheless, as SHG is a coherent and almost instantaneous process and the plasmonic response is also fast, we can also approximately use Eq. (D29) for the instantaneous SHG emission rate. In this scenario, $\chi^{(2)}$ and E_{ex} would be a function of time.

To get the average emission rate, we need to integrate the instantaneous emission rate over a single laser period and then, multiply it by f_{inc} . We also consider that the total emission rate equals the summation of emission rates from individual modes. Then, we get:

$$I_{SHG} = \frac{\pi}{2} |\epsilon_0 v_{inc}|^2 f_{inc} \sum_p \gamma_p^{SHG} \eta_p \propto f_{inc} \left(\frac{16v_{inc}^2}{c^3} \right) \sum_p \gamma_p^{SHG} \eta_p, \quad (D30)$$

where $\gamma_p^{SHG} \propto \sigma_p(2\omega_{inc}) \int_{-\infty}^{+\infty} \left| \iint_{\partial_m} \chi^{(2)}(t) (E_{ex}(t) \cdot \hat{n})^2 \cdot (E_p \cdot \hat{n})^* dS \right|^2 dt$.

In our experiments, the excitation direction only breaks the symmetry in the x-direction. Following that, $(E_{ex} \cdot \hat{n})^2$ is a symmetric (even) function in the y direction while it is non-symmetric in the x direction, regardless of the incident polarization (Figure D10). Furthermore, considering the structural symmetry of the NPCs with respect to the x and y axes (in-plane), their x-polarized plasmonic modes have an antisymmetric $E_p \cdot \hat{n}$ profile with respect to the y axis and vice versa (Figure D10). Therefore, γ_p^{SHG} is ideally zero for y-polarized plasmonic modes and SHG should ideally be x-polarized for both S and P incident polarizations.

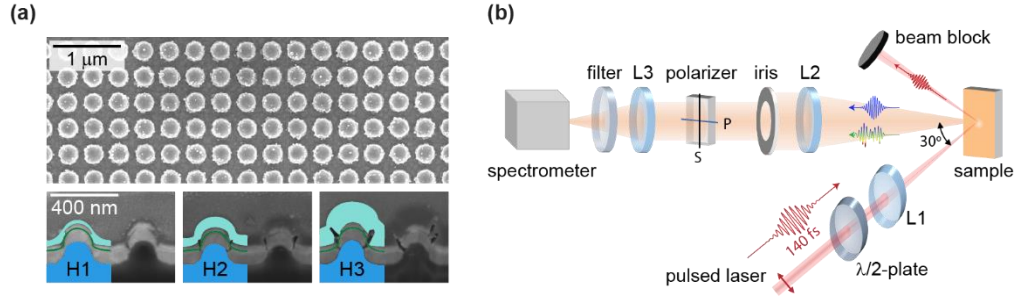


Figure D1. (a) Top-view and cross-sectional view SEM pictures of H1, H2, and H3 samples. The samples are only different in terms their TiO₂ thickness. (b) The experimental setup for the nonlinear optical measurements. L1, L2, and L3 are convex lenses for laser condensation, emission collection, and coupling to the spectrometer, respectively. The optical filter has a ~490-890 nm pass band. The polarizer on the output path only exists when measuring the emission polarization.

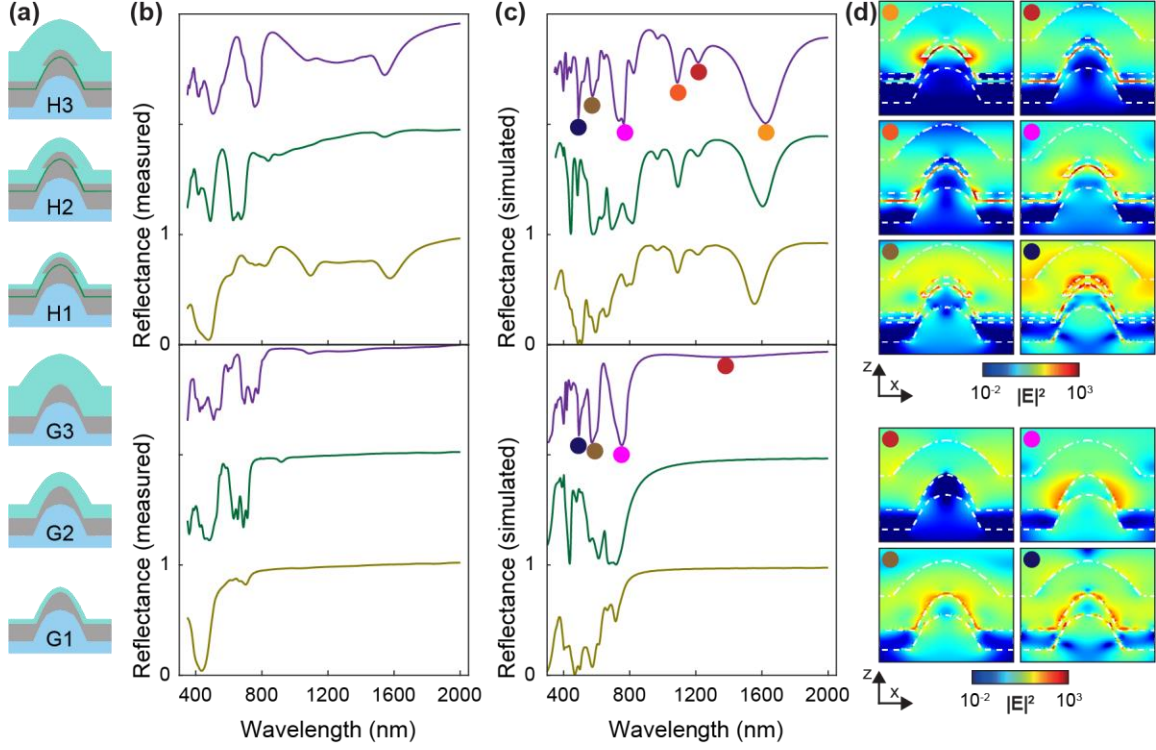


Figure D2. (a) 2D schematics of the nanolaminate plasmonic crystals (NPCs) used in this work. H1-H3 consist of a corrugated Ag-SiO₂-Ag nanolaminate array coated by 25 nm, 60 nm, and 130 nm TiO₂ cladding layers, respectively (Figure 5.1(c)). G1-G3 are similar except not possessing the top SiO₂ and Ag layers. (b, c) Measured (b) and FDTD-simulated (c) reflectance spectra of the samples. Due to having the ground plane layer, transmission is negligible. Hence, $R=1-A$, where R and A denote the reflectance and absorbance, respectively. (d) FDTD-simulated near-field $|E|^2$ profiles corresponding to the resonances marked in part (c).

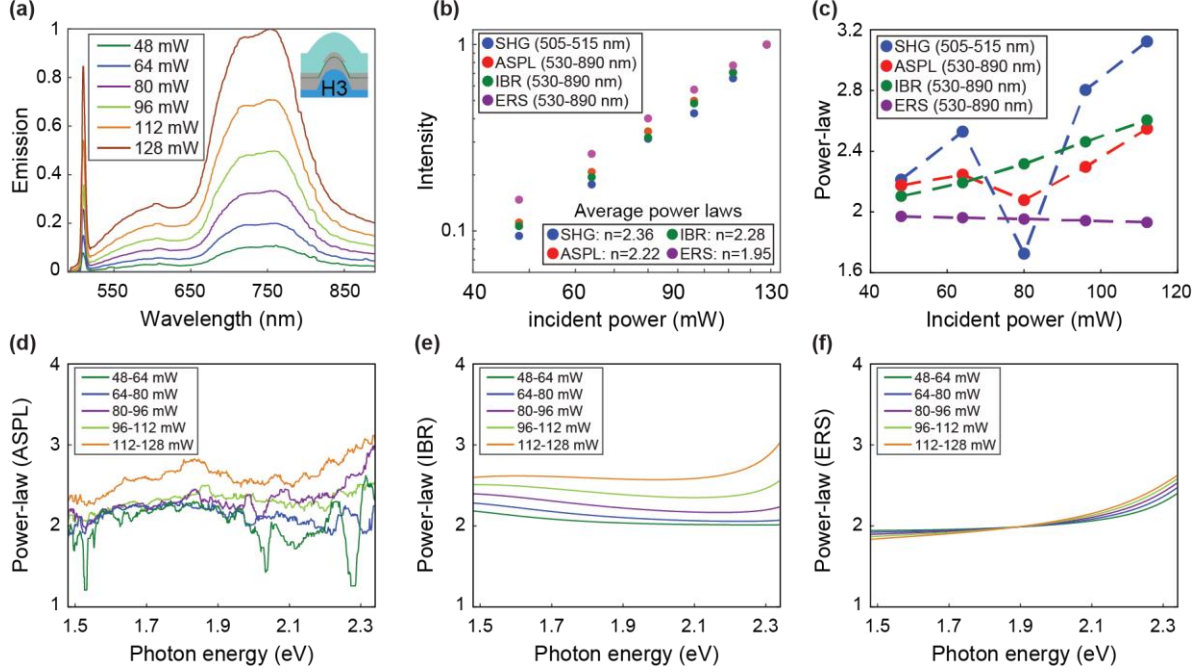


Figure D3. (a) H3 nonlinear emission spectra for fixed incident wavelength (1020 nm) and polarization (P) but different incident powers ranging from 48 mW up to 128 mW. (b) SHG (experimental), ASPL (experimental), IBR (model), and ERS (model) integrated intensities as a function of the incident power. The axes are in logarithmic scale. The power-laws (n) are acquired by exponential fitting ($R^2 > 0.99$). (c) The SHG, ASPL, IBR, and ERS power-laws as a function of the incident power (P_{inc}). ASPL and SHG power-laws generally go up as P_{inc} increases. The anomaly at 80 mW is possibly due to non-linear resonance effect, though further investigation is needed. IBR power-law also goes up with P_{inc} . However, ERS power-law is a decreasing function of P_{inc} . (d-f) ASPL (d), IBR (e), and ERS (f) spectral power laws at different P_{inc} levels. Again, ASPL and IBR power-laws generally go up with P_{inc} . However, ERS power-law below ~ 1.9 eV is a decreasing function of P_{inc} . Also, ERS power-law below ~ 1.9 eV cannot go above 2, unlike ASPL and IBR power-laws.

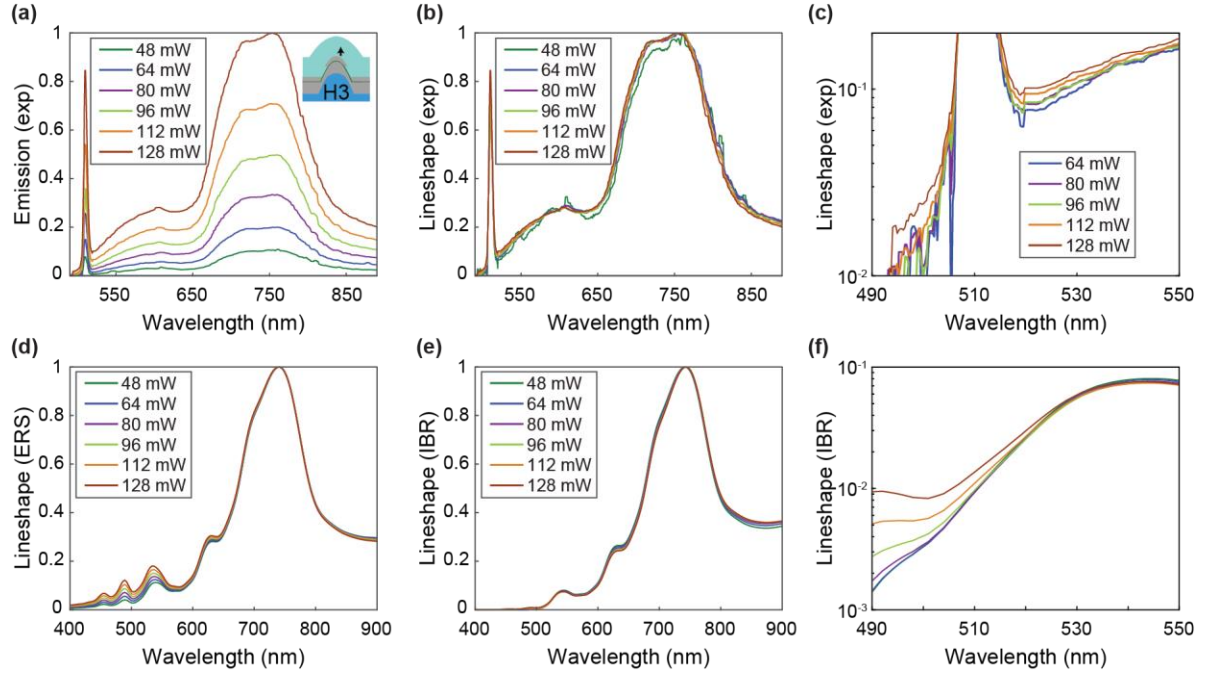


Figure D4. (a) H3 nonlinear emission spectra for fixed incident wavelength (1020 nm) and polarization (P) but different incident powers ranging from 48 mW up to 128 mW. (b) Spectral lineshapes for different incident powers. (c) Magnified lineshapes from part (b). (d-e) Spectral lineshapes extracted from the spectra calculated based on the ERS (d) and IBR (e) models. (f) Magnified lineshapes from part (e).

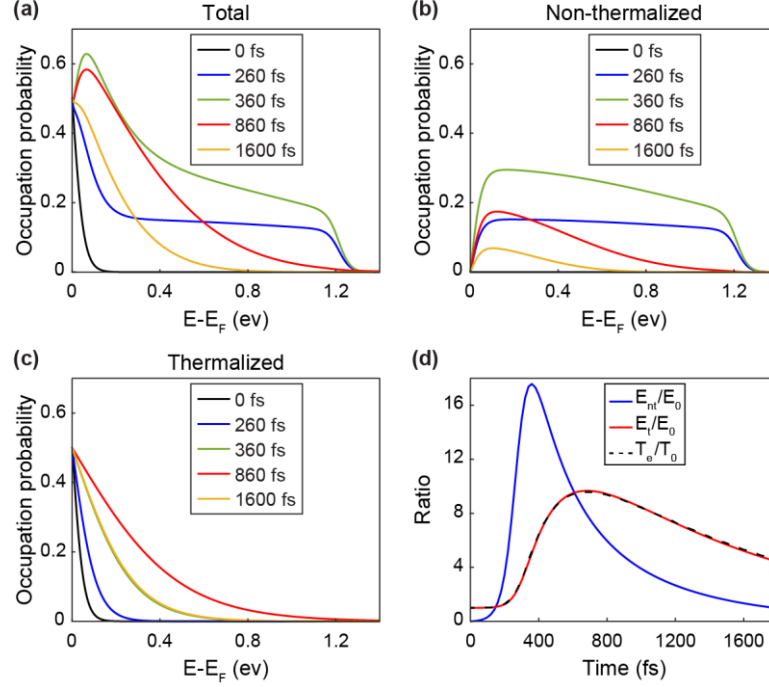


Figure D5. Time evolution of the electron distribution for a system with $M = 0.26$ excited by a laser pulse ($\Delta t_{inc} = 140$ fs, $\lambda_{inc} = 1020$ nm, and $P_{inc} = 128$ mW) that peaks at $t = 260$ fs. (a-c) Total (a), non-thermalized (b), and thermalized (c) electron energy distributions at different times before, during, and after the excitation. (d) Energy stored in the non-thermalized (blue curve) and thermalized (red curve) hot electrons over time. The dashed black curve shows the temperature of the thermalized hot electrons over time. $T_0 = 300$ K and $E_0 = \frac{\sqrt{2}}{\pi^2 \hbar^3} \left(\frac{m}{|q|} \right)^{3/2} \int_{E_F}^{\infty} \frac{1}{\exp\left(\frac{\epsilon - E_F}{k_B T_0}\right) + 1} \epsilon^{3/2} d\epsilon$ represent the temperature and energy of the native (pre-excitation) electron distribution, respectively.

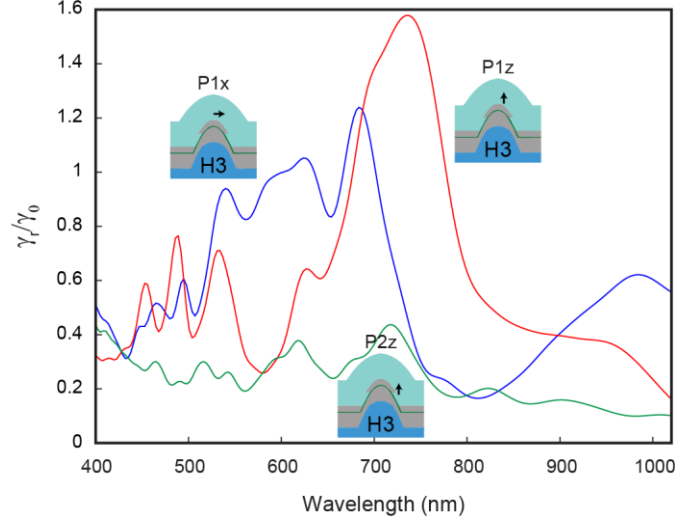


Figure D6. FDTD simulations show that $F_l(r, \lambda) = \gamma_r/\gamma_0$ highly depends on the wavelength λ as well as the dipole's position r and direction l . P1z curve decently mimics the resonances in the experimental lineshapes of Figure 5.3(d) in the main text.

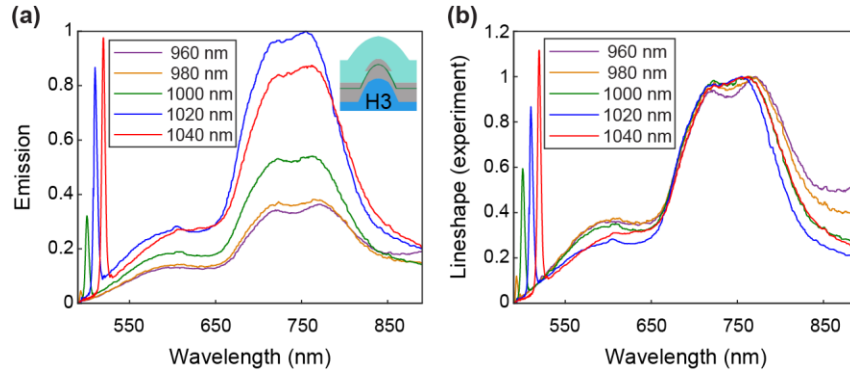


Figure D7. (a) H3 nonlinear emission spectra for fixed incident power (128 mW) and polarization (P) but different incident wavelengths ranging from 960 nm up to 1040 nm. (b) Spectral lineshapes corresponding to part (a).

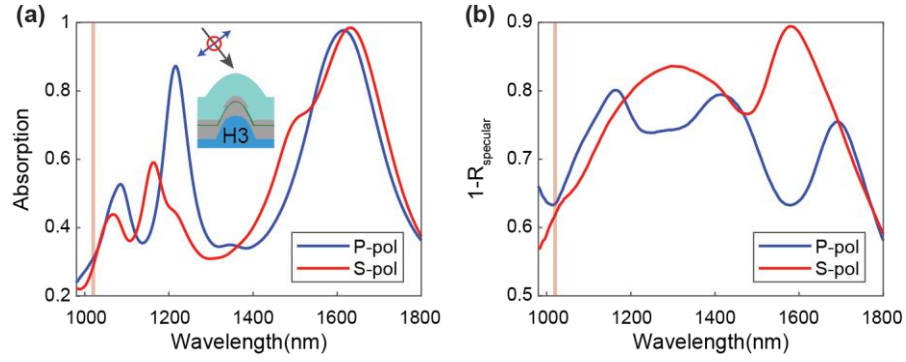


Figure D8. (a) FDTD-simulated absorption spectra for the H3 sample under S-polarized and P-polarized 30°-angled plane wave excitations. (b) Experimental $1-R_{\text{specular}}$ of the sample, where R_{specular} is the specular reflectance measured using an ellipsometry setup. The two figures indicate that S and P incident polarizations cause comparable absorption levels at $\lambda_{\text{inc}} = 1020 \text{ nm}$.

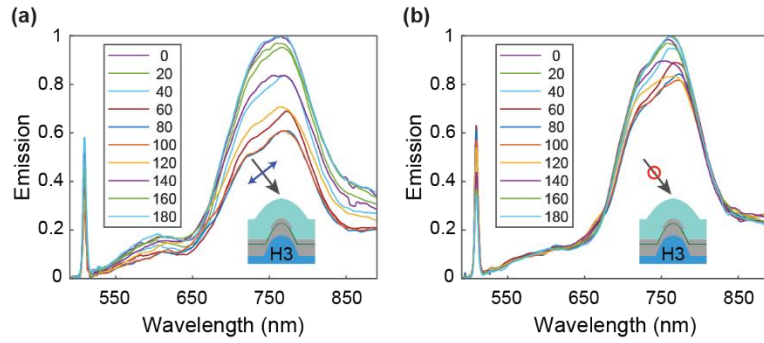


Figure D9. Emission spectra for different excitation and emission polarizations.

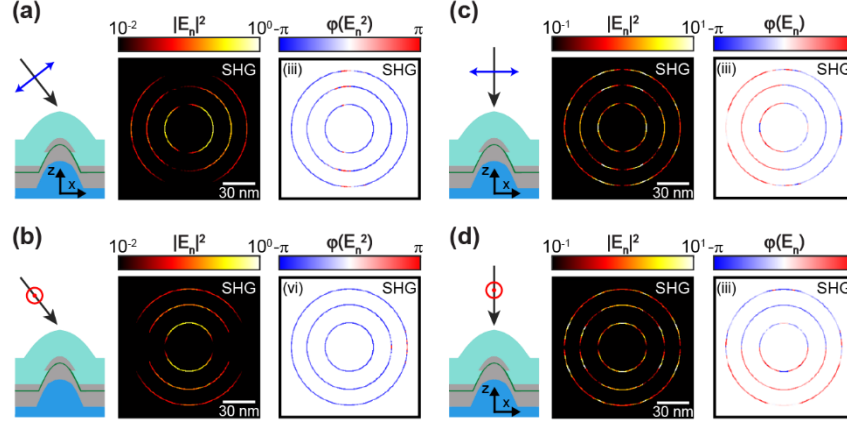


Figure D10. (a-b) $(E_{ex} \cdot \hat{n})^2$ distributions at the dome level for S and P polarized excitations (at $\lambda_{inc} = 1020 \text{ nm}$). (c-d) $E_p \cdot \hat{n}$ distributions at the dome level for normal excitation (at $\lambda_{inc} = 768 \text{ nm}$) with two perpendicular polarizations.

Table D1. Comparison of the second harmonic generation (SHG) and anti-stokes photoluminescence (ASPL) general behaviors in this work

Non-linear process	Coherent	Power-law (P)	Incident wavelength-dependence	Incident polarization dependence
SHG	Yes	- Weak-excitation regime: $P = 2$. - Mid- and strong-excitation regimes: $P > 2$.	- Higher intensity modulation. - Spectral shift.	- Higher intensity modulation. - Higher modification of the emission polarization.
ASPL	No	- Weak-excitation regime: $1 < P < 2$. - Mid-excitation regime: $P \approx 2$. - Strong-excitation regime: $P > 2$.	- Lower intensity modulation. - ASPL cut-off around the SHG wavelength. - ASPL lineshape modification.	- Lower intensity modulation. - Lower modification of the emission polarization. - ASPL lineshape modification.

Chapter 6: Summary and outlook

Chapters 1-5 presented a coherent and comprehensive picture on the fundamentals, design strategies, fabrication, and applications of “multiresonant plasmonic systems with spatial mode overlap”. In this chapter, we first summarize the important materials in the previous chapters and then, discuss the related future works on applications of multiresonant plasmonic systems with spatial mode overlap.

6.1. Summary

Chapter 1 motivated the topic with focusing on the plasmonic applications where multiresonant systems can outperform their single-resonant counterparts. In applications involved with multiphoton non-linear optical processes at nanoscale, multiresonant plasmonic systems with spatial mode overlap can enhance the excitation process through field confinement at the fundamental wavelengths and enhanced the emission process through increasing the photonic density of states (Purcell effect) at the emission wavelengths. Furthermore, by enabling wavelength-multiplexed operations through exploitation of the different resonant wavelength bands, multiresonant plasmonic systems open interesting opportunities in combining several different types of plasmonics enabled/enhanced modalities (sensing, spectroscopy, switching, etc.) into the same nanoscale optical devices.

Chapter 2 summarized the recent advances in the study of the multiresonant plasmonic systems with spatial mode overlap and extensively examined their operation theory, architecture, and design strategies. The chapter first briefly reviewed some basic concepts, including the different types of plasmonic modes, mode hybridization, and the geometrical symmetry effects on the optical properties. The chapter then discussed how one can build the multiresonant plasmonic systems with spatial mode overlap, with an emphasis on the mode hybridization between closely-assembled metallic nanostructures as the key strategy. According to the localization characteristics of the elementary modes in their building blocks, the chapter then classifies the multiresonant plasmonic systems into those based on the optical coupling between: (1) two or more localized modes, (2) localized and delocalized modes, and (3) two or more delocalized modes. Pros and cons of various architectures in each category in terms of fabrication and overall performance for multiresonant enhancement were also examined. Multiresonant systems based on the coupled

localized modes are most suitable when compactness in footprint and volume is required, but the systems using the delocalized-localized mode hybridization are preferred when 3D device miniaturization is not critical.

Chapter 3 developed the Black-box Coupled-Mode Theory (BBCMT), a versatile analysis framework derived from the modal expansion of the fields in Maxwell's equations to analyze the electromagnetic interactions of open, lossy, and dispersive resonators. The key idea in BBCMT development is employing the conjugated Lorentz's reciprocity theorem to normalize the modes and obtain the coupled-mode equations. By directly connecting the field products to Poynting's theorem, this approach allows defining a resonator's Hamiltonian matrix that characterizes its modes' electromagnetic interactions, energy storage, and absorption. BBCMT considers both the non-resonant and resonant responses of a resonator to accurately model its scattering and absorption. Furthermore, the chapter introduces the background perturbation method to evaluate the non-resonant responses from numerical simulations or experimental results. After deriving the formulations for single and coupled resonators, the chapter presents some examples to demonstrate how BBCMT can facilitate the design and analysis of electromagnetic resonant systems with complicated dynamics, especially in plasmonics and metamaterials.

Chapter 4 introduced the nanolaminate plasmonic crystals (NPCs), two-tier metamaterials consisting of closely-packed metal-insulator-metal nanodome and nanohole arrays that can support many (~ 10) plasmonic modes with spatial overlap and high excitability under free-space light illumination in 400 – 1400 nm. Wafer-scale fabrication of NPCs is demonstrated through a combination of nanoimprinting lithography and multilayered physical vapor deposition techniques. Furthermore, NPCs' unique performance and tunability as multiresonant plasmonic systems is evidenced by far-field optical measurements, in good agreement with numerical simulations. Coupled-mode theory analysis and numerical simulations reveal that highly-excitability and spatial overlap of the NPC modes originate in the synergistic effects of the strong near-field coupling between the less-excitability modes in their nanodome and nanohole arrays and the ground-plane-like loading effect of the nanohole array on the nanodome array modes. NPCs can serve as a high-performance nanophotonics platform for multiresonant enhancement of the multiphoton nonlinear optical processes with multiple excitation/emission transitions in the Visible-Near-Infrared (Vis-NIR) spectral range.

Chapter 5 demonstrated the NPCs' application in uncovering the mechanisms of the second harmonic generation (SHG) and broadband anti-Stokes photoluminescence (ASPL) from plasmonic structures excited by ultrafast pulsed lasers. This chapter's work was primarily enabled by taking the NPCs design to the next level, such that their plasmonic modes cover the whole Vis-NIR spectral range and become independently controllable at the excitation ($> 950\text{ nm}$) and emission ($< 950\text{ nm}$) wavelengths. We then experimentally investigated the effects of the incident laser power, wavelength, and polarization on the intensity, spectral shape, and polarization of the NPCs' non-linear emission. Furthermore, to analyze the experimental results, we developed novel PL models based on the intraband recombination (IBR) and electronic Raman scattering (ERS) pictures that consider the time evolution of the hot carriers' energy distribution due to Landau damping as well as electron-electron and electron-phonon interactions. When needed, the models are further expanded to include the effects of the hot carriers' spatial distribution as well. This chapter also develops an advanced SHG model based on the black-box coupled-mode theory that characterizes the contribution by multiple plasmonic modes at both the fundamental and second harmonic wavelengths. The most important findings of this chapter are as follows: 1- plasmonic ASPL is dominated by the IBR process; 2- Rather than radiative electronic transitions, ASPL and SHG photons come from the decay of the surface plasmons that provide the Purcell enhancement at the emission wavelengths; 3- By affecting the energy and spatial distributions of the microscopic non-linear sources, excitation conditions highly impact the portion of the non-linear energy coupled into each plasmonic mode; 4- Structural defects could highly affect the non-linear emission properties, especially for SHG which is highly sensitive to the system symmetries.

6.2. Outlook

As future work, applications of the NPCs and other multi-resonant out-of-plane structures can be further explored. First, such systems can potentially be utilized as efficient platforms for non-linear optical sensing with ultrahigh sensitivity and ultrahigh spatial resolution. Second, we can investigate their application as active and multimode optical systems that combine different functionalities into a single device.

6.2.1. Non-linear optical sensing

Plasmonic resonances are very sensitive to the size and shape of the structure supporting them as well as the refractive index of their environment. In this regard, plasmonic systems can be used to

detect the variations in any physical parameter, such as concentration and temperature, that can affect these parameters. Upon surface functionalization with specific antibodies and other biological and chemical probes, plasmonic structures can also be used as detection tools down to a single-molecule resolution. Most of the plasmonic sensors developed so far are passive devices that rely on linear processes such as scattering and absorption as the optical probe^{361, 362}. In such devices, a monochromatic light beam hits the plasmonic nanoantennas covered with the analyte and the transmitted or reflected intensity at the same wavelength is measured. A refractive index change Δn at the nanoantenna surface then shifts the plasmonic resonances, which directly modulates the detected intensity by the ratio $\Delta I/I$. Alternatively, the broadband response of the nanoantenna can be measured to detect the resonance frequency shifts $\Delta\omega$. The device sensitivity $\Delta I/I\Delta n$ can be higher when a non-linear signal is used as the optical probe as in this scenario, the signal generation process involves more electronic transitions and shifting of the plasmonic modes affects each transition step individually. This scheme has already been demonstrated using single-resonant plasmonic systems^{310, 363}. Nevertheless, plasmonic modes are more sensitive to the refractive index change when they are narrower or closer to resonance. Hence, we speculate that $\Delta I/I\Delta n$ can be much further improved when multiresonant plasmonic systems with spatial mode overlap and narrow resonances are utilized as the nonlinear sensing platform. As a future work, this hypothesis can be tested using the NPCs designed in chapter 5.

6.2.2. Active and Multimode optical devices

Typically, gap plasmon modes are supported by metal-insulator-metal (MIM) structures with closely assembled metal nanoparticles. Yet, we interestingly found that the insulator gap does not need to be fully dielectric for magnetic dipolar gap plasmon modes. The reason is that these modes have an electric field node at the center of the gap and when the gap material lies in that region, the magnetic dipole mode does not notice its presence (appendix C.1). Considering this strategy, we demonstrated through numerical simulations that fully metallic MIM plasmonic structures can also be realized (appendix C.1). NPCs consisting solely of conductive metallic materials can open the door to a plethora of potential applications. For example, such devices can combine the electrical recording and Raman biochemical analysis at nano-bio interfaces, can serve as electrochemical electrodes capable of optical sensing and spectroscopy, and be employed in integrated solar cells and batteries. Our next step in this line of research is coming up with strategies of fabricating the fully metallic MIM systems.

NPCs offer several degrees of freedom in materials and geometrical features and thus, can be tailored for the optimized performance in almost every plasmonic application that does not require 3D device miniaturization. However, they are less suitable for in vivo biological applications that require nanoscale footprints and volumes. Instead, multiresonant MIM nanoantennae^{364, 365} can be used for such applications. Through theoretical analyses and numerical simulations³⁶⁴ (appendix C.2), we could demonstrate that the magnetic dipole mode in such devices can provide large absorption cross sections combined with large field enhancements in the dielectric gaps. Furthermore, MIM nanoantennae can effectively communicate with the far-field via their high-quantum-efficiency electric dipole mode. The explained qualities are also experimentally confirmed³⁶⁵. As a future work, in vivo application of the MIM nanoantennae for simultaneous photothermal therapy and Raman spectroscopy can be investigated.

Finally, a more advanced future work would be combining the active and multiresonant plasmonics. By incorporating functional materials such as nonlinear dielectric materials, phase-change materials³⁶⁶, and emissive gain media within the NPCs' dielectric layers, active plasmonic devices with wavelength-multiplexed multifunctional capabilities can potentially be created. When these active materials are also electrically active (sensitive to electric field, voltage, etc.) or have properties that can be controlled by electronic modulation³⁶⁶, one can potentially utilize NPCs as platforms for electro-optic devices (e.g., ultrafast switches) as well.

Appendix E

E.1. Conductive Gap-Plasmon Nanocavity

(This appendix is an expanded version of the conference paper “Safiabadi Tali SA, Zhou W. Conductive Gap-Plasmon Nanocavity. In Laser Science 2018 Sep 16 (pp. JTU2A-58). Optical Society of America.”)

While Raman spectroscopy is of considerable interest for label-free molecular analysis in biological systems, it is limited by intrinsically small cross section of the Raman signals. In this regard, plasmonic nanostructures can enhance the local electromagnetic fields by several orders of magnitude to achieve Surface enhanced Raman Spectroscopy (SERS)³⁶⁷. On the other side, high-performance electrical recording of bioelectrical signals at subcellular resolution is important for studying neural systems. In this aspect, combining electrical recording and Raman biochemical analysis at nano-bio interface can be a very useful approach to correlate the electrophysiological activities of neurons with their biochemical environments/conditions. Moreover, we can use plasmonic nanostructures to enhance local photothermal conversion efficiency and achieve transient nanoscale optoporation on the cell membranes for delivering molecules into the living cells or allowing intracellular access of nanotransducers³⁶⁸. In this work, with the aim of establishing hybrid optical and electrical nanodevices for interfacing with cells and cellular networks at subcellular resolution, we propose a conductive gap-plasmon nanocavity structure based on stacked metallic or conductive oxide nanodisks, which are inspired by Metal-Insulator-Metal (MIM) nanostructures.

Figure E1(a) analyzes the FDTD-simulated gap material effect on the optical response of a single-gap out-of-plane plasmonic nanocavity (shown in the inset). SiO₂ has the same index ($n=1.5$) as the background and serves as the reference. We see that the system response below 750 nm have little dependence on the gap material, while the opposite is true for the response above 750 nm. The reason for insensitivity of the sub-750 nm resonances to the gap material is their belonging to their domination by the electric dipole mode and other high order modes with small fields inside the gap. The resonance above 750 nm belongs to the gap magnetic dipole mode which also has an electric field node at the center of the gap, where the nanodisk with 32 nm diameter is located (Figure E1(b)). In this regard, the nanodisk only partially overlaps with the magnetic dipole mode

and hence, even when the nanodisk is metallic, the mode does not get killed. Nevertheless, the nanodisk presence still affects the mode resonance properties. Please note that almost all the natural materials are non-magnetic at the optical frequencies. Hence, the nanodisk mainly perturbs the mode electric field and cannot directly affect the mode magnetic field (Figure E1(b)).

Figure E2 shows the resonance wavelength, absorption and scattering cross sections, and the maximum intensity enhancement of the magnetic dipole mode for the different gap materials. Al, Ti, and Au clearly perturb the mode due to their large index mismatch to the background. We further see that the resonance wavelength for all Al, Ti, and Au shifts to the blue side, which can be traced to their negative $Re(\epsilon)$ by a simple resonator perturbation analysis based on BBCMT. On the contrary, despite ITO is also conductive, we interestingly see that this material almost gives the same response as the reference SiO_2 . The reason is that ITO, as a result of its low free electron density, has a low plasma frequency which causes it to behave like a dielectric at optical frequencies. In this regard, the index mismatch to the background is much smaller for ITO compared to the metallic materials such as Al, Ti, and Au. Among the three metals, Au is the preferred choice as it has the highest conductivity and gives the highest intensity enhancement.

Figure E3 compares the optical and electrical performances of ITO and Au as a function of the gap nanodisk diameter. The optical performance is evaluated by the maximum intensity enhancement inside the gap when the magnetic dipole mode is at resonance. The electrical performance is evaluated by the conductivity of the gap nanodisk in the z direction. For both materials, the optical performance is a decreasing function of D_{gap} while the electrical performance is an increasing function of D_{gap} . In terms of optical performance, ITO generally outperforms Au but the two materials are comparable up to $D_{gap} \sim 20 \text{ nm}$. However, electrical performance of Au is almost two orders of magnitude better than ITO for all D_{gap} values. Hence, Au overall gives higher optical and electrical performances than ITO.

In conclusion, our numerical study has demonstrated how one can make the conductive gap-plasmon nanocavity systems that can simultaneously function as a nanoelectrode as well as a plasmonic nanoantenna/nanocavity. The first method is using the metal oxides like ITO, which almost act like a dielectric at optical frequencies but are conductive at lower frequency bands. The second method is using a noble metal (like Au) with small diameter, which preserves the optical performance of the gap mode while simultaneously offering a high gap conductivity. Ultimately,

practical and application-specific considerations, such as fabrication feasibility and material compatibility, must also be taken into account besides performance to choose the proper gap material. As an application example, Figure E4 schematically illustrates how conductive gap MIM systems can be used as electrochemical electrodes with and optical sensing capability.

Methods. The simulations for this work were done using Lumerical FDTD software with Perfectly Matched Layer (PML) boundary conditions. The background refractive index was set to 1.5. Also, we chose the Johnston and Christy model ²²⁶ for silver, Palik models for Gold, Titanium, and Aluminum ²⁸³, Moreland model for ITO ³⁶⁹, and $n=1.5$ for SiO₂.

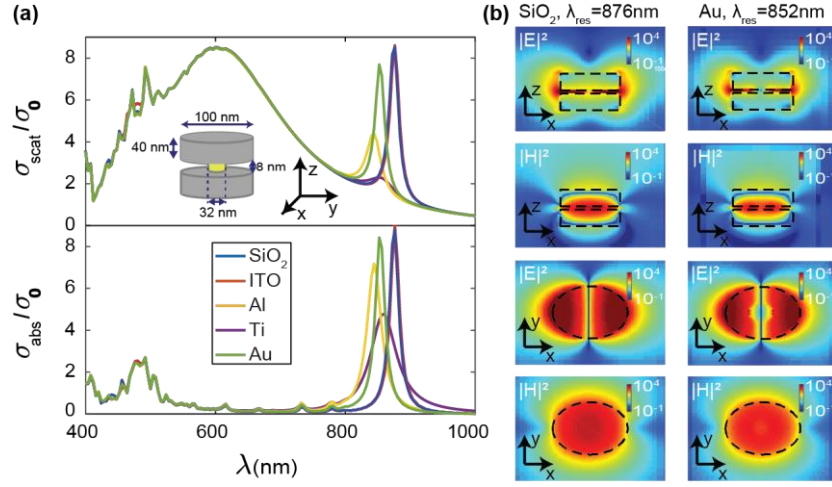


Figure E1. (a) Normalized scattering and absorption spectra of the MIM nanocavity system with SiO₂, ITO, Al, Ti, and Au as the gap materials. (b) Electric and magnetic intensity profiles of SiO₂ (same index as the background) and Au in the x-z and x-y gap cross sections. SiO₂ has the same index (n=1.5) as the background and hence, its optical response serves as the reference.

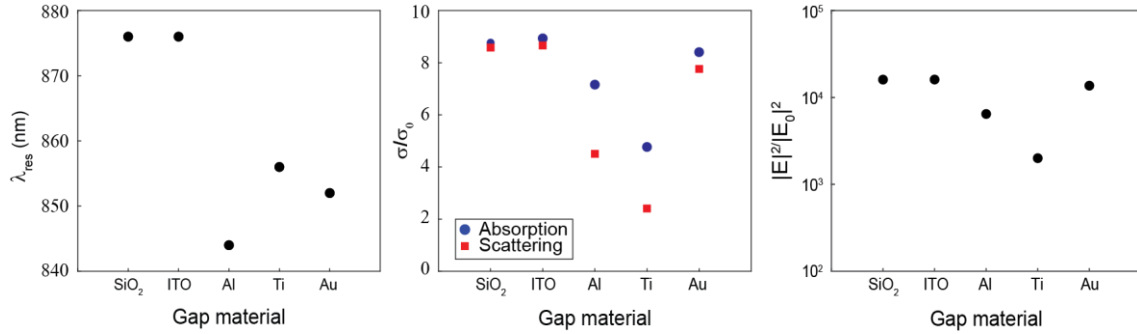


Figure E2. Resonance wavelength (a), scattering and absorption spectra (b), and intensity enhancement (c) of the magnetic dipole mode for different gap materials.

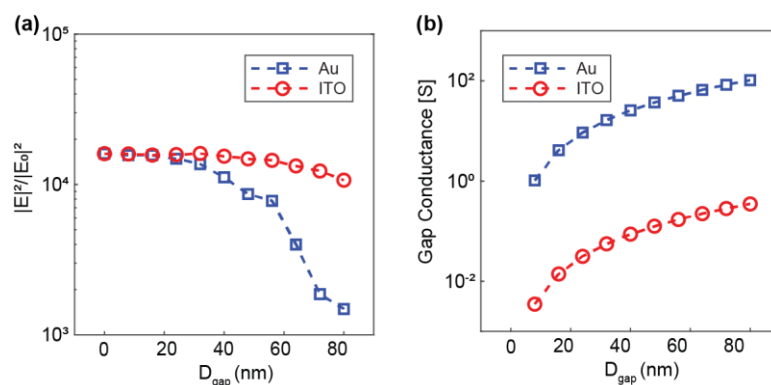


Figure E3. Optical (a) and electrical (b) performances of ITO and Au as a function of the gap nanodisk diameter.

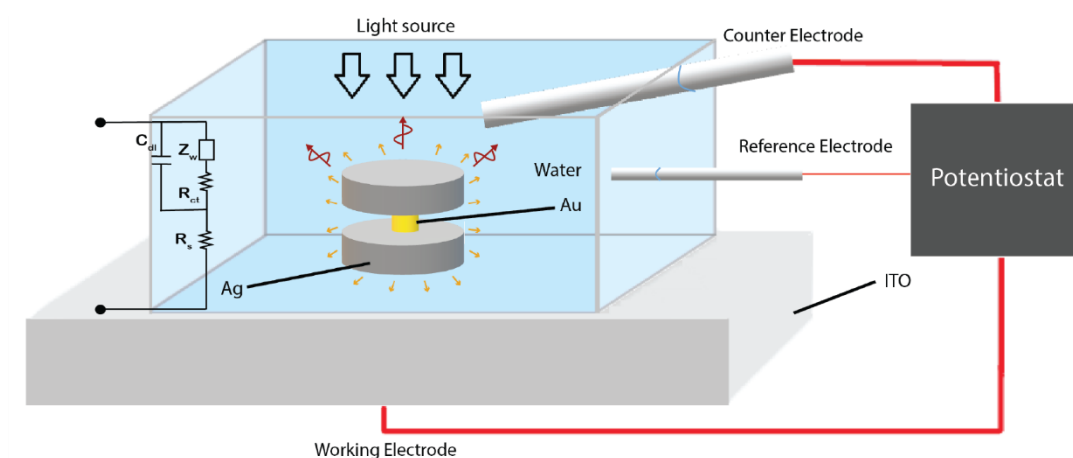


Figure E4. Conductive gap MIM systems can be used as electrochemical electrodes with and optical sensing capability.

E.2. Fixed-Size Double-resonant Nanolaminate Plasmonic Nanoantennas with Wide Spectral Tunability and High Optical Cross-sections

(This appendix is a summary of the paper “Qian Y, Safiabadi Tail SA (co-first author), Mejia E, Zhou W. Fixed-size double-resonant nanolaminate plasmonic nanoantennas with wide spectral tunability and high optical cross-sections. *Optik*. 2021 Mar 1;230:166332.”)

By supporting localized surface plasmon (LSP) modes, plasmonic nanoantennas based on metal-dielectric nanostructures can trap and concentrate light at the nanoscale to enhance both linear and nonlinear optical processes for various applications in areas ranging from information technology to energy and healthcare^{1, 370-374}. Due to the short LSP lifetimes (2–10 fs), the plasmon energy localized in nanoantennas depletes quickly through radiative decay pathways as free-space photons and nonradiative decay pathways as local heating³⁷⁵⁻³⁷⁷. In general, the use of relatively brighter LSP modes is advantageous for plasmonic enhancement of elastic/inelastic scattering and emission processes in applications such as scattering based biosensing/bioimaging, surface-enhanced Raman spectroscopy (SERS), fluorescence spectroscopy, and nonlinear optics light sources^{5, 285, 372, 373, 378}. On the other hand, using relatively darker LSP modes is preferable for nanolocalized photothermal heating processes in applications, such as solar energy photothermal conversion, photothermal cancer therapy, and photothermal neural activation^{374, 379-381}.

Here, we propose and numerically demonstrate that fixed-size nanolaminate plasmonic nanoantennas (NLPNAs) consisting of vertically-stacked metal/insulator layers can support two highly excitable LSP modes with electrical dipole (ED) and magnetic dipole (MD) characteristics (Figure E5). By simply controlling the thickness ratio between the individual metal and insulator layers, the resonant wavelengths of both ED and MD modes can be tuned between ~700 nm and ~1000 nm, while preserving the overall size and shape. While the ED mode in NLPNAs can have large scattering cross-sections suitable for applications based on plasmonic emission/scattering processes, the MD mode has large absorption cross-sections desirable for applications based on plasmonic photothermal effects (Figure E6). Numerical simulations and theoretical analyses reveal that NLPNAs' double-resonance tunability originates from the out-of-plane geometric dependence of the elementary ED and MD modes in their insulator-metal-insulator (IMI) and metal-insulator-metal (MIM) building blocks. Furthermore, due to the intimate vertical stacking of IMI and MIM

building blocks, the optical coupling strength among elementary ED and MD modes in IMI and MIM building blocks can also be modulated by changing the metal-to-insulator thickness ratio (t/h) in NLPNAs (Figure E7). The proposed NLPNAs can be fabricated by the electron-beam evaporation of alternating metal and insulator thin films through nanohole array deposition masks^{295, 382}, with nanometer-scale thickness accuracy.

Having a fixed-size, NLPNAs can maintain a consistent nano-bio interface with cells and cellular systems across separate experiments³⁸³⁻³⁸⁷. In this regard, NLPNAs are potentially useful for multifunctional wavelength-multiplexed nano-biodevices. For example, they can be used for simultaneous surface-enhanced Raman spectroscopy³⁸⁸ and photothermal cell activation^{97, 389}. By having a nanoscale size and supporting LSP modes with tunable resonant wavelengths in the NIR biological window (NIR-I: 700–900 nm, NIR-II: 1000–1350 nm, and NIR-III: 1550–1870 nm), NLPNAs are also suitable for in-vivo biomedical applications requiring deep light penetration in tissues³⁹⁰⁻³⁹².

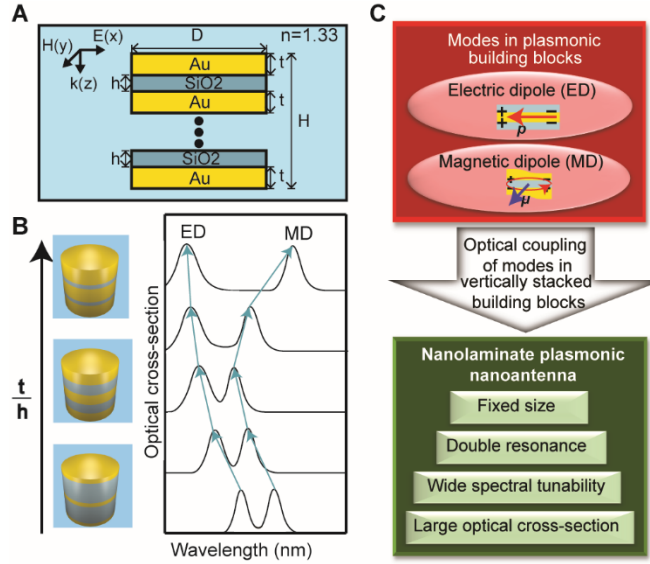


Figure E5. Fixed-size double-resonant NLPNAs. (A) Cross-sectional schematic of a fixed-size nanolaminate plasmonic nanoantenna with a fixed-diameter (D) and a fixed-height (H) in water ($n = 1.33$) under x-polarized normal incident light. The nanolaminate plasmonic nanoantenna consists of alternating layers of Au thickness (t) and SiO₂ thickness (h) nanodisks. (B) Schematic illustration of the evolution of resonant wavelengths for hybridized electric dipole (ED) and magnetic dipole (MD) modes in a fixed-size nanolaminate plasmonic nanoantenna at different Au-SiO₂ thickness ratios (t/h). (C) Scheme of the mode hybridization strategy for engineering the double-resonant optical properties of fixed-size NLPNAs. NLPNAs consist of two types of plasmonic building blocks in the vertical stack, which are the insulator-metal-insulator (IMI) nanostructures, supporting the electric dipole (ED) modes, and the metal-insulator-metal (MIM) nanostructures, supporting the magnetic dipole (MD) modes.

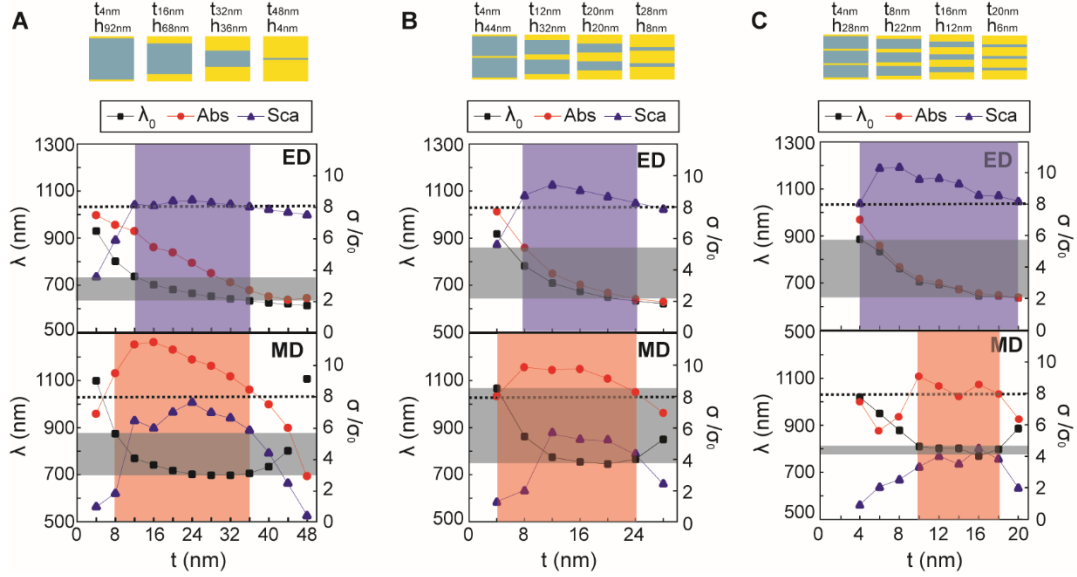


Figure E6. Spectral tunability of fixed-size double-resonant NLPNAs with different numbers of vertically stacked MIM building blocks by controlling the metal-to-insulator thickness ratio (t/h). (A-C) The dependence of the resonant wavelength and the peak absorption/scattering cross-sections of the ED mode and the MD mode on the Au layer thickness (t) for fixed-size NLPNAs with (A) one insulator layer, (B) two insulator layers, and (C) three insulator layers, in water ($n=1.33$). The diameter and the total height of NLPNAs with different numbers of Au-SiO₂-Au building blocks are fixed as ~ 100 nm. In the top panel of (A-C), the vertical shaded blue bands depict the range of Au layer thickness (t) for the ED mode with high peak scattering ($\sigma_{sca}/\sigma_0 \geq 8$), and horizontal shaded grey bands represent the tunable resonant wavelength range for a high scattering regime. In the bottom panel of (A-C), the vertical shaded red bands depict the range of Au layer thickness (t) for the MD mode with high peak absorption ($\sigma_{abs}/\sigma_0 \geq 8$), and horizontal shaded grey bands represent the tunable resonant wavelength range for the MD mode with the peak absorption $\sigma_{abs}/\sigma_0 \geq 8$.

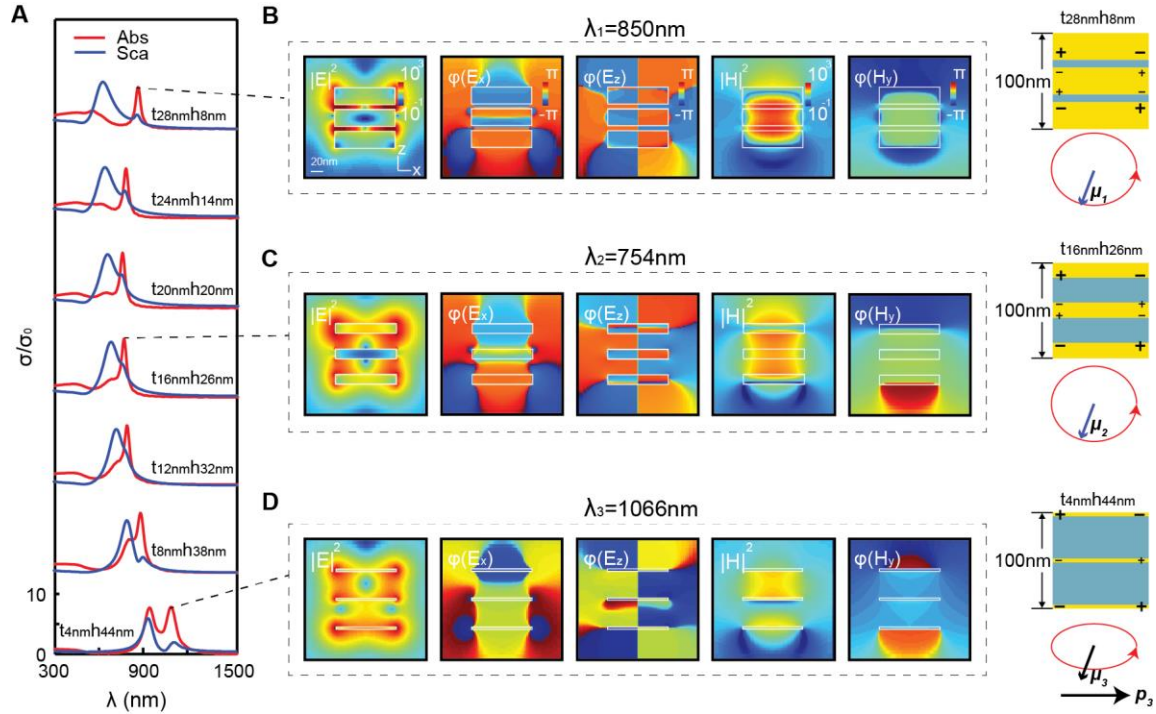


Figure E7. Far-field and near-field optical properties of fixed-size MIMIM NLPNAs with different metal-to-insulator thickness ratios (t/h). (A) FDTD-calculated spectra of normalized absorption and scattering cross-sections for fixed-size Au-SiO₂-Au-SiO₂-Au nanoantennas in water ($n=1.33$) with different thicknesses for Au (t) and SiO₂ (h) layers, which have the fixed diameter (D) and the height (H) of ~ 100 nm. (B-C) FDTD-calculated distribution maps of $|E|^2$, $\phi(E_x)$, $\phi(E_z)$, $|H|^2$, and $\phi(H_y)$ for the MD related modes of fixed-size Au-SiO₂-Au-SiO₂-Au nanoantennas with different thicknesses of Au and SiO₂ layers in water ($n=1.33$), including (B) $t = 28$ nm and $h = 8$ nm, (C) $t = 16$ nm and $h = 26$ nm, and (D) $t = 4$ nm and $h = 44$ nm.

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