Development of High-Performance Optofluidic Sensors on Micro/Nanostructured Surfaces

Weifeng Cheng

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Jiangtao Cheng, Chair
Yang Liu
Xiaoyu Zheng
Todd Lowe

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Abstract

Optofluidic sensing utilizes the advantages of both microfluidic and optical science to achieve tunable and reconfigurable high-performance sensing purpose, which has established itself as a new and dynamic research field for exciting developments at the interface of photonics, microfluidics, and the life sciences. With the trend of developing miniaturized electronic devices and integrating multi-functional units on lab-on-a-chip instruments, more and more desires request for novel and powerful approaches to integrating optical elements and fluids on the same chip-scale system in recent years. By taking advantage of the electrowetting phenomenon, the wettability of liquid droplet on micro/nano-structured surfaces and the Leidenfrost effect, this doctoral research focuses on developing high-performance optofluidic sensing systems, including optical beam adaptive steering, whispering gallery mode (WGM) optical sensing, and surface-enhanced Raman spectroscopy (SERS) sensing.

A watermill-like beam steering system is developed that can adaptively guide concentrating optical beam to targeted receivers. The system comprises a liquid droplet actuation mechanism based on electrowetting-on-dielectric, a superlattice-structured rotation hub, and an enhanced optical reflecting membrane. The specular reflector can be adaptively tuned within the lateral orientation of 360°, and the steering speed can reach ~353.5°/s. This work demonstrates the feasibility of driving a macro-size solid structure with liquid microdroplets, opening a new avenue for developing reconfigurable components such as optical switches in next-generation sensor network.

Furthermore, the WGM sensing system is demonstrated to be stimulated along the meridian plane of a liquid microdroplet, instead of equatorial plane, resting on a properly designed nanostructured
chip surface. The unavoidable deformation along the meridian rim of the sessile microdroplet can be controlled and regulated by tailoring the nanopillar structures and their associated hydrophobicity. The nanostructured superhydrophobic chip surface and its impact on the microdroplet morphology are modeled by Surface Evolver (SE), which is subsequently validated by the Cassie-Wenzel theory of wetting. The influence of the microdroplet morphology on the optical characteristics of WGMs is further numerically studied using the Finite-Difference Time-Domain method (FDTD) and it is found that meridian WGMs with intrinsic quality factor Q exceeding $10^4$ can exist. Importantly, such meridian WGMs can be efficiently excited by a waveguiding structure embedded in the planar chip, which could significantly reduce the overall system complexity by eliminating conventional mechanical coupling parts. Our simulation results also demonstrate that this optofluidic resonator can achieve a sensitivity as high as 530 nm/RIU. This on-chip coupling scheme could pave the way for developing lab-on-a-chip resonators for high-resolution sensing of trace analytes in various applications ranging from chemical detections, biological reaction processes to environmental protection.

Lastly, this research reports a new type of high-performance SERS substrate with nanolaminated plasmonic nanostructures patterned on a hierarchical micro/nanostructured surface, which demonstrates SERS enhancement factor as high as $1.8 \times 10^7$. Different from the current SERS substrates which heavily relies on durability-poor surface structure modifications and various chemical coatings on the platform surfaces which can deteriorate the SERS enhancement factor (EF) as the coating materials may block hot spots, the Leidenfrost effect-inspired evaporation approach is proposed to minimize the analyte deposition area and maximize the analyte concentration on the SERS sensing substrate. By intentionally regulating the temperature of the SERS substrate during evaporation process, the Rhodamine 6G (R6G) molecules inside a droplet with an initial concentration of $10^{-9}$ M is deposited within an area of 450 $\mu$m$^2$, and can be successfully detected with a practical detection time of 0.1 s and a low excitation power of 1.3 mW.
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General Audience Abstract

Over the past two decades, optofluidics has emerged and established itself as a new and exciting research field for novel sensing technique development at the intersection of photonics, microfluidics and the life sciences. The strong desire for developing miniaturized lab-on-a-chip devices and instruments has led to novel and powerful approaches to integrating optical elements and fluids on the same chip-scale systems. By taking advantage of the electrowetting phenomenon, the wettability of liquid droplet on micro/nano-structured surfaces and the Leidenfrost effect, this doctoral program focuses on developing high-performance optofluidic sensing systems, including optical beam adaptive steering, whispering gallery mode (WGM) optical sensing, and surface-enhanced Raman spectroscopy (SERS) sensing. During this doctoral program, a rotary electrowetting-on-dielectric (EWOD) beam steering system was first fabricated and developed with a wide lateral steering range of 360° and a fast steering speed of 353.5°/s, which can be applied in telecommunication systems or lidar systems. Next, the meridian WGM optical sensing system was optically simulated using finite difference time domain (FDTD) method and was numerically validated to achieve a high quality-factor $Q$ exceeding $10^4$ and a high refractive index sensitivity of 530 nm/RIU, which can be applied to the broad areas of liquid identification or single molecule detection. Lastly, a SERS sensing platform based on a hierarchical micro/nano-structured surface was accomplished to exhibit a decent SERS enhancement factor (EF) of $1.81 \times 10^7$. The contact angle of water droplet on the SERS substrate is $134°$ with contact angle hysteresis of $\sim 32°$. Therefore, by carefully controlling the SERS surface temperature, we employed Leidenfrost evaporation to concentrate the analytes within an extremely small region, enabling the high-resolution detection of analytes with an ultra-low concentration of $\sim 10^{-9}$ M.
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Chapter 1  Introduction

1.1 Motivation

The term of optofluidic firstly came up in the early of 21st century, which is a multidisciplinary subject involving microfluidics, photonics, and surface science to accomplish high-performance optical sensing or signal transmission. As the liquid media for optical transmission is amorphous and reconfigurable comparing to the solid optical transmission unit, optofluidic sensing systems enable tunable and high-resolution sensing to meet variable sensing requirements, including single molecule detection\(^1,2\), tunable lens\(^3,4\), and reconfigurable imaging systems\(^5,6\), etc. In recent years, with the trend of electronic device miniaturization, the development of optofluidic focuses on lab-on-a-chip devices for accurate liquid manipulation and high sensitive analyte sensing, such as electrowetting-on-dielectric (EWOD) devices\(^7\) for liquid manipulation, whispering gallery mode (WGM) optical sensing system\(^8\) for liquid refractive index measurement, and surface enhanced Ramen spectroscopy sensing (SERS)\(^9\) for particle identification. With the motivation of improving the performance of currently reported optofluidic sensing systems, this doctoral research aims to utilize the knowledge of optofluidic to solve the problem of optical beam steering using EWOD, meridian WGM optical sensing, and high-resolution SERS sensing on hierarchical micro/nanostructured substrate, respectively.

Firstly, with the rapid progress of multifunctional sensor network and electronic networking devices, reconfigurable beam steering components are indispensable to support network systems operating with high adaptability and with various functions. Currently, almost all such components are made of solid parts whose structures are rigid, and hence their functions are difficult to be reconfigured. Also, optical beam steering is still a very challenging problem compared to
RF/microwave beam steering. Hence, developing a high-performance reconfigurable optical beam steering system is highly expected. During recent years, several novel fluidic-based beam tuning mechanisms have been developed especially for optical beam steering.

**Figure 1-1.** Currently reported liquid-based beam steering systems.¹⁰⁻¹⁴

Some typical liquid-based beam steering systems are illustrated in Figure 1-1. Among them, the beam tuning system driven by electrowetting on dielectric (EWOD),¹⁵⁻¹⁷ which is defined as the change in the contact angle between an electrolyte and a dielectric surface due to an applied electric potential between them, shows distinct advantages. EWOD-based digital operations have demonstrated great potential in actuating and manipulating liquid droplets due to EWOD’s unique characteristics of prompt response (tens of ms), low power consumption (µW - mW), and programmable operations. Based on EWOD, tunable liquid prisms can reflect incident beams to the desired direction by controlling the orientation of a reflecting membrane located on a droplet surface or embedded at a fluid-fluid interface.¹³,¹⁹⁻²³ The maximum tilting angle among these tunable prism configurations has reached ~22°.¹⁰ As a comparison, a functional dielectrophoresis (DEP)-driven liquid prism was shown to steer beams only within ±0.87°.¹⁴ Furthermore, a liquid-liquid light steering device actuated by dielectrowetting was developed and its maximum beam steering angle can reach ±22.7°.¹¹ In addition to the liquid-prism-based steering mechanism, an EWOD-driven rotating shaft device was developed to modulate a membrane reflector within a range of ±30°,¹² indicative of an apparent improvement over the liquid prism modules. Generally,
liquid-based beam tilting and steering systems driven by EWOD require high stability of the fluid-fluid interface or the bulk fluids. In this respect, modulation of the embedded reflector at the fluid-fluid interface usually has a relatively low stability and is consequently hard to achieve full-range tracking and agile steering. Therefore, tuning devices capable of achieving fast, stable and accurate responses for adaptive and wide range beam steering are still desired.

Secondly, for the optical sensor using whispering gallery mode (WGM), it had been shown that optical WGMs can be present along the circular rim in the equatorial plane of a sessile microdroplet, and this phenomenon had been leveraged for biosensing demonstrations. However, optical coupling to such equatorial modes for their excitation and monitoring is mostly based on tapered fiber coupling, prism coupling or angle-polished fiber coupling,\textsuperscript{24} as shown in Figure 1-2. The optimum gap between the cavity and the waveguide is within 50 nm to 100 nm. Therefore, those coupling mechanisms demandingly require precise and complex alignment systems adjacent to the equatorial surface of the WGM resonator, which are usually bulky and hard to be applied on lab-on-chip devices. Consequently, many researchers strive to develop a WGM system which can reduce the coupling complexity and maintain high sensitivity of the optical WGM sensor at the same time.

\textbf{Figure 1-2.} Different optical Whispering Gallery Mode coupling mechanism. (a) Prism coupling. (b) Polished fiber coupling. (c) Tapered fiber coupling.\textsuperscript{24}
Lastly, Surface-enhanced Raman spectroscopy (SERS) has emerged to be an ultrasensitive molecular detection technique for (bio-)chemical analyses.\textsuperscript{25-27} A recent effort in SERS research is to achieve a fast and ultrasensitive detection of analytes at ultralow concentrations for applications ranging from point-of-care biomedical diagnosis, food, and water quality analyses, and to environmental monitoring.\textsuperscript{27-30} The diffusion-limited transport processes, however, makes it very challenging to effectively deliver analytes of sub-nanomolar-level low-concentrations into sparse sub-10-nm-scale hot spots on the SERS substrates within a relatively short detection time window.\textsuperscript{31,32}

![Surface physical modification (F.D. Angelis, 2011)](image1.png) ![Adoption of lubricant (S. Yang, 2016)](image2.png)

**Figure 1-3.** Typical approaches to concentrate analytes on SERS substrate.\textsuperscript{33,34}

To overcome the diffusion limit, researchers have created superhydrophobic SERS substrates to maintain a high contact angle (> 150°) of analyte droplets during the natural evaporation process, which can allow an increased surface density of analyte molecules deposited into a reduced footprint area (< 50×50 μm\(^2\)) for ultrasensitive SERS detection\textsuperscript{35-38}, as shown in Figure 1-3 (left). Despite promising results, superhydrophobic SERS substrates typically require surface coatings/modifications of hydrophobic layers on the hydrophilic plasmonic metal nanostructures. The surface-modified hydrophobic layers can impede analyte molecules to access SERS hotspots, introduce interfering Raman signals of hydrophobic materials layers, and deteriorate the SERS detection performance. Other than applying surface physical modification to concentrate the analytes, another approach adopts coating a lubricant layer on top of the nanostructures of SERS
substrate,\textsuperscript{34} as illustrate in Figure 1-3 (right). The liquid-liquid contact interface can dramatically concentrate the analyte and result in the detection of the analyte solution with an initial concentration of $10^{-15}$ M.\textsuperscript{34} However, the employment of lubricant layer may lead to chemical reactions with the target analyte in certain cases, and consequently alter the molecule configurations of the analyte. Therefore, it becomes a hot topic of developing a new approach to accomplish high-solution SERS sensing avoiding the durability-poor surface physical modification approach and the lubricant coating method.

1.2 Objectives

The primary objectives of this investigation are to:

➢ Develop a high-performance optical beam steering system with comprehensive merits:
  • Fast steering speed, wide steering range and high steering accuracy
  • Compact platform size and low power consumption
➢ Exploit the WGM system with the light coupling mechanism from the meridian periphery:
  • Investigate the relationship between the droplet contact angle and the quality factor $Q$ of the meridian WGM sensing system
➢ Design the hierarchical plasmonic mico/nanostructured SERS sensing platform and improve the SERS sensing ability in both lateral and vertical direction:
  • Accomplish SERS detection of ultra-low concentration solution

1.3 Challenges

The following challenges are faced in the investigation:

➢ Design the electrode pattern of electrowetting device to manipulate the droplet to move in a circular manner and actuate the reflecting membrane for beam steering
• Optimum design of the electrode unit for the best droplet actuation with fast and smooth motion
  ➢ Optimize the nanopillar size and nanopillar gap to support the droplet with a desired contact angle and morphology so that the meridian WGM can be formed
  ➢ Concentrate the analyte inside a droplet by evaporation as a deposition on the SERS substrate for SERS sensing

1.4 Approaches

The following approaches are used to overcome the challenges mentioned in this study:

➢ Adopt annuals-shaped electrode pattern made up by 24 trapezoid electrode units to achieve driving the reflecting membrane to steer 360° based on electrowetting
➢ Design the trapezoid electrode unit with interlock teeth structure for smooth manipulation of the droplet
➢ Simulate the droplet morphology on nanostructured surface using Surface Evolver, and conduct the optical WGM modelling using the droplet model as the WGM cavity by FDTD
➢ Minimize the analyte deposition area by utilizing the heat-assisted evaporation approach inspired by Leidenfrost effect, and ultimately accomplish SERS detection of R6G solution with initial ultra-low concentration

1.5 Contributions

The primary contributions of this research include:

For the rotary EWOD optical beam steering system:

➢ The concept of rotary EWOD system is put forward, which enables the droplet to fulfill a circular motion.
The feasibility of a miniaturized droplet-based beam steering system is theoretically and experimentally verified.

The rotary EWOD beam steering system is demonstrated, which can steer optical beam signal with a steering range of 360°, a max steering speed of 353.5°/s, a low actuation AC voltage of 40V – 20Hz, and a low power consumption of $10^{-5}W$.

For the meridian WGM optical sensing system:

- The lab-on-a-chip feasible WGM resonator is created by the integrating of the micro-droplet on superhydrophobic surface with WGM system coupling from meridian periphery, which can significantly reduce the overall system complexity.
- The meridian WGMs with high intrinsic quality factors of $Q > 10^5$ can exist according to the FDTD simulation.
- This optofluidic resonator performs a refractive index sensitivity of ~ 530 nm/RIU.

For the hierarchical plasmonic micro/nanostructured SERS sensing platform:

- The micro- and nano- structured substrate with multi-metal layer is fabricated as the SERS substrate.
- The controllable heating evaporation approach is developed to minimize the droplet deposition area and maximize the molecule concentration.
- The proposed SERS substrate can detect the molecule in an ultra-low concentration solution in $10^{-9}$ M by using the heat-assisted evaporation approach.

1.6 Outline

- Chapter 1 provides the motivation, objectives, challenges, approaches and contributions of this doctoral research, and lists the outline of this dissertation.
- Chapter 2 gives background knowledge and an overview of optical beam steering, WGM sensing, SERS sensing, and relevant scientific background.
➢ Chapter 3 presents the design, theoretical analysis and experimental test of an adaptive optical beam steering and tuning system based on electrowetting driven fluidic rotor.

➢ Chapter 4 presents the simulating analysis of meridian whispering gallery modes sensing in a sessile microdroplet on micro/nanostructured superhydrophobic chip surfaces.

➢ Chapter 5 presents the development of a Leidenfrost-evaporation-assisted ultrasensitive SERS sensing platform using hierarchical plasmonic micro/nanostructures.

➢ Chapter 6 provides the confusions for the investigation and discusses the future work.
Chapter 2  Background and Literature Review

2.1 Background for Optical Beam steering

During the past two decades, the development of multifunctional sensing network, swift signal transmission systems, and advanced wireless communication techniques has grown rapidly. Their applications are ubiquitous in our daily lives, ranging from optical switches\textsuperscript{39-41}, laser beam security networks\textsuperscript{42}, in-home WiFi antenna networks\textsuperscript{43}, global positioning systems (GPS)\textsuperscript{44} to autonomous vehicle remote control\textsuperscript{45}. To make these advanced sensing and telecommunication networks feasible in a more complex environment, a higher level of beam signal transmission standards, e.g., avoidance of signal mitigation over a longer transmission distance and alleviation of the multi-path fading phenomenon, needs to be carefully addressed. In this regard, adaptive beam steering technology has been highly demanded since it can effectively guide the concentrating beams to the desired paths and protect the network from noise disturbance.

Compared to radio frequency (RF)/microwave beam steering via various antenna techniques, optical beam steering is still a very challenging problem. A high-performance optical beam steering system with comprehensive merits such as low insertion loss, fast steering speed, wide steering range, high steering resolution, less system complexity, and compact platform size is highly demanded. During recent years, several novel fluidic-based beam tuning mechanisms have been developed especially for optical beam steering. Among them, the beam tuning system driven by electrowetting on dielectric (EWOD),\textsuperscript{15-17} which is defined as the change in the contact angle between an electrolyte and a dielectric surface due to an applied electric potential between them, shows distinct advantages. EWOD-based digital operations\textsuperscript{18} have demonstrated great potential in actuating and manipulating liquid droplets due to EWOD’s unique characteristics of prompt response (tens of ms), low power consumption (μW - mW), and programmable operations. Based
on EWOD, tunable liquid prisms can reflect incident beams to the desired direction by controlling the orientation of a reflecting membrane located on a droplet surface or embedded at a fluid-fluid interface.\textsuperscript{13,19-23} The maximum tilting angle among these tunable prism configurations has reached \(22^\circ\).\textsuperscript{10} As a comparison, a functional dielectrophoresis (DEP)-driven liquid prism was shown to steer beams only within \(\pm 0.87^\circ\).\textsuperscript{14} Furthermore, a liquid-liquid light steering device actuated by dielectrowetting was developed and its maximum beam steering angle can reach \(\pm 22.7^\circ\).\textsuperscript{11} In addition to the liquid-prism-based steering mechanism, an EWOD-driven rotating shaft device was developed to modulate a membrane reflector within a range of \(\pm 30^\circ\),\textsuperscript{12} indicative of an apparent improvement over the liquid prism modules. Generally, liquid-based beam tilting and steering systems driven by EWOD require high stability of the fluid-fluid interface or the bulk fluids. In this respect, modulation of the embedded reflector at the fluid-fluid interface usually has a relatively low stability and is consequently hard to achieve full-range tracking and agile steering. Therefore, tuning devices capable of achieving fast, stable and accurate responses for adaptive and wide range beam steering are still desired.

Inspired by capillary rotors with annular-shaped electrode designs,\textsuperscript{22} we put forward a novel optical concentrating beam steering system based on EWOD. The whole system comprises an annular EWOD platform with an open-plate configuration, a superlattice-structured rotation hub, and an enhanced optical reflecting membrane attached to the hub as the beam reflector. The EWOD platform is fabricated by sequentially depositing an annular array of Au electrodes, a thin film of Si\(_3\)N\(_4\) dielectric, and a thin layer of hydrophobic fluoropolymer on a glass substrate. The rotary hub is made of silicone oxycarbide ceramic with an octet-truss superlattice structure of ultralight weight (~8 mg), ultrahigh strength (9 MPa) and ultrahigh stiffness (950 MPa), which is additively manufactured by scanning optics projection micro-stereolithography (SOP\(\mu\)SL).\textsuperscript{46} A low frequency alternative current (AC) voltage is applied to actuate a liquid microdroplet via EWOD along the annular loop to activate the specular reflector, to which the liquid droplet is adhered. A resistor-capacitor (RC) circuit network analysis of the EWOD system indicates that the EWOD
driving force is in the order of hundreds of μN and its power consumption is ~10^{-5}-10^{-4} W. As such, the annular array of EWOD electrodes can be programmably activated to circulate a liquid droplet for digitally actuating the membrane reflector. Importantly, this EWOD-driven “watermill” is able to laterally rotate the reflector by 360° without the constraint of contact angle saturation\textsuperscript{47-49}, which outperforms most existing liquid-based actuation devices reported in the literature.\textsuperscript{12-14,19-22} In this paper, the general setup of the rotary EWOD steering system and the fabrication of the superlattice hub are firstly introduced; then, a theoretical analysis of the EWOD driving force and the resistant force are discussed for feasibility validation. Lastly, the adaptive optical beam tuning on the rotary EWOD system is experimentally demonstrated. In particular, the testing results of beam steering range, tuning speed, angular actuation resolution and repeatability, and the specular reflectance of the reflector are reported.

2.2 Background for Electrowetting-on-Dielectric

The phenomenon of electrowetting or electrowetting-on-dielectric (EWOD) is a widely adopted approach to manipulate the droplet or liquid-liquid interface. From the wetting perspective, a solid surface can be generally classified as hydrophobic surface (contact angle $\theta > 90^\circ$) and hydrophilic surface (contact angle $\theta < 90^\circ$), as illustrated in Figure 2-1. The three surface tensions, solid-vapor interfacial tension $\gamma_{SV}$, solid-liquid interfacial tension $\gamma_{SL}$, and liquid-vapor interfacial tension $\gamma_{LV}$, respectively, operate together at the three-phase contact line and result in the equilibrium state of the droplet with a specific contact angle $\theta$. When a droplet rests on top of a flat surface with an initial certain contact angle and a voltage is applied between the droplet and the surface, the droplet contact angle will decrease and end up with a new equilibrium contact angle, in other words, the voltage can reduce the surface energy and enhance the surface wettability, which is the phenomenon called as electrowetting.
Figure 2-1. Droplet on a surface. The three interfacial tensions work together at the triple line to maintain tangent force equilibrium.

Electrowetting-on-dielectric (EWOD) refers to the phenomenon of changing the droplet contact angle by applying a voltage between a droplet and a dielectric layer, as demonstrated in Figure 2-2.

Figure 2-2. Schematic of electrowetting-on-dielectric (EWOD).

Berge was the first researcher who conducted the EWOD experiments back in the 1990s. He gave the EWOD equation by combining Lippmann equations with the Young equation:

\[ \cos \theta(V) = \cos \theta_0 + \frac{\varepsilon V^2}{2\gamma_{LV}d} \]  \hspace{1cm} (2 - 1)
where $\theta(V)$ is the contact angle after applying a voltage $V$, $\theta_0$ is the contact angle without applying any voltage, $\varepsilon$ is the dielectric constant of the dielectric layer, $d$ is the thickness of the dielectric layer. Equation (2-1) has been found to be in good consistency with the experimental results when the applied voltage is low (e.g. <100 V), and Lippmann-Young equation is the fundamental equation to quantitively describe EWOD.

EWOD is a powerful and promising method to realize reconfigurable lab-on-a-chip devices. With a rapid development in recent years, applications driven by EWOD have been achieved in various fields, including tunable liquid micro-lens, electronic display technology, and beam steering systems. Beyond that, EWOD is also widely applied in bio-medical and chemical sensing devices because of its fast and accurate droplet manipulation with the droplet volume ranging from nanoliters to microliters.

2.3 Background for Whispering Gallery Mode Sensing

Ultrasensitive, label-free, cost-effective, compact and deployable sensing systems are critical for medical diagnostics, environmental monitoring and homeland security applications. Chip scale optical sensing systems integrating photonic, electrical, and fluidic functions are especially intriguing for label-free sensing applications due to the high sensitivity of optical sensors, the compactness of chip scale systems, and the low-cost fabrication techniques that are amenable to well-developed mass production.

Optical whispering gallery modes (WGMs) are morphology-dependent resonances occurred in a micro-cavity (or micro-resonator) and can be used for ultrasensitive optical detection. The utilization of high quality (high $Q$-factor) resonances in biosensing offers specific advantages such as a small sample volume, low concentration of analytes and high sensitivity. Generally, an optical micro-cavity is simply composed of a solid dielectric medium and can take various morphologies such as spheres, disks, toroids and capillary tubes. As a result of their compact mode volume
in micron scale and ultrahigh $Q$-factor, WGM micro-cavities enable significant (Raman or fluorescent) signal amplification due to the strong light–analyte interactions thereon. Detection of single viruses and other biomolecules has been demonstrated by monitoring the frequency shift of a WGM upon even trace amount of target analytes anchoring on the resonator surface.\textsuperscript{67} Since the refractive index of the optical cavity should be higher than the surrounding medium to confine the light inside by total internal reflection, silicon or glass are commonly used in case the surrounding medium is water or just ambient air. The vast majority of previous WGM works were performed on solid resonators such as glass beads and silica disks/toroids. Despite the high $Q$-factor of solid WGM resonators, most of the light is confined inside their dielectric bulk and only the evanescent field can interact with the analytes adhered on the external surface of resonators, thereby limiting the further enhancement of $Q$-factor. Hitherto, demonstration of feasibility of high performance WGMs sensing in a fluidic environment was achieved only in rare cases, in which the cavity tube was filled with analyte solution or a bead-like resonator was immersed in the sample liquid and WGMs were monitored by a wavelength-swept laser. However, when the micro-resonator is surrounded by an aqueous solution, its $Q$-factor is further decreased due to the reduced refractive-index contrast resulting in more radiation loss. Moreover, these solid resonators are not readily amenable to biosensing in fluidic carriers, e.g., red cells in serum. Therefore, it is desirable to use liquid medium containing analytes itself as the optical cavity that enables more intimate and more intense interactions between the target analytes and the stimulated WGMs.

A liquid microdroplet with its characteristic size shorter than its capillary length,\textsuperscript{71} i.e., $\sim$2.7 mm for water, can naturally form nearly perfect spherical shape with exceptionally smooth surface due to the dominant surface tension effect of liquid. This intriguing trait endows the microdroplet an ideal microcavity candidate of an impressive quality factor. Owing to their biocompatibility, structural flexibility and electrical tunability, liquid microdroplet resonators have attracted increasing interests in the optical sensing field.\textsuperscript{59,61,72-83} For a microdroplet-based resonator, apart from the desired high $Q$-factor of the microcavity, an efficient and facile coupling scheme is still
necessary especially for chip-level implementations. So far, either tapered fiber coupling or free-space beam coupling are the most commonly utilized coupling methods in nearly all the WGMs-related work.\textsuperscript{60,74,78,79} In either coupling method, precise alignment of the tapered fiber or free-space beam adjacent to the equatorial surface of a resonator is required. Hence, they are not very facile to implement in a complex sample matrix. Although it has been more than 40 years since the first suggestion of droplet resonator sensors, the practical applications of this potentially powerful technique are still quite limited.\textsuperscript{83} Therefore, unlike their solid counterparts, to realize a feasible microdroplet-based high performance sensing system, a robust, stable and facile optical coupling method must be developed.

Easy in light-coupling, stable in mechanics, convenient in implementation and preserving a high optical performance are key factors required for the high $Q$-factor optical sensing. The WGMs along the meridian rim of a liquid microdroplet resting on a superhydrophobic surface meet most of those requirements. In particular, such meridian WGMs can be dexterously stimulated by a strip waveguide embedded in the substrate surface. Even though a superhydrophobic surface that can sustain a droplet with the contact angle as high as nearly 180° has been demonstrated,\textsuperscript{84} the meridian plane of a sessile microdroplet resting on a surface is still inevitably deformed. Besides maintaining the microdroplet within tens of microns in diameter, the deformation in the meridian plane can be controlled by tailoring the surface roughness of the substrate and hence the microdroplet’s wettability.

In this research, we show that WGMs can be agilely excited and adaptively sustained along the meridian circumference of a liquid microdroplet sitting on a nanostructured superhydrophobic surface. To study the influence of nanoscale roughness on the microdroplet morphology including contact angle and local interface curvature and its impact on WGMs sensitivity, we conducted wetting characterization on the superhydrophobic surface by Surface Evolver (SE) and the Finite-Difference Time-Domain (FDTD) simulation of WGMs performance in this configuration. It is also shown that an embedded strip waveguide underneath the sessile droplet can efficiently
stimulate such modes in a facile manner, offering a novel and robust optofluidic platform for ultrahigh Q-factor sensing of trace chemicals and biomolecules.

2.4 Background for Droplet Wetting on Roughness Surfaces

As discussed in section 2.2, the droplet contact angle $\theta$ results from the balance of the three surface tensions, solid-vapor interfacial tension $\gamma_{SV}$, solid-liquid interfacial tension $\gamma_{SL}$, and liquid-vapor interfacial tension $\gamma_{LV}$, respectively. The droplet contact angle $\theta$ is expressed by Young’s equation:

$$
\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}
$$

(2 – 2)

On a flat surface, the droplet contact angle can be increased by coating a layer of hydrophobic material (such as fluoropolymer) on the original surface, but the maximum contact angle of a droplet on flat surface is reported as $\sim 120^\circ$. To further increase the contact angle, microstructure or nanostructure is required to be featured on the surface. The behavior a water droplet resting on a micro or nanostructured surface is schematically illustrated in Figure 2-3. The water droplet can either penetrate the pillars and fill into the cavities (in Wenzel state) or suspend on top of the pillars and be supported by the air cushion inside the cavities (in Cassie-Baxter state).

![Figure 2-3. Schematic of droplet wetting on micro- or nano-structured surface. (a) Wenzel state; (b) Cassie-Baxter state.](image-url)
The droplet contact angle on micro- or nano-structured surface is called as the apparent contact angle. $\theta^W$ and $\theta^C$ represent the droplet apparent contact angles when the droplet is in Wenzel state or in Cassie-Baxter state, respectively.

For the droplet in Wenzel state, the apparent contact angle $\theta^W$ can be depicted by the Wenzel equation:

$$cos\theta^W = r cos\theta$$

(2 – 3)

where $r$ represents the surface roughness, and $\theta$ refers to Young’s angle on the flat surface with the identical material.

The surface roughness $r$ is defined by the liquid-solid surface contact area divided by the droplet projected area, therefore, for a roughness surface $r$ is always more than 1. According to the Wenzel equation, $\theta^W > \theta > 90^\circ$ when the surface is hydrophobic; and $\theta^W < \theta < 90^\circ$ when the surface is hydrophilic. The micro- or nano- structures enhance both hydrophobicity and hydrophilicity depending on the wettability of the flat surface with the identical material.

The decrease in the contact angle hysteresis is attributed to the switching from the Wenzel to the Cassie–Baxter state because of the increased air fraction leading to the suspension of water droplet on top of the asperities as shown in figure 2-3(b). The suspension of water droplet is also described as a composite state.

For the droplet in Cassie-Baxter state, the apparent contact angle $\theta^C$ can be described using the Cassie-Baxter equation:

$$cos\theta^C = f(1 + cos\theta) - 1$$

(2 – 4)

where $\theta^c$ is the apparent contact angle; $f$ is the solid-liquid fraction, which is defined as pillar top surface area divided by the droplet projected area. The solid-liquid fraction $f$ is always less than 1, and is not a function of the pillar height. For the droplet in Cassie–Baxter state, the apparent
contact angle \( \theta^C \) is a sole function of the solid-liquid fraction \( f \) for a given surface with the contact angle \( \theta \), and increases with the decreasing solid-liquid fraction \( f \).

In order to obtain superhydrophobic surface with the apparent contact angle \( \theta^C > 150^\circ \) and the contact angle hysteresis < 5\(^\circ\), in practical, the hierarchical two-tier structure with nanopillars on top of micropillars is usually adopted to further decrease the solid-liquid fraction \( f \) so that the apparent contact angle \( \theta^C \) can be enlarged over 150\(^\circ\) with the droplet maintaining in Cassie-Baxter state.

2.5 Background for Surface Enhanced Ramen Spectroscopy Sensing

Surface-enhanced Raman spectroscopy (SERS) has emerged to be an ultrasensitive molecular detection technique for (bio-)chemical analyses.\(^{25-27}\) By increasing both laser excitation and inelastic Raman scattering rates from analyte molecules in hot spots of intense optical fields, plasmonic nanostructures can achieve a significant SERS enhancement factor (EF) above \( 10^7 \).\(^{86-88}\) In particular, metal-insulator-metal (MIM) nanocavities with sub-10 nm plasmonic nanogaps can support gap surface plasmon modes,\(^{89,90}\) and allow extremely hot spots with SERS EFs up to \( 10^{10} \).\(^{91}\)

A recent effort in SERS research is to achieve a fast and ultrasensitive detection of analytes at ultralow concentrations for applications ranging from point-of-care biomedical diagnosis, food, and water quality analyses, and to environmental monitoring.\(^{27-30}\) The diffusion-limited transport processes, however, makes it very challenging to effectively deliver analytes of sub-nanomolar-level low-concentrations into sparse sub-10-nm-scale hot spots on the SERS substrates within a relatively short detection time window.\(^{31,32}\) To overcome the diffusion limit, researchers have created superhydrophobic SERS substrates to maintain a high contact angle (> 150\(^\circ\)) of analyte droplets during the natural evaporation process, which can allow an increased surface density of analyte molecules deposited into a reduced footprint area (< 50 \times 50 \mu m^2) for ultrasensitive SERS detection.\(^{35-38}\) Despite promising results, superhydrophobic SERS substrates typically require
surface coatings/modifications of hydrophobic layers on the hydrophilic plasmonic metal nanostructures. The surface-modified hydrophobic layers can impede analyte molecules to access SERS hotspots, introduce interfering Raman signals of hydrophobic materials layers, and deteriorate the SERS detection performance.

In this work, we report a new ultrasensitive SERS detection strategy enabled by Leidenfrost evaporation of analyte droplets on hierarchical plasmonic micro/nanostructures without the need for any hydrophobic surface coatings. The Leidenfrost effect describes that a liquid droplet sitting on a superheated surface can be levitated by a self-evaporated vapor layer underneath that also functions as a thermal barrier to prevent the droplet from boiling. As illustrated in Figure 1, compared to natural evaporation, Leidenfrost evaporation of analyte droplets results in a much smaller analyte deposition footprint on hierarchical plasmonic micro/nanostructures and thus leads to a much higher analyte molecule density and more intense SERS signals from the detection region. Hierarchical plasmonic micro/nanostructures are essential to enable Leidenfrost evaporation-assisted ultrasensitive SERS detection by 1) providing plasmonic nanostructures as SERS hot spots with high SERS enhancement factors (EFs) >10⁷, and 2) providing micro/nanopillar structures to facilitate the Leidenfrost evaporation of liquid droplets with a minimized liquid-solid contact area subject to reduced substrate heating temperature. By increasing the substrate temperature from the room temperature beyond a threshold temperature of ~120 °C to introduce the sufficient levitating force from the evaporated vapor, a liquid droplet on the hierarchical plasmonic micro/nanostructures can switch from the Wenzel state, featured with a relatively small contact angle of ~140° and a large final deposition area of ~4 mm², to the Cassie state featured with a relatively larger contact angle of ~170° and a much smaller final deposition area of ~450 μm². By carefully controlling the substrate heating process, we demonstrate that it is possible to levitate up only the circumferential region of a liquid droplet, i.e., in the Cassie state, while pinning the central region of a droplet on the hierarchical plasmonic micro/nanostructures, i.e., in the Wenzel state. Throughout such a dynamically tuned Leidenfrost
evaporation process, the analyte droplet maintained in the Cassie-Wenzel hybrid state can continuously shrink on a fixed position, leading to a remarkably minimized analyte deposition footprint for ultrafast and ultrasensitive SERS detection without the need for any additional surface treatments.

Figure 2-4. Schematic of Leidenfrost effects assisted ultrasensitive SERS detection of analyte molecules using hierarchical plasmonic micro/nanostructures.
Chapter 3 Adaptive Optical Beam Steering and Tuning System Based on Electrowetting-Driven Fluidic Rotor

3.1 Chapter Introduction

With the rapid progress of multifunctional sensor network and electronic networking devices, reconfigurable beam steering components are indispensable to support network systems operating with high adaptability and with various functions. Currently, almost all such components are made of solid parts whose structures are rigid, and hence their functions are difficult to be reconfigured. Also, optical beam steering is still a very challenging problem compared to RF/microwave beam steering. In this paper, we present a watermill-like beam steering system that can adaptively guide concentrating optical beam to different receivers. The whole system comprises a liquid droplet actuation mechanism based on electrowetting-on-dielectric (EWOD) with an open-plate configuration, a superlattice-structured rotation hub, and an enhanced optical reflecting membrane attached to the hub as the beam reflector. The rotary hub is made of silicone oxycarbide ceramic with an octet-truss superlattice structure of ultralight weight (~8 mg), ultrahigh strength (9 MPa) and ultrahigh stiffness (950 MPa) and is additively manufactured by scanning optics projection micro-stereolithography (SOPμSL). A low frequency AC voltage is applied to transport a water microdroplet along the annular electrode loop to activate and rotate the specular reflector, to which the liquid droplet is adhered. A resistor-capacitor (RC) circuit network model of the EWOD system indicates that the EWOD driving force is in the order of hundreds of μN and its power consumption is ~10⁻⁵-10⁻⁴ W. The experimental results show that the specular reflector can be adaptively and agilely tuned within the lateral orientation of 360°, and the steering speed can reach as high as ~353.5°/s. This work demonstrates the feasibility of driving a macro-size, solid structure with liquid micro-droplets, opening a new avenue for developing adaptive and reconfigurable
components in modern sensor network.


### 3.2 Electrowetting on Dielectric Platform Design

We designed an annular array of electrowetting on dielectric (EWOD) electrodes on a glass substrate to implement the circular transport of a liquid droplet. The open-plate EWOD configuration\(^\text{15}\) was adopted in this study to manipulate the locomotion of a liquid droplet, and the EWOD-driven droplet could successively rotate the reflecting membrane which is attached to the central hub. As shown in Figure 3-1(a), the 24 ring-arrayed trapezoidal elements are evenly patterned on the substrate. To achieve facile droplet actuation and continuous droplet movement with a relatively low driving voltage, interdigitated teeth are implanted along the radial edges of each electrode element so that the leading edge of the droplet can easily reach the next-to-be activated electrode unit. The inner diameter of the annulus electrode is 7 mm, and the outer diameter is 15 mm. As the array of EWOD electrodes are uniformly distributed, each trapezoidal unit spans 15° with an outer edge of 2 mm and an inner edge of 1 mm; the length and the width of the teeth structure are 0.7 mm and 0.1 mm, respectively. The overall size of each electrode unit is 2.5 mm by 3.8 mm as shown in Figure 3-1 (b). In addition, the gap between each pair of adjacent elements needs to be reasonably small so that the three-phase contact line on the next-to-be-actuated element can be sufficiently long to generate a strong driving force.\(^\text{95}\) Consequently, we made the gap between each pair of interwoven teethes protruding from neighboring electrode elements to be 30 μm.
Figure 3.1. Design of rotary electrowetting on dielectric (EWOD) electrode pattern. (a) Layout of the annular array of EWOD electrodes with leads. (b) Trapezoidal electrode element with interdigitated teethes.

3.3 Design of Superlattice Rotary Hub and Reflecting Membrane

The overall EWOD-based optical beam steering system consists of an annular EWOD substrate, a rotational hub, and a reflecting membrane as shown in Figure 3-2(a). The adaptive beam steering is achieved by tuning the reflecting membrane through the EWOD-actuated liquid droplet. To enable smooth and facile rotation of the reflecting membrane, the 3D printed superlattice structure as illustrated in Figure 3-2(b) was adopted as the rotary hub with ultralow weight and superior mechanical properties. Thus a stretch-dominated cellular structure of the octet-truss superlattice\textsuperscript{96} was fabricated using SOP\textsubscript{µ}SL system as shown in Figure 3-2(c),\textsuperscript{97} which is capable of fabricating large-volume, high-resolution complex superlattice structures. The ultraviolet (UV)-curable siloxane resin was formulated based on previous work\textsuperscript{97} and was added into the resin bath to form the pre-ceramic parts. The 3D hub design was sliced into a sequence of 2D patterns, which were sequentially transmitted to a spatial light modulator (SLM) and were illuminated with UV light from a light-emitting diode (LED) array. The exposed resin formed a cured layer imaging the shape of the 2D slice, and then the z-axis elevator was lowered to recoat a thin film of the liquid resin
for the subsequent 2D slice exposure. The 2D image projection step was then repeated to form the whole 3D structures as designed. Pre-ceramic parts were subsequently pyrolyzed in a tube furnace at 1000° C with ultra-high-purity Argon gas to form the superlatticed SiOC ceramic, as shown in Figure 3-2 (d) and (e).

Figure 3-2. Schematic of rotary electrowetting on dielectric (EWOD) optical beam steering system. (a) the assembled EWOD rotor system; (b) the superlattice hub design; (c) the scanning optics projection microstereolithography (SOPµSL) system; (d) the pre-ceramic hub. (e) the pyrolyzed SiOC hub. The SOPµSL system is employed for reducing the weight of the hub while maintaining its ultrahigh stiffness.

The relative density, $\bar{\rho}$, of the octet-truss lattice can be calculated as $\bar{\rho} = 6\sqrt{2} \left(\frac{b}{l}\right)^2$, where $b$ is the strut thickness of the lattice and $l$ is the node-to-node length. Therefore, the relative density of the as-formed lattice structure is 14%. Based on the volume of the hub (~24 mm$^3$) and the density of the base material (2.2 g cm$^{-3}$ for SiOC), the weight of the latticed hub is only ~7.4 mg. The strength of the hub $\sigma_{eff} \sim \alpha \bar{\rho} \sigma_s$ and its stiffness $E_{eff} \sim \beta \bar{\rho} E_s$, where $\sigma_s$ and $E_s$ are the strength and the
Young’s modulus of SiOC, respectively; $\alpha$ and $\beta$ are pre-factors. Therefore, the superlatticed rotary hub printed by SOP$\mu$SL has a high strength $\sigma_{eff} = 9$ MPa and an ultra-high stiffness $E_{eff} = 950$ MPa.

To reduce the friction between the shaft and the hub, silicone oxycarbide (SiOC) and stainless steel were adopted as the hub and the shaft materials, respectively, since the friction coefficient between steel and ceramic is as low as 0.1 ~ 0.2. The outer diameter of the hub was designed to be 2.4 mm, and the inner diameter was designed to be 1.2 mm in order to fit the stainless steel shaft. An elliptical part was integrated on to the bottom end of the hub to further reduce the friction between the hub and the shaft base as shown in Figure 3-2 (b). A vertical edge of 0.12 mm thick protruding out of the hub sidewall was pre-fabricated to attach the reflection plate. Figure 3-2 (a) shows the assembled rotary EWOD device, on which a liquid droplet actuated by EWOD drags the reflector membrane (3M Vikuiti™ enhanced specular reflector) to rotate around the central shaft for beam-steering purpose. Additionally, the reflection plate was spin-coated with a thin layer of hydrophobic fluoropolymer (FluoroPel™ PFC1101V-FS, Cytonix) so that the liquid droplet could not spread over the reflector surface upon contacting it.

3.4 Electrowetting Driving Force and Resistant Force Analysis

The EWOD driving force versus the resistant force, which mainly includes the hub-shaft rotating friction and the droplet liquid-substrate friction, were analyzed to verify the feasibility of the droplet actuation. In this work, an AC voltage was applied to manipulate the droplet transport since it can effectively mitigate dielectric polarization and prevent liquid electrolysis, as demonstrated in our previous work. To analyze the EWOD driving force, a water droplet straddling two electrodes on the EWOD platform as shown in Figures 3-3(a) and 3-3(b) was studied. Each trapezoidal electrode element with teeth is simplified as a sector-shaped unit in this analysis. One of the co-planar electrodes was activated with the leading edge of the droplet formed on it, and the
adjacent electrode was assigned as the ground. Phenomenologically, the electrostatic energy stored in the dielectric layer under the droplet leads to a change in the apparent contact angle, inducing electrohydrodynamic (EHD) force inside the droplet to drive it toward the activated electrode. On the other hand, the EWOD driving force can be analyzed via the lumped-parameter method based on an equivalent RC circuit of the EWOD system\(^{100}\), as shown in Figure 3-3(a).

The area of the droplet on the actuated electrode, \(A_a\), and that on the grounded electrode, \(A_g\), can be determined by the droplet position angle \(\theta\), which is formed between the center of the droplet and the gap of the two electrodes. As illustrated in Figure 3-3(b), \(A_a\) and \(A_g\) are calculated as:

\[
A_a(\theta) = \frac{2 \cos^{-1} \left( \frac{R \sin \theta}{r} \right)}{2} r^2 - R \sin \theta \cdot r \cdot \sin \left( \frac{2 \cos^{-1} \left( \frac{R \sin \theta}{r} \right)}{2} \right) \\
A_g(\theta) = \pi r^2 - A_a(\theta)
\]  

(3 - 1)

(3 - 2)

where \(r\) is the droplet radius and \(R\) is its radial distance from the shaft. In the lumped-parameter method, each dielectric part including the water droplet itself is considered as a RC component or RC group. For the co-planar configuration of EWOD, the RC circuit model consists of five RC components connected in series as shown in Figure 3-3(a). The resistances and capacitances of each RC component, which are dependent of \(A_a\) and \(A_g\), are needed in order to calculate the equivalent total capacitance of the RC network.

In Figure 3-3(a) of the main text, the resistance and capacitance for each RC group are given as the following:

\[
C_{fg} = \frac{\varepsilon_0 \kappa_f A_g}{h_f}, \quad C_{sg} = \frac{\varepsilon_0 \kappa_s A_g}{h_s}, \quad C_{fa} = \frac{\varepsilon_0 \kappa_f A_a}{h_f}, \quad C_{sa} = \frac{\varepsilon_0 \kappa_s A_a}{h_s}, \quad C_w = \frac{\varepsilon_0 \kappa_w A_w}{h_w}
\]

\[
R_{fg} = \frac{h_f}{\sigma_f A_g}, \quad R_{sg} = \frac{h_s}{\sigma_s A_g}, \quad R_{fa} = \frac{h_f}{\sigma_f A_a}, \quad R_{sa} = \frac{h_s}{\sigma_s A_a}, \quad R_w = \frac{h_w}{\sigma_w A_w}
\]  

(3 - 3)
where $C_{fg}$ and $R_{fg}$ are the capacitance and resistance of the fluoropolymer layer on the grounded electrode, respectively; $C_{fa}$ and $R_{fa}$ are the capacitance and resistance of the fluoropolymer layer on the actuated electrode, respectively; $C_{sg}$ and $R_{sg}$ are the capacitance and resistance of the dielectric Si$_3$N$_4$ layer on the grounded electrode, respectively; $C_{sa}$ and $R_{sa}$ are the capacitance and resistance of the dielectric Si$_3$N$_4$ layer on the actuated electrode, respectively; $C_w$ and $R_w$ are the capacitance and resistance of the water droplet, respectively; $\varepsilon_0$ is the vacuum permittivity; $\kappa_s$ and $\sigma_s$ are the dielectric constant and the electrical conductivity of the dielectric material Si$_3$N$_4$, respectively; $\kappa_f$ and $\sigma_f$ are the dielectric constant and the electrical conductivity of the fluoropolymer (FluoroPel$^\text{TM}$ PFC1101V-FS), respectively; $\kappa_w$ and $\sigma_w$ are the dielectric constant and the electrical conductivity of water, respectively; $A_a$ is the area of the droplet on the actuated electrode; $A_g$ is the area of the droplet on the grounded electrode; $A_w$ is half of the contact area between the water droplet and the substrate, which is approximated to $(A_a + A_g)/2$; $r$ is the radius of the droplet; $h_s$ is the dielectric layer thickness; $h_f$ is the fluoropolymer layer thickness; and $h_w$ is the center-to-center distance between $A_a$ and $A_g$.

Table 3-1. Parameters for rotary EWOD force analysis

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum permittivity</td>
<td>$\varepsilon_0 = 8.854 \times 10^{-12}$ F/m</td>
</tr>
<tr>
<td>Si$_3$N$_4$ dielectric constant and electrical conductivity and thickness</td>
<td>$\kappa_s = 7.5$  \n $\sigma_s = 10^{-8}$ S/m \n $h_s = 120$ nm</td>
</tr>
<tr>
<td>FluoroPel$^\text{TM}$ PFC1101V-FS dielectric constant and electrical conductivity and thickness</td>
<td>$\kappa_f = 1.9$  \n $\sigma_f = 10^{-13}$ S/m \n $h_f = 200$ nm</td>
</tr>
<tr>
<td>DI water dielectric constant and electrical conductivity</td>
<td>$\kappa_w = 80.10$ \n $\sigma_w = 2.4 \times 10^{-4}$ S/m</td>
</tr>
<tr>
<td>Radius of the droplet</td>
<td>$r = 3$ mm</td>
</tr>
</tbody>
</table>
Table 3-1 shows the value of each parameter used in the EWOD driving force calculation.

![Diagram](image)

**Figure 3-3.** Schematic of electrowetting lumped energy analysis. (a) Side view and (b) top view of a droplet straddling two electrodes with an applied potential difference. The whole electrowetting on dielectric (EWOD) system can be considered as a resistor-capacitor (RC) circuit network for EWOD force analysis. For simplicity, the effect of interdigitated teeth structures along the radial edges of each electrode is ignored in this analysis. (c) EWOD driving force versus droplet transport angle $\theta$. (d) EWOD system power consumption versus droplet transport angle $\theta$.

The five RC groups are connected in series, so the total impedance is the summation of the impedances of five components:

$$Z_{tot} = Z_{fg} + Z_{fa} + Z_{tg} + Z_{ta} + Z_w = \frac{1}{R_{tot} + \frac{1}{j\omega C_{tot}}} \quad (3-4)$$
By expressing the total impedance $Z_{tot}$ with the capacitances and resistances of each component, the equivalent total capacitance of the RC network, $C_{tot}$, can be derived. With the value of $C_{tot}$ and $Z_{tot}$ obtained, the total electrostatic energy stored in the RC network 

$$E = \frac{1}{2} C_{tot} V_{RMS}^2$$

and the power consumption of the EWOD system $P_{tot} = \frac{V_{RMS}^2}{Z_{tot}}$ can be estimated, where $V_{RMS} = \frac{1}{2} V_{pk-pk}$ is the root-mean square of the applied square-wave AC voltage, and $V_{pk-pk}$ is the peak to peak voltage referring to the amplitude of the square wave. We applied $V_{pk-pk} = 40$ V at 20 Hz in the experimental tests, so $V_{RMS} = 20$ V in the force analysis. Therefore, the electrostatic energy stored in the system increases with the square of the applied voltage magnitude. As the equivalent total capacitance is a function of the droplet position angle $\theta$, which is formed between the droplet centroid and the electrode gap, and the angular frequency $\omega$ of the AC voltage, i.e., $C_{tot} \sim f(\theta, \omega)$, the EWOD driving force on the droplet can be calculated by taking the derivative with respect to $\theta$, i.e., $F_{ewod} = \frac{dE(\theta)}{d\theta}$. The EWOD driving force on the droplet and the power consumption are plotted against the position angle $\theta$ in Figures 2(c) and 2(d), respectively. Since the fan angle of each electrode sector is $15^\circ$, Figure 3-3(c) and 3-3(d) are plotted in the range of $-7.5^\circ$ to $7.5^\circ$, corresponding to a full step of the droplet movement.

As shown in Figure 3-3(c), RC network analysis indicates that (1) the magnitude of EWOD driving force is in the order of hundreds of $\mu$N; (2) the EWOD force is always directed toward the central gap between the two straddled electrode units; and (3) the magnitude of EWOD force barely changes with the low AC frequencies (< 25 Hz). From Figure 2(d), it can be concluded that: (1) the power consumption of the EWOD system increases with increasing AC frequency; (2) the magnitude of the power consumption is in the order of $\sim 10^{-5} - 10^{-4}$ W; (3) the maximum power consumption during each step of droplet actuation happens at the central gap between the two straddled electrode units. This RC network analysis elucidates the observed droplet movement characteristics actuated by EWOD and the power consumption of the EWOD system.
To calculate the required driving force to rotate the membrane reflector, we denote the inner diameter of the hub as $d_1$, the outer diameter of the hub as $d_2$, the distance between the droplet and the axis of the shaft as $l$, the moment of inertia of the hub as $J_{hub}$, and the torque induced by the rotational friction between the shaft and the hub as $\tau_f$. Since the droplet drags the reflecting membrane, which is attached to the hub, the rotation angle of the hub is equal to the droplet position angle $\theta$. Assuming the moment of inertia of the thin reflector membrane is negligible, we can apply the following governing equation for the rotation of the hub:

$$J_{hub}\ddot{\theta} + \tau_f - F_{droplet}l = 0 \quad (3-5)$$

where $F_{droplet}$ is the driving force on the reflector exerted by the water droplet. The friction torque $\tau_f$ can be derived from the following:

$$\tau_f = \int_0^{2\pi} F_f \frac{d_1}{2} d\theta \quad (3-6)$$

where $F_f = \mu G$ is the friction between the shaft and the rotary hub, $\mu \approx 0.1$ is the friction coefficient between the steel shaft and the ceramic hub, and $G$ is the gravity of the rotary hub and the reflector membrane. Combining equations (3-5) and (3-6), we estimated the required minimum driving force exerted by the EWOD-actuated droplet on the membrane reflector as $F_{droplet} \approx 2.5 \times 10^{-5} \text{ N}$.

The other resistant force due to friction between the droplet and the EWOD platform can be scaled as:

$$F_{liquid-solid friction} \sim \pi r \gamma (\cos \theta_{adv} - \cos \theta_{rec}) \quad (3-7)$$

where $\gamma = 0.072 \text{ N m}^{-1}$ is surface tension of water, $r = 3 \text{ mm}$ is the droplet radius, $\theta_{adv} \approx 130^\circ$ is the droplet advancing contact angle due to electrowetting, $\theta_{rec} \approx 105^\circ$ is the droplet receding contact angle on the substrate. Substituting these parameter values into equation (3-7), the droplet-substrate friction force $F_{liquid-solid friction} \approx 1 \times 10^{-5} \text{ N}$. Since the EWOD driving force $F_{EWOD}$
from the droplet can be as high as $3 \times 10^{-4}$ N, which is an order of magnitude higher than the force needed to rotate the hub (i.e., $F_{EWOD} \gg F_{droplet} + F_{liquid-solid \ friction}$), we are certain that the EWOD-actuated water droplet can facilely drive the reflection plate toward the specific orientation as desired.

3.5 Fabrication of Rotary EWOD Substrate

This rotary EWOD platform fabrication process mainly includes the following sequential steps: electrode array deposition, dielectric layer coating, hydrophobic layer spin-coating, and flex cable attachment. The annular array of EWOD electrodes were fabricated on a glass slide (Corning 26005, Ted Pella). First, a thin layer of S1813 photoresist (Dow® Electronic Materials MICROPOSIT™) was spin-coated on the glass substrate, and then the photoresist layer was hardened by soft baking at 115°C for 1 min. Next, the annular array of electrodes was patterned in the photoresist by exposing ultraviolet (UV) light through the electrode mask in a photolithography system (Karl Süss MA6). After patterning the electrode array via photolithography, the three layers of 5-nm-thick Ti, 120-nm-thick Au, and 5-nm-thick Ti were successively deposited on the glass substrate using e-beam evaporation (Kurt J. Lesker PVD 250). Then, the electrode pattern was presented by dipping the substrate into the developer solution AZ 400K. A 120-nm-thick Si$_3$N$_4$ dielectric layer was subsequently deposited on the top of the electrode array by PECVD (Trion Orion III). With a low deposition rate of 49 nm/min, the chemical vapor deposition process can effectively mitigate the formation of pinholes in the dielectric layer, which would otherwise lead to undesired liquid electrolysis during EWOD operations. Then, a 50-nm-thick fluoropolymer (FluoroPel™ PFC1101V-FS, Cytonix) was spin-coated on the dielectric layer. The hydrophobic coating gives rise to a larger contact angle of ~112° for the water droplet and smaller contact friction, which is desirable for EWOD droplet manipulation. Finally, the 24 leads of the electrodes were bonded with the flex cable using a hot bar soldering system (PHM 1-1, Fancort Industries).
For EWOD operations, the EWOD rotary device was connected to a custom-designed, multi-channel controller, which provides 0–50V of DC/AC voltages on 128 channels.\textsuperscript{53}

### 3.6 Steering Speed, Steering Range, and Signal Transmission Loss

The EWOD rotary steering system was assembled after the fabrication of each component such as the EWOD platform and the superlattice rotary hub. Then the steering speed and range of the EWOD-driven reflecting membrane were tested on this EWOD rotary system. Since water is one of the most widely used electrowetting fluids, we adopted deionized (DI) water in this work for demonstrating the feasibility of actuating a macroscale reflecting membrane by a microdroplet as the proof of concept. To slow down the evaporation process of a water droplet, a proper amount of glycerol can be added into water to form glycerol–water mixture. For practical applications, ionic liquids are good alternatives due to their extremely low vapor pressure (as low as $\sim10^{-12}$ mm Hg), negligible evaporation rate, and high electrical conductivity.\textsuperscript{102} Figure 3-4(a) shows the setup of the EWOD beam steering system, including the annular array of EWOD control electrodes, the superlattice rotary hub, the membrane reflector, and a DI water droplet as the actuation medium. The assembled rotary device has the dimension of 5 cm x 7.5 cm x 2.5 cm, which can be made more compact by further condensing electrode elements and leads. In the open plate configuration of EWOD, the footprint of the droplet is required to span at least 3 electrode units so that the droplet can be continuously actuated forward.\textsuperscript{53} According to this actuation criterion and the electrode unit size, a DI water droplet of about 50 μL was adopted by us for EWOD actuation. A square-wave AC voltage of 40 V\textsubscript{AC} with a low frequency of 20 Hz was applied to actuate the droplet while preventing dielectric layer polarization.\textsuperscript{16} The droplet was consecutively driven forward by successively powering the electrode elements under the leading edge of the droplet. For beam steering purpose, the droplet was attached to the reflector and dragged the reflector to rotate to the desired orientation via the digital actuations of EWOD, as illustrated in Figure 3-4(b). By sequentially turning on the electrode units in a clockwise direction, the whole rotating (steering)
process of the reflection plate was captured by a camera (Canon VIXIA HF R700) as shown in Figures 3-4(c) to 3-4(f).

Figure 3-4. Experimental test of rotary electrowetting on dielectric (EWOD) beam steering system. (a) Rotary electrowetting on dielectric (EWOD) beam steering system. The dashed white parallelogram indicates the reflecting membrane. (b) Side view of the droplet adhered to the reflecting membrane; (c)-(f) the snapshots of the reflecting membrane at different orientations. The dashed line in each snapshot indicates the top edge of the reflecting membrane. (g) Steering speed of the reflecting membrane driven by EWOD in response to the intermittent and synchronized square-wave alternating current (AC) signals. The
dashed line indicates the average angular velocity and the average linear velocity. (h) Experimentally measured specular reflectance of the reflecting membrane with and without the fluoropolymer coating.

The real-time steering speed was obtained by post-image processing of the captured movie. Assuming the initial orientation of the reflection plate is $0^\circ$ at $t = 0$ s, Figures 3-4(b) – 3-4(f) show the snapshots of the droplet with the reflecting membrane in four different orientations due to the EWOD digital actuations. Accordingly, Figure 3-4(g) displays both the angular velocity and the linear velocity of the membrane corresponding to the synchronized input square-wave AC signal. The experimental results show that: (1) the reflector can be stepwise tuned with a pace of $7.5^\circ$ in each EWOD actuation, which is mainly contingent on the electrode element fan angle; (2) the actuation manner of the droplet and hence the reflecting membrane is pulse-like with the maximum transient angular steering velocity as high as $353.5^\circ$ s$^{-1}$ (the maximum droplet linear velocity is 33.9 mm s$^{-1}$) and the average angular steering velocity during a full circle of trail is $\sim 21.7^\circ$ s$^{-1}$; (3) the dynamic response of the droplet lags behind the input AC signal about 0.02s because of the droplet inertia; and (4) the EWOD rotary device enables $360^\circ$ lateral steering of the reflector around the shaft without contact angle saturation effect. It is noteworthy that the water droplet oscillates in response to the AC input signals during each step of EWOD actuations. Such droplet oscillations can be effectively mitigated by applying a higher frequency AC voltage in EWOD with compromised power consumption. The angular steering resolution can be further improved by designing finer electrode elements with a smaller sector angle, i.e., $< 7.5^\circ$.

Another vital factor of a beam steering system is the insertion loss of the system. Insertion loss is the signal power loss that arises as a result of inserting a certain device (e.g., reflecting membrane) in the signal transmission path.$^{103}$ Mathematically, it is the logarithmic ratio of the power entering, $P_{in}$, to the power coming out of the beam steering system, $P_{out}$, expressed in dB:

$$Insertion\ loss\ (dB) = 10 \log \frac{P_{in}}{P_{out}} \quad (3 \text{ – 8)}$$
Any beam steering system with substantial amount of transmission power loss can significantly degrade the overall performance of the system. Furthermore, lower insertion loss implies lower energy requirements, leading to enhanced energy efficiency of the system. The signal transmission performance of our EWOD rotary system mainly depends on the specular reflectance of the reflecting membrane (3M Vikuiti™ enhanced specular reflector). In order to prevent the droplet spreading over the reflecting membrane, the reflecting membrane was coated with a thin hydrophobic layer of fluoropolymer (FluoroPel™ PFC1101V-FS, Cytonix) during the experiment. The specular reflectances of the reflecting membrane with and without the fluoropolymer coating as shown in Figure 3-4(h) were measured in a broadband wavelength of 200 nm to 1000 nm using the spectrophotometer (Cary 5000 UV-vis-NIR).

The measured specular reflectance indicates that the optimum wavelength of this reflecting membrane is in the range of ~ 400 nm – 800 nm. In this optimum spectrum, the average specular reflectance of the membrane without the fluoropolymer coating $\rho_{avg-no~coating}$ can reach as high as 98.2%. In comparison, the average specular reflectance of the membrane with coating $\rho_{avg-coating}$ is ~ 86.8%. Therefore, the reflecting membrane without any coating has a superb intrinsic reflectance, while the hydrophobic coating slightly degrades the specular reflectance of the reflector. It is thus concluded that the insertion loss of this rotary EWOD beam steering system is only ~1.5 dB in the broadband spectrum of 400 nm–800 nm. To have a better performance of signal transmission and even lower insertion loss, we can apply a thinner coating of fluoropolymer on a high specular reflectance membrane or make a hydrophobic-hydrophilic hybrid surface treatment.

### 3.7 Optical Beam Tuning and Steering Accuracy

Based on the EWOD rotary device, we conducted beam steering tests by adaptively redirecting an incident laser beam to the target photodetectors located at three different directions, as shown in
Figure 3-5(a). The red laser beam with an intensity of 1.18mW at λ = 635 nm was adopted as the signal source. Three photodiodes, i.e., PD1 (ThorLab DET100A), PD2 and PD3 (ThorLab S120c), were used as the signal detectors with the aperture size of 9.5 mm in diameter and the light detecting resolution of 0.001 mW, and they were placed 25 cm away from the EWOD rotary hub at the directions of 96°, 127°, and 221°, respectively (the incident direction of the laser beam was set as 0°). To deduct the ambient light influence, the three photodetectors were first calibrated to filter out the effect of the background light. The reflecting membrane in contact with the droplet was tuned clockwise to steer the incident beam to PD1, PD2 and PD3 in sequence. The illumination lasted for ~ 1s on each receiver, as reflected by the three pulses in Figure 3-5(b). Driven by the square-wave AC voltage (40V<sub>AC</sub>, 20Hz), the EWOD rotary system fulfilled the desired beam steering via adaptively modulating the orientations of the rotating membrane. More accurate characterization of the steered beam spot position can be achieved by measuring the beam center position.

Reflecting membrane steering repeatability and reflecting membrane angular tuning resolution of the EWOD rotary device are key characteristics of the electrowetting-driven beam steering systems. As such, a reference electrode was arbitrarily chosen from the 24 electrodes and the orientation of its left edge of the reference electrode was set as 0°. Thus, the reflecting membrane steering accuracy was evaluated by EWOD tuning the position of the reflecting membrane (attached with the droplet) repetitively between two adjacent electrodes and inspecting the alignments of the membrane with the targeted orientations at -7.5°, 0°, and +7.5°, respectively, as shown in Figure 3-5(c). To this end, fifty trials for each orientation as demonstrated by Supplementary Movie 3 were performed by EWOD actuating the droplet both clockwise and counter-clockwise in order to align the membrane with the three orientations. With the reflecting membrane relative steering error defined as $\varepsilon_{relative} = \frac{\theta_{measured} - \theta_{targeted}}{\theta_{measured}} \times 100\%$, the statistical results as shown in Figure 3-5(d) indicate that the average relative positioning error for each case
are $\varepsilon_{-7.5^\circ} = 0.32\%$, $\varepsilon_{0^\circ} = -0.06\%$, and $\varepsilon_{+7.5^\circ} = -0.37\%$, the maximum relative positioning error measured in the total one hundred and fifty trails is 0.8% ($\max \varepsilon_{-7.5^\circ} = 0.76\%, \max \varepsilon_{0^\circ} = 0.24\%, \text{and} \; \max \varepsilon_{+7.5^\circ} = -0.8\%$), and the maximum standard deviation of the steering relative positioning error is 0.25% ($\sigma_{-7.5^\circ} = 0.23\%, \sigma_{0^\circ} = 0.16\%, \text{and} \; \sigma_{+7.5^\circ} = 0.25\%$). The small reflecting membrane relative steering error indicates the superb steering repeatability of the EWOD rotary system, and the low relative error standard deviation indicates the high precision of the EWOD-based digital tuning. As noticed, the majority of relative positioning errors for the $-7.5^\circ$ case are positive whereas most of the relative positioning errors are negative for the case of $+7.5^\circ$ steering, resulting mainly from the concentricity misfit between the rotary hub and the center of the annular electrode loop. The concentricity error can be mitigated by dwindling the diameter of the shaft so that the shaft can be more accurately concentric with the center of the annular electrodes. Furthermore, optimizing the inner diameter of the rotary hub to be more compatible with the shaft size is another approach to reducing the circular runout of the rotary hub during steering and in the meantime maintaining a low pivoting friction. As per the mechanism of specular reflection, the stepwise adjustable beam steering angle is double of the orientation change of the reflecting membrane, which is $15^\circ$ of tuning in this case. Accordingly, the beam steering error is magnified twice relative to the reflecting membrane steering error as well. In the future work, we will further improve the beam steering performance by optimizing the rotary hub dimension and making the rotary hub concentric with the annular array of electrodes. In short, the EWOD rotary system is able to adaptively orient the reflection membrane with a relatively high steering accuracy ($\varepsilon_{\text{relative}} < 0.52\%$).
Figure 3-5. Optical beam steering test and characterization of reflecting membrane steering accuracy. (a) Beam steering setup based on the rotary electrowetting on dielectric (EWOD) platform. (b) Steered beam signals detected by the three distributed photodiode receivers. (c) The three aimed orientations (-7.5°, 0°, and +7.5°) of the reflecting membrane on the rotary EWOD platform for steering accuracy and repeatability testing. (d) The relative error of the reflecting membrane steering angle. Each box chart and error bar show an average and standard deviation of fifty measurements conducted by tuning the reflecting membrane to three target directions.

In general, the main quantities defining the performance of a liquid-based beam steering system are the maximum steering angle, the maximum steering angular velocity, and the magnitude of actuation voltage (power consumption). The experimental results of our EWOD rotary beam steering system are compared with the state-of-the-art liquid-based beam steering devices as shown in Table 3-2. Our rotary EWOD system is unique and provides outstanding performance.
over the existing liquid-based beam steering systems, most of which are based on light refraction to achieve beam steering with a relatively high insertion signal loss, a high actuation voltage, a limited steering range and steering speed. The main merits of our rotary EWOD system can be summarized as: (1) Integration of rotary EWOD actuation mechanism with a low friction superlattice hub to achieve adaptive beam steering by reflection with low insertion loss. In contrast to beam steering by light refraction, the beam steering by tuning the reflecting membrane orientation via EWOD can significantly mitigate the dispersion and aberration of beam signals during transmission, leading to an insertion loss as low as ~1.5dB; (2) Innovative rotary electrode design for EWOD actuation and rotation with a large beam steering range. The annulus-shaped EWOD electrodes enables the reflecting membrane fulfill a full loop of rotation without the limitation of contact angle saturation\textsuperscript{47}. So far, there is no other liquid-based beam steering systems that can achieve 360° full range beam steering as this work; (3) Optimum design of the electrode shape, size and gap, and the dielectric layer thickness to achieve low actuation voltage and power consumption. By comparing the droplet actuation performances with different dielectric layer materials and various designs of the electrode unit, the rotary EWOD system is optimally designed using the trapezoid electrode unit with interdigitated teeth (Supplementary Figure 1b) and using Si$_3$N$_4$ as the dielectric layer, leading to a low actuation voltage of 40 V\textsubscript{AC} and a low power consumption on the order of $\sim 10^{-5} - 10^{-4}$ W.
Table 3-2. Comparison with the state-of-the-art liquid-based beam steering devices

<table>
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<tr>
<th>Reference</th>
<th>Working principle</th>
<th>Steering range (°)</th>
<th>Max steering speed (°/s)</th>
<th>Voltage requiring (V)</th>
<th>Aperture size (mm)</th>
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<td>-</td>
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<td>0~360</td>
<td>353.5</td>
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</tbody>
</table>

### 3.8 Applications of EWOD Rotors for Optical Switch

The rotary EWOD beam steering system can be integrated to form an optical switching system for signal and data communication applications, as shown in Figure 3-6. The optical switching array enables long distance optical signal transmission with significant energy savings by keeping the signal transmission in the optical domain, i.e., the signals keep transmission through optical fibers and switches instead of through an optical-to-electrical-to-optical (OEO) conversion cycle. By tuning the reflecting membrane orientation of each rotary EWOD module, each input optical signal can be adaptively directed to a specific output port of an optical fiber. Besides the EWOD response time limit (tens of milliseconds), the signal steering speed is subject to the reflecting membrane size and mass. With a larger reflecting membrane, it takes longer time to orient the incident signal, therefore there is a trade-off between the steering speed and the EWOD module size. Since the EWOD-based optical switching system is amenable to different configurations, the rotary EWOD beam steering system can meet various optical signal transmission demands, such as signal transmission system miniaturization, multichannel signal transmission, and rapid optical signal switching, etc.
3.9 Chapter Summary

Beam steering is a widely investigated and used technology in optics, RF/microwave transmission and wireless communications, et al. In recent years, there has been a resurgent interest in this area because of the demanding needs from many critical future photonics applications such as lidar for automated driving and 3D sensing for virtual reality (VR). As such, there have appeared numerous techniques to solve the problems associated with current beam steering schemes based on bulk optics. However, most of these schemes still suffer from limited angular range, low speed and high optical loss, in contrast to the standard bulk-optic solutions that can cover almost all angles with very low loss.
In this work, we demonstrate an adaptive optical beam steering system based on the digital operations of an EWOD-driven fluidic rotor. Compared with other liquid-based beam steering devices, the EWOD rotary platform integrated with the 3D printed superlattice hub endows the system with the widest lateral steering range (360°), the fastest response (~ 353.5 °/s), the lowest voltage requirement (~ 40 V), and the lowest power consumption (~10^{-5} W). Via the specular reflection mode of beam steering, there is no optical aberration incurred during the beam transmission. Importantly, the full range steering is not constrained by the contact angle saturation effect of EWOD, which generally plays an inextricable role in conventional EWOD systems. Actually, by integrating EWOD-controlled liquid prism in to the system, the beam can be guided not only laterally but also omnidirectionally.

Moreover, the employment of this high performance EWOD-controlled fluidic rotor instead of the conventional motor-driven technique will facilitate the next generation development of reconfigurable electronic systems\textsuperscript{108,109} and optical switching systems with high adaptability. As such, this EWOD-driven beam steering system can be used for photonic synthetic aperture radar (SAR)\textsuperscript{110,111} applications. The typical setup of photonic SAR systems requires the steering of the optical beam around the target. Due to the bulky setup of the state-of-the-art photonic systems, it is very difficult to achieve this goal using conventional optical components and schemes. Inspiringly, the compact EWOD beam-steering devices can be easily integrated into the photonic SAR system to achieve adaptive optical beam steering for photonic SAR measurements. Therefore, it is our belief that this EWOD-based work could contribute to the photonics community by offering an alternative solution to beam steering.
Chapter 4  Meridian Whispering Gallery Modes (WGM) Sensing in A Sessile Microdroplet on Micro/Nanostructured Superhydrophobic Chip Surfaces

4.1 Chapter Introduction

A liquid microdroplet could be a naturally simple, miniaturized and effective optical cavity by itself due to the intriguing optofluidic properties associated with its surface-tension-induced spherical shape. It had been shown that optical whispering gallery modes (WGMs) can be present along the circular rim in the equatorial plane of a sessile microdroplet, and this phenomenon had been leveraged for biosensing demonstrations. However, optical coupling to such equatorial modes for their excitation and monitoring is mostly based on either tapered fiber coupling or free-space beam coupling, each of which demandingly requires precise alignment of the tapered fiber or the free-space beam adjacent to the equatorial surface of the resonator. In this paper, we show that WGMs could also be stimulated along the meridian plane of a liquid microdroplet resting on a properly designed nanostructured chip surface. The geometrical morphology and optical characteristics of a microdroplet cavity are critical to achieve a high quality Q factor and therefore to realize high-resolution in situ and in vivo monitoring of trace analytes. The unavoidable deformation along the meridian rim of the sessile microdroplet can be controlled and regulated by tailoring the nanopillar structures and their associated hydrophobicity. The nanostructured superhydrophobic chip surface and its impact on the microdroplet morphology are modeled by Surface Evolver (SE), which is subsequently validated by the Cassie-Wenzel theory of wetting. The influence of the microdroplet morphology on the optical characteristics of WGMs is further numerically studied using the Finite-Difference Time-Domain method (FDTD) and it is found that meridian WGMs with intrinsic quality factor Q exceeding 104 can exist. Importantly, such
meridian WGMs can be efficiently excited by a waveguiding structure embedded in the planar chip, which could significantly reduce the overall system complexity by eliminating conventional mechanical coupling parts. Our simulation results also demonstrate that this optofluidic resonator can achieve a sensitivity as high as 530 nm/RIU. This on-chip coupling scheme could pave the way for developing lab-on-a-chip resonators for high-resolution sensing of trace analytes in various applications ranging from chemical detections, biological reaction processes to environmental protection.


4.2 Microdroplet Resonator Morphology Modeling

For sensitive bioassay applications, a perfectly round liquid droplet is the ideal optical cavity in favor of the generation of high $Q$-factor WGMs. In the presence of gravity, however, a sessile water droplet on a hydrophobic surface takes the shape of spherical dome as its contact angle cannot reach beyond $120^\circ$.\textsuperscript{112} In particular, the morphology of the sessile droplet, whose degree of deformation can be reflected by the droplet’s contact angle and the ratio of droplet’s vertical height to lateral width, has a significant impact on the meridian WGMs generation. In order to alleviate gravity-induced flattening, the characteristic size of a sessile droplet should be much shorter than the capillary length, i.e., a small Bond number\textsuperscript{113}, so that surface tension becomes dominant to determine the droplet morphology, which makes the droplet close to a spherical shape with a higher value of the WGM quality factor. Moreover, for the purpose of reducing the optical radiation loss and saving the computational cost, a liquid droplet of 20 $\mu$m in diameter is selected by us for the optical meridian WGM study.
On the other hand, micro/nanoscale roughness decorated on a smooth surface has considerable influence on a fluid’s wettability thereon. Therefore, introducing nano/micro-structures onto a smooth hydrophobic surface can enhance its hydrophobicity to ultrahydrophobicity or even to superhydrophobicity\textsuperscript{94,114-116}, which can sustain a water microdroplet with a contact angle exceeding 150°. In this regard, the wettability of a liquid microdroplet on a solid surface is determined collectively by the interfacial energies between the solid, liquid and air phases and the solid surface roughness. Figure 4-1 is the schematic of a liquid microdroplet sitting on a rough substrate with an array of nanopillars. Actually, the effects of surface roughness on contact angle were first reported in the seminal work of Wenzel\textsuperscript{117} regarding a sessile droplet penetrating the surface roughness and the work of Cassie and Baxter\textsuperscript{118} regarding a droplet sitting atop surface roughness, respectively. Both works introduced an apparent contact angle $\theta_A$ on a rough surface, which is related to the intrinsic contact angle $\theta_Y$ on a flat surface, as shown in Figure 4-1.

**Figure 4-1.** Schematic of droplet morphology and interfacial tensions on a micro/nanostructured surface, where $a$ is the width of square pillars, $s$ is the gap between pillars, $h$ is the pillar height, $h_{\text{sag}}$ stands for the sagging of droplet base in to the roughness interstices, $h_{\text{gap}}$ is the space between the droplet curvature and the base surface of roughness interstices, $\theta_Y$ is the intrinsic contact angle on a flat surface, and $\theta_A$ is the apparent contact angle on a rough surface. $\gamma_{\text{ls}}$, $\gamma_{\text{sv}}$, and $\gamma_{\text{lv}}$ are the interfacial tensions of the liquid-solid interface, the solid-air interface, and the liquid-air interface.
While $\theta_Y$ is determined by the interfacial tensions, i.e., Young’s equation, $\theta_A$ is dependent on the liquid’s interfacial tensions and the surface roughness in a combined manner. In this study, we assumed the liquid microdroplet cavities sit in the Cassie state with ultrahigh mobility. Based on the energy minimization principle, the Cassie-Baxter relation can be derived as:\textsuperscript{119}

\[ \cos \theta_A = -1 + f(1 + \cos \theta_Y) \]  
\[ (4 - 1) \]

where \( f = \frac{a^2}{(a + s)^2} \) is the fraction of solid-liquid contact.

Besides the optofluiddic properties of the micro-resonator itself, understanding and developing such a microdroplet-based cavity system necessitates detailed information of the microdroplet morphology such as local interface curvature, local variation in the contact angle, and their evolutions with the changes of the geometrical shape or wettability of surface roughness. Therefore, the three-dimensional morphologies of sessile microdroplets resting on top of nanopillared surfaces are modeled by Surface Evolver (SE) in this work. Surface Evolver is a finite element method (FEM) based liquid morphology analyzing software.\textsuperscript{120} After defining the initial droplet profile, Surface Evolver evolves the surface toward the state with minimal surface energy by a gradient descent method.

The morphology of a sessile droplet in the Cassie-Baxter state depends on both the solid-liquid contact fraction \( f \) \textsuperscript{119} and the micro/nanopillar arrangement or configuration\textsuperscript{121,122}. For simplifying the modelling of droplet morphology and quantitatively analyzing the droplet contact angle, the apparent contact angle $\theta_A$ is modulated by adjusting the structural parameters of the nanopillar array based on equation (4-1). In this study, the textured surface is conformably coated by a thin layer of fluoropolymer (PFC1601V, Cytonix), so the intrinsic contact angle $\theta_Y$ is constrained at 112°,\textsuperscript{119} the water-air interfacial tension $\gamma_{lv}$ is 0.072 N/m and the gravity acceleration $g$ is 9.81 m/s$^2$ in the simulation. Surface Evolver distinguishes the inner and outer surface directions of a droplet surface by the surface normal, and the outer droplet surface is subject to the interfacial tension, including the liquid-solid tension and the liquid-air tension. Thus, a microdroplet in the Cassie-
Baxter state would require assigning energy boundary conditions to the wetted portion of the nanopillars plus the free microdroplet-air interface. Accordingly, the difference between the liquid-solid interfacial tension and the solid-air interfacial tension $\gamma_{ls} - \gamma_{sv}$ defines the energy boundary condition of the wetted nanopillar surface, and the liquid-air interfacial tension $\gamma_{lv}$ defines the microdroplet free facets. In practice, the energy of a nanopillar facet is implemented as a line integral applied to the edges of all nanopillar facets as suggested by Brakke.\textsuperscript{120} Area of each facet is sequentially modified by the local surface energy and the global energy. The propagation of constraints during refinement is handled internally by Surface Evolver. Every energy minimization step conducts a sequence of iteration, mesh refine, and vertex averaging. Finally, the Newton-Raphson method\textsuperscript{123} of energy minimization is executed for computation convergence. The convergence is regarded as achieved when the surface energy decrement is less than $10^{-19}$ units. In this SE model, a microdroplet of 20 μm in diameter in the final equilibrium state consists of ~30,000 individual nodes and the node number varies with the nanopillar geometries.

By adjusting the geometric parameters of the nanopillars, six different morphologies of water microdroplets in the Cassie-Baxter state with apparent contact angle $\theta_A$ ranging from 140° to 170° are achieved (see the morphology column in Figure 4-6). Those microdroplet-based cavity models were adopted as the micro-cavities for the meridian WGMs simulation in this study. For the comparison purpose, all the microdroplet cavities were simulated with their lateral spreading radius $r \sim 10 \, \mu m$. The related geometrical information of the microdroplets and the nanopillar patterns are listed in Table 4-1.
Table 4-1. SE simulation results of sessile microdroplet morphologies on rough surfaces

<table>
<thead>
<tr>
<th>Case</th>
<th>$f$</th>
<th>Theoretical $\theta_A$ (°)</th>
<th>Simulated $\theta_A$ (°)</th>
<th>$a$ (nm)</th>
<th>$s$ (nm)</th>
<th>$h$ (nm)</th>
<th>$r$ (µm)</th>
<th>$l$ (µm)</th>
<th>$h_{sag}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.375</td>
<td>140</td>
<td>141.7</td>
<td>615</td>
<td>390</td>
<td>53.7</td>
<td>10</td>
<td>13.07</td>
<td>3.7</td>
</tr>
<tr>
<td>2</td>
<td>0.290</td>
<td>145</td>
<td>146.5</td>
<td>527</td>
<td>452</td>
<td>57.1</td>
<td>10</td>
<td>11.75</td>
<td>7.1</td>
</tr>
<tr>
<td>3</td>
<td>0.215</td>
<td>150</td>
<td>151.2</td>
<td>411</td>
<td>476</td>
<td>57.5</td>
<td>10</td>
<td>10.64</td>
<td>7.5</td>
</tr>
<tr>
<td>4</td>
<td>0.151</td>
<td>155</td>
<td>156.3</td>
<td>329</td>
<td>518</td>
<td>60.3</td>
<td>10</td>
<td>9.32</td>
<td>10.3</td>
</tr>
<tr>
<td>5</td>
<td>0.097</td>
<td>160</td>
<td>161.5</td>
<td>271</td>
<td>601</td>
<td>63.1</td>
<td>10</td>
<td>7.86</td>
<td>13.1</td>
</tr>
<tr>
<td>6</td>
<td>0.025</td>
<td>170</td>
<td>170.9</td>
<td>126</td>
<td>668</td>
<td>69.8</td>
<td>10</td>
<td>6.35</td>
<td>19.8</td>
</tr>
</tbody>
</table>

As shown in Figure 4-2, the average difference between the theoretical contact angles predicted by Cassie-Baxter equation (Eq. 4-1) and the SE simulation results is only 1.35°, indicating all the six simulated models are in the Cassie state. We are also interested in the microdroplet local curvature within pillar intervals where sagging might exist. In our simulation, the smallest sagging depth $h_{sag}$ is ~3.7 nm for the case with $\theta_A = 141.7^\circ$; the biggest sagging depth is ~ 19.8 nm for the case with $\theta_A = 170.9^\circ$. The extent of sagging is governed by the balance of the internal Laplace pressure force and the capillary force. The Laplace pressure pushes the liquid interface into the surface interstices whereas the capillary force functions as the counteracting force. The sagging extent is related to the intrinsic contact angle $\theta_Y$ of the microdroplet and the geometry of surface textures. For a microdroplet sitting on a relatively sparsely pillared surface, the microdroplet-pillar contact line length is shorter compared to a microdroplet on the densely textured surface. As a result, the capillary force as an antiwetting force becomes relatively small so that the sagging depth tends to increase, which is consistent with our SE results as shown in Table 1. With the detailed morphology obtained, we studied the optical sensitivity of the microdroplet-based cavity.
Figure 4-2. Comparison of theoretical contact angles with simulated contact angles by Surface Evolver.

The main goal of this work is to analyze the relationship between the droplet contact angle (hence droplet morphology) and the optical WGM performance, and is not to study the factors that have impacts on the droplet contact angle. Nevertheless, we can adjust the droplet contact angle by tuning the space ratio of the pillars, which is one of the approaches that can be adopted to modify the droplet contact angle. Indeed, the arrangement of the pillars has a huge impact on the droplet contact angle.
Figure 4-3. Comparison between the Surface Evolver simulation and the experimental results of droplet morphology on a rough surface. (a) droplet morphology by Surface Evolver simulation; (b) sessile droplet on structured surface; (c) SEM image of the pillared surface.

To validate our Surface Evolver (SE) modelling, we compared the simulation results of Surface Evolver with the theoretical values of the Cassie-Baxter law (as shown in Figure 4-2) and with the experimental observation as shown in Figure 4-3. Since it is difficult to fabricate the nanopillars with a neat shape and a precisely controlled pillar gap, the micropillars are employed for the SE modeling validation. In the experiment, the contact angle of a sessile droplet on the structured surface was measured by the optical tensiometer (Attension® Theta). The square micropillars with the side length of 10 μm and the pillar gap of 80 μm were fabricated by DRIE, and were subsequently spin-coated with a thin layer of fluoropolymer (FluoroPel 1601V) whose intrinsic contact angle (CA) is 112°, as shown in Figure 4-3(c). The water droplet on the substrate turns out
to be in the Cassie-Baxter state, which is consistent with the simulation result as shown in Figure 4-3(a). Furthermore, the relative contact angle difference between the SE simulated result (CA=161.5°) and the experimental result (CA=163° ± 2.3°) is less than 1%, indicating the high reliability of our SE modelling approach presented in this paper.

4.3 WGMs Excitation Along Meridian Plane of Microdroplet

Firstly, as a reference to the deformed cases, an ideal spherical water microdroplet with a radius of 10 μm was considered as the optical microcavity in the FDTD simulation. Our FDTD simulation approach is validated by comparing with the theoretical and experimental WGM results in the literature, which shows an excellent agreement with each other. The wavelength of ~750 nm was chosen in the FDTD simulation due to its low water absorption. In this undeformed spherical cavity, \( q \) stands for the number of field maxima in the radial direction. The field distributions of its modes with \( q = 1, 2, 3 \) and 4 are illustrated in Figure 4-4 and exhibit a perfect spherical symmetry. For the deformed microdroplet cavities with different contact angles, the modes stimulated in their meridian planes are mainly the deformed WGMs (see their resonant mode field distributions in Figure 4-5 and Figure 4-6). These deformed meridian WGMs show the following features: (i) Although the deformation of microdroplets affects the mode field distribution losing spherical symmetry, each mode in the deformed cavity could be easily traced back to the undeformed mode with the same \( q \) by scrutinizing modes' appearance similarity in Figure 4-4 and Figure 4-5; (ii) Similar to an undeformed microdroplet, the deformed microdroplet cavity can also support many meridian WGMs with different \( q \) values. The allowed modes in a deformed microdroplet do not always start from \( q = 1 \) and heavily depend on the degree of droplet deformation. As shown in Figure 4, the least \( q \) for the allowed modes in the deformed microdroplet with a large \( \theta_A \) of 170.9° starts from 1 while it is from 2 in the deformed microdroplet with \( \theta_A = 161.5° \). This phenomenon can also be verified by their normalized intensity spectrum as illustrated in Figure 4-6. For example, the narrow peaks corresponding to the least \( q = 1, 2, 3, \) and 4 for the
cases with $\theta_A = 170.9^\circ$, $161.5^\circ$, $151.2^\circ$ and $146.5^\circ$ respectively are observed; (iii) In each deformed microdroplet, the mode with the least $q$ dominates the whole field distribution because its mode quality factor $Q$ is much higher than the $Q$ values of other modes with larger $q$ values. Therefore, we only consider the mode with the least $q$ in the following discussion. This feature is shown by the normalized intensity spectrums of the deformed microdroplets as illustrated in Figure 4-6. For instance, even though the modes with $q = 3, 4$ also exist in the microdroplet of $\theta_A = 170.9^\circ$ as shown in Figure 4-5(a), only the peaks corresponding to the modes of $q = 1$ and 2 are observed in Figure 4-4, in which the mode with the least $q = 1$ exhibits the narrowest and highest peak implying the largest $Q$ factor.

**Figure 4-4.** The mode field distributions of the undeformed water microdroplet cavity of 10 $\mu$m in radius with different $q$ values. $q$ is the number of field maxima in the radial direction. $d$ is the distance from the cavity centroid to the principle maxima of the undeformed WGMs with different $q$ values.
Figure 4-5. The resonant mode field distribution inside the deformed microdroplets: (a) the deformed $q = 1, 2$ and 3 meridian WGMs in the microdroplet with $\theta_\Lambda = 170.9^\circ$; (b) The microdroplet cavity morphology and the deformed $q = 2$ and 3 meridian WGMs in the microdroplet of $\theta_\Lambda = 161.5^\circ$. 
Figure 4-6. The microdroplet cavity morphology, the intensity spectrum, and the least $q$ meridian WGM field distribution for each microdroplet.

The feature (ii) mentioned above for the deformed microdroplets can be further understood by analyzing the distance $d$ from the cavity centroid to the principle maxima of the undeformed WGMs with different $q$ values and the distance $d'$ from the centroid to the baseline of the deformed microdroplet with different contact angles. Quantitatively, the distances $d$ are calculated to be 9.642 μm, 9.009 μm, 8.556 μm and 8.152 μm for the undeformed modes with $q = 1, 2, 3$ and 4,
respectively (see the blue dashed lines in Figures 4-7(b) and 4-7(c)). However, the distance $d'$ are 9.43 μm, 9.1 μm, and 8.148 μm for microdroplets with $\theta_A = 170.9^\circ$, 161.5°, and 151.2°, respectively. For the microdroplet cavity of $\theta_A = 170.9^\circ$, its $d'$ value of 9.43 μm is less than but close to the undeformed distance $d$ of 9.642 μm for $q = 1$. Phenomenologically, this shorter distance $d'$ would lead to a deformed meridian WGM of $q = 1$ deviating from the undeformed counterpart. This depressed distance, on the other hand, indicates that other deformed modes with higher $q$ can still be generated, as evidenced by the existence of the higher order modes in Figure 4-5(a). Moreover, with further decreasing $d'$, it would block the generation of deformed meridian WGM of $q = 1$. Thus, the microdroplet of $\theta_A = 161.5^\circ$ cannot form the mode of $q = 1$ due to the short distance $d' = 9.1\mu m$. Similar to the microdroplet of $\theta_A = 161.5^\circ$, which cannot achieve meridian WGM of $q = 1$, the microcavities with a relatively smaller $\theta_A$ are constrained to generate deformed meridian WGMs with larger $q$ values.

![Figure 4-7](image)

**Figure 4-7.** (a) The contours of sessile microdroplet profiles. (b) The variations of the baseline length $l$ and the centroid-to-baseline distance $d'$ of the deformed water microdroplets with $r = 10 \mu m$. The blue dashed
lines indicate the distances $d$ from the principle maxima of the modes to the cavity centroid for undeformed modes of $q = 1, 2, 3$ and 4, respectively. (c) The cross sections of the deformed microdroplet cavities with different $\theta_A$. The blue dashed lines are the positions of the principle maxima for the undeformed modes of $q = 1, 2, 3$ and 4, respectively.

The performance of an optical resonator is evaluated by the quality factor $Q$ that is related to the dissipation rate of photons confined in the cavity. Generally, $Q$ factor is associated with the spectrum of the resonator cavity through the formula $Q = \frac{\lambda_{\text{res}}}{\Delta \lambda_{\text{FWHM}}}$, where $\lambda_{\text{res}}$ and $\Delta \lambda_{\text{FWHM}}$ are the resonant wavelength and the full width at the half-maximum of individual resonant peaks in the spectrum, respectively. With regard to the WGMs along the meridian periphery of a microdroplet resonator resting on a superhydrophobic surface, the total quality factor $Q_{\text{total}}$ can be physically formulated by:

\[
\frac{1}{Q_{\text{total}}} = \frac{1}{Q_{\text{intrinsic}}} + \frac{1}{Q_{\text{coupling}}} \tag{4-2}
\]

\[
\frac{1}{Q_{\text{intrinsic}}} = \frac{1}{Q_{\text{ab}}} + \frac{1}{Q_{\text{rad}}} + \frac{1}{Q_{\text{ss}}} + \frac{1}{Q_{\text{def}}} \tag{4-3}
\]

where $Q_{\text{intrinsic}}$ is the intrinsic quality factor of the deformed cavity, $Q_{\text{ab}}$ due to the liquid absorption-related loss, $Q_{\text{rad}}$ due to the curvature radiation-related loss, $Q_{\text{ss}}$ due to the surface roughness scattering-related loss, $Q_{\text{def}}$ due to the deformation-related loss and $Q_{\text{coupling}}$ due to the tunneling loss when using a waveguide to inject energy into the microcavity’s near field.
Theoretically, the curvature radiation-related loss factor $Q_{\text{rad}}$ is $> 10^{11}$ and the scattering-related loss is safely negligible for the undeformed fundamental WGM with $q = 1$.\textsuperscript{74,79} The material absorption-loss dominates the upper limit of the intrinsic quality factor and this contribution can be expressed as $Q_{\text{ab}} = 2\pi n / \alpha_{ab}$,\textsuperscript{74,79} where water refractive index $n = 1.33$ and water absorption coefficient $\alpha_{ab} \approx 2.6 \text{ m}^{-1}$ at the working wavelength. The resulting $Q_{\text{ab}} \approx 4.3 \times 10^6$ sets the upper limit of $Q_{\text{intrinsic}}$, which is in the order of $10^6$ for the undeformed spherical microdroplet cavity. Therefore, the intrinsic $Q_{\text{intrinsic}}$ of a sessile microdroplet cavity cannot reach beyond this upper bond due to the inevitable deformation along its meridian rim as shown in Figure 4-8. For example, regarding deformed meridian WGM with the least $q = 2$ in the cavity of $\theta_A = 161.5^\circ$, $Q_{\text{intrinsic}} = 1.1 \times 10^4$; with regard to the deformed meridian WGM of $q = 3$, $Q_{\text{intrinsic}} = 1.2 \times 10^3$ for the case of $\theta_A = 151.2^\circ$. Besides, in the undeformed cavity, a large $q$ mode is associated with a relatively low $Q_{\text{intrinsic}}$ value due to the large radiation loss. Its $Q_{\text{intrinsic}}$ values are estimated to be $4 \times 10^5$, $1 \times 10^4$, $2 \times 10^3$ for the high order modes of $q = 2, 3, 4$, respectively. Similarly, a microcavity with a smaller contact angle may lead to deformed meridian WGMs with large $q$ values and consequently a relatively lower $Q_{\text{intrinsic}}$. Therefore, the field energy loss increases as the contact angle of the
deformed microdroplet cavity decreases. Moreover, $Q_{\text{intrinsic}}$ of the deformed meridian WGM is smaller than that of the undeformed cavity in the same mode, which shows this deformed meridian WGM has more energy loss compared to the same order undeformed mode. Obviously, such loss mainly results from the microdroplet deformation. The deformation-related loss dominates the intrinsic quality factor of the deformed microdroplets and this deformation-related loss is mainly caused by two factors: (i) the WGMs have a mismatch at the junction between the microdroplet base and the microdroplet above the pillar section, and (ii) the distance $d'$ resulted from the cavity deformation generates a large radiation-related loss. In Figure 4-6 and Figure 4-7, as the contact angle $\theta_A$ decreases, the baseline length $l$ increases and the distance $d'$ decreases, indicating a stronger mode mismatch (i.e., the deviated distribution of field maxima in the radial direction of the meridian plane), a larger radiation-related loss and consequently a smaller $Q_{\text{intrinsic}}$ factor. To better describe how the contact angle related-deformation influences $Q_{\text{intrinsic}}$, we define two aspect ratios in the meridian plane as $\eta_1 = (r - d') / r$ and $\eta_2 = l / 2r$, where $r$ is the lateral radius of the deformed droplet and $l$ is the baseline length as shown in Figure 4-6. Compared to a perfectly spherical cavity, smaller values of $\eta_1$ and $\eta_2$ indicate the mitigated deformation of a microdroplet cavity; whereas $\eta_1 = 0$ and $\eta_2 = 0$ are associated with a perfectly circular rim of the meridian cross-section of the microdroplet. For example, a sessile microdroplet with $\theta_A = 170.9^\circ$ has the aspect ratios of $\eta_1 = 5.7\%$ and $\eta_2 = 28.5\%$, indicative of a relatively small deformation. If the contact angle further decreases, the aspect ratio will increase, resulting in a larger deformation and a lower $Q_{\text{intrinsic}}$. As shown in Figure 4-8, when $\theta_A$ varies from $161.5^\circ$ to $151.2^\circ$, $\eta_1$ changes from $9.0\%$ to $18.5\%$, and $\eta_2$ increases from $36.3\%$ to $50.9\%$, demonstrating a remarkable increase in the cavity deformation. Thus, it is not surprising to observe that $Q_{\text{intrinsic}}$ falls from $1.1 \times 10^4$ to $1.2 \times 10^3$ as $\theta_A$ decreases from $161.5^\circ$ to $151.2^\circ$. 

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4.4 Lab-on-a-chip Coupling Scheme to Microdroplet Cavity

Due to the intriguing existence of the high $Q$-factor WGMs along the meridian plane of a sessile microdroplet, such modes could be excited in a more facile way, which is very different from the current schemes based on tapered fiber coupling or free-space beam coupling along the equatorial periphery. In this respect, a strip waveguide$^{134-136}$ embedded in a chip underneath the microdroplet can be utilized for coupling light into the meridian plane of the microdroplet cavity. This on-chip stationary coupling scheme without mechanical moving parts, e.g., motor-driven nanostage, would be realized by designing the strip waveguide on a nanoroughness-decorated chip surface, making it highly favorable for lab-on-a-chip applications. As shown in Figure 4-9, the sessile microdroplet rests on top of a superhydrophobic chip surface with an embedded strip optical waveguide. The nanopillar array, fabricated by deep reactive ion etching or thermally dewetting platinum film on a solid substrate, function as the superhydrophobic chip surface. This planar chip plays dual roles in this configuration: one is to mechanically support the deformed microdroplet on the surface without additional complex position-stabilizing equipment and the other is to accommodate the built-in waveguide for adaptive optical coupling.

![Image of a chip with a microdroplet and a strip waveguide](image.png)

**Figure 4-9.** Schematic and operation principles of the sessile microdroplet cavity system on a chip. We put forward to use meridian WGMs sensing of trace analytes contained in a liquid microdroplet. Coupling light
or radiation into the microdroplet is accomplished by placing it on a chip surface that incorporates a planar optical waveguide, along with electrodes that can tune the morphology of the microdroplet cavity via electrowetting to optimize the coupling.

There are two basic requirements for an efficient light-coupling scheme: one is through the phase (or the effective refractive index $n_{\text{eff}}$) matching, and the other is by the sufficient spatial overlap of the evanescent electromagnetic fields between the mode of the sessile microdroplet cavity and that of the strip waveguide. Therefore, it is necessary to firstly investigate the effective refractive index $n_{\text{eff}}$ of the deformed microdroplet and then the strip waveguide is designed accordingly. However, the $n_{\text{eff}}$ of the deformed microdroplet cannot be directly calculated due to its loss of spherical symmetry. Instead, the $n_{\text{eff}}$ of an undeformed spherically symmetric microdroplet cavity can be readily calculated by FEM. Moreover, as discussed in section 4.3, the deformed meridian WGM with different $q$ values can be traced back to the undeformed mode with the same $q$. Therefore, the $n_{\text{eff}}$ of the deformed meridian WGM should be close to that of the undeformed counterpart. It is reasonable that the strip waveguide is firstly designed to match the $n_{\text{eff}}$ of the undeformed microdroplet and is then adjusted to match the deformed microdroplet. For a microdroplet with radius of 10 µm, the $n_{\text{eff}}$ of the undeformed modes with $q = 1, 2$ and $3$ are calculated to be 1.2806, 1.2790 and 1.2743, respectively. Therefore, the $n_{\text{eff}}$ of the waveguide was initially estimated around 1.28, based on which we can find the optimum waveguide geometry for matching the deformed microcavity. Besides, based on the refractive index of water, SiO$_2$ and porous silicon dioxide (p-SiO$_2$) were selected as the component materials for the strip waveguide and the substrate, respectively. The variation of the $n_{\text{eff}}$ of the strip waveguide with height $H$ and width $W$ is plotted in Figure 4-10, from which the values of $H = 0.525$ µm and $W = 0.8$ µm, for example, are matching $n_{\text{eff}} = 1.28$. 

137,138
Figure 4-10. The dependence of the calculated effective refractive index $n_{\text{eff}}$ of the proposed strip waveguide on geometrical parameters of the waveguide and undeformed microdroplet cavity size. The black lateral dash line indicates $n_{\text{eff}} \sim 1.28$ of the underformed microdroplet with a radius of 10 $\mu$m.

The coupling between the strip waveguide and the microdroplet cavity can be analyzed by the coupled-mode theory. The amplitude of the input power in the waveguide and the amplitude of the output power in the waveguide are $E_i$ and $E_o$, respectively. Thus, the field transmission coefficient, which is the ratio of $E_o$ to $E_i$, can be described by: $^{139}$

$$ T = \frac{E_o}{E_i} = \frac{\sqrt{1-k^2} \exp\left[-\left(\frac{\alpha}{\beta}+j\beta\right) L\right]}{1-\sqrt{1-k^2} \exp\left[-\left(\frac{\alpha}{\beta}+j\beta\right) L\right]} $$

(4 - 4)

where $\alpha$ is the amplitude loss coefficient of the electric field in the microdroplet, and $k$ is the coupling power loss factor between the waveguide and the microdroplet. The effective propagation constant $\beta$ in the microdroplet is defined by $\beta = (2\pi/\lambda)n_{\text{eff}}$, where $n_{\text{eff}}$ is the effective refractive index of the microdroplet, and $L$ is the circumference along the meridian plane of the microdroplet. On resonance, $\beta L = 2m\pi$, where $m$ is an integer. In case $1 - k^2 = \exp(-\alpha L/2)$,
the numerator becomes zero and therefore the transmitted optical power at the output of the waveguide goes to zero on resonance, i.e. the critical coupling.

The transmitted optical power at the output of the waveguide relies heavily on the microdroplet-waveguide interface geometry, often termed as the gap with a height $h_{\text{gap}}$ between the base of the deformed microdroplet and the waveguide. The influence of $h_{\text{gap}}$ on the optical performance of the system with $\theta_A = 161.5^\circ$, $W = 0.7 \mu\text{m}$, $H = 0.6 \mu\text{m}$, and with $\theta_A = 161.5^\circ$, $W = 1.0 \mu\text{m}$, $H = 0.6 \mu\text{m}$, respectively, are investigated by the FDTD method. It can be seen in Figure 10(a) that the critical coupling condition is achieved at $W = 0.7 \mu\text{m}$, $H = 0.6 \mu\text{m}$, $h_{\text{gap}} \sim 100 \text{ nm}$, in which less than 4% of the input power succeeds in transmission. The waveguide with $W = 1.0 \mu\text{m}$, $H = 0.6 \mu\text{m}$ is not an ideal configuration because more than 11% of the input power evolves to the waveguide transmission. However, $Q_{\text{total}}$ of the system with $W = 1.0 \mu\text{m}$, $H = 0.6 \mu\text{m}$ is larger than that of the system with $W = 0.7 \mu\text{m}$, $H = 0.6 \mu\text{m}$ at any given $h_{\text{gap}}$. Moreover, after $Q_{\text{total}}$ increases to a certain level with increasing $h_{\text{gap}}$, it does not change significantly with $h_{\text{gap}} > 150 \text{ nm}$. It is also noteworthy that further increasing $h_{\text{gap}}$ is unfavorable to storing energy in the microdroplet because more power goes to the waveguide transmission at a larger gap. Therefore, a trade-off between the stored energy in the microdroplet and the quality factor $Q_{\text{total}}$ is necessary. For this microdroplet-waveguide system, the combination of $W = 1.0 \mu\text{m}$, $H = 0.6 \mu\text{m}$, and $h_{\text{gap}} = 100 \text{ nm}$ allows for a relatively high $Q_{\text{total}}$ in conjunction with a large amount of energy stored in the microdroplet. It is worth noting that in the above analysis of the relationship between $h_{\text{gap}}$ and the optical WGM performance, the variation of $h_{\text{gap}}$ has no direct effect on the droplet morphology since all the microdroplets under consideration are in the Cassie-Baxter state and the pillar height $h$ is larger than the droplet sagging depth $h_{\text{sag}}$. Nevertheless, the optimal waveguide parameters of $W$, $H$, and $h_{\text{gap}}$ can be a guidance for designing the nanopillar height and the strip waveguide. In practice, even the pillar height is fixed, $h_{\text{gap}}$ can be adjusted by adaptively tuning $h_{\text{sag}}$ via electrowetting-on-dielectric (EWOD).\textsuperscript{15,140}
Figure 4-11. (a) Normalized transmission power and $Q_{\text{total}}$ against $h_{\text{gap}}$ with $W = 0.7 \, \mu m$, $H = 0.6 \, \mu m$ and $W = 1.0 \, \mu m$, $H = 0.6 \, \mu m$ for the microdroplet with $\theta_A = 161.5^\circ$. (b) Normalized transmission power, (c) $Q_{\text{total}}$, (d) resonant wavelength versus height $H$ and width $W$ while $\theta_A = 161.5^\circ$, $h_{\text{gap}} = 100 \, \text{nm}$. (e) The morphology, the resonant mode field distribution, transmission spectra of the deformed microdroplet with $\theta_A = 161.5^\circ$.

Besides, in order to understand how the system coupling is affected by the waveguide geometry, the simulated transmission power and the total quality factor $Q_{\text{total}}$ as well as the resonant wavelength for the system with eight waveguide widths at three different waveguide heights ($H = 0.55, 0.60, 0.70 \, \mu m$) are plotted in Figure 4-11. Here, the microdroplet apparent contact angle $\theta_A$ and the gap thickness $h_{\text{gap}}$ are fixed at $161.5^\circ$ and $100 \, \text{nm}$, respectively. With the waveguide width $W$ increasing from 0.6 $\mu m$ to 1 $\mu m$, the normalized transmission power in the waveguide and the quality factor $Q_{\text{total}}$ increase. This is because that the mode confinement factor in the waveguide
becomes larger with increasing $W$, leading more power to waveguide transmission; whereas the electric field in the waveguide extends less into the microdroplet, leading to a smaller coupling strength and thus a higher $Q_{\text{total}}$. With further increasing of $W$, $Q_{\text{total}}$ increases only slightly for the system with height $H = 0.55$ or $0.60 \mu$m. This is due to the fact that further increasing in $W$ cannot lead to a smaller coupling strength. For the system with $H = 0.70 \mu$m, the quality factor $Q_{\text{total}}$ decreases with further increasing of the waveguide width $W$. On the other hand, $W = 1.0 \mu$m with $H = 0.60 \mu$m is the better waveguide combination for achieving a relatively high $Q_{\text{total}}$ with mitigated transmission as shown in Figures 4-11(b) and 4-11(c). Moreover, for $W = 1.0 \mu$m and $H = 0.60 \mu$m, the transmission spectrum and the mode field distribution are plotted in Figure 4-11(e). As expected, the mode type stimulated by the waveguide is the deformed $q = 2$ meridian WGM. Furthermore, $Q_{\text{total}}$ of the deformed microdroplet cavity systems with $\theta_A = 170.9^\circ$, $161.5^\circ$, $151.2^\circ$, and $146.5^\circ$ are plotted in Figure 4-8, respectively. The results show that $Q_{\text{total}}$ of the deformed microdroplet cavities is smaller than their $Q_{\text{intrinsic}}$ due to the coupling loss incurred by waveguide coupling. The $Q_{\text{total}}$ of the deformed microdroplet cavities with $\theta_A > 151.2^\circ$ exceeds $10^3$, which can fulfill the basic requirements of a variety of sensing applications. Moreover, the $Q_{\text{total}}$ of this microdroplet-based cavity system with $\theta_A = 161.5^\circ$ and $170.9^\circ$ can reach an impressive value of above $10^4$, which can meet the requirements for advanced biosensing.

4.5 Refractive Index Sensing Performance of The Deformed Microdroplet Resonators

According to this study, a liquid microdroplet dwelling on a well-structured substrate can sustain resonant WGMs of high $Q$ factors along its deformed meridian periphery, which are stimulated by a strip waveguide underneath. Therefore, this optofluidic system can provide a robust and stable platform of refractive index sensor. Moreover, in contrary to solid micro-resonators using evanescent-tail field for sensing, this optofluidic system directly exploits the enhancement of the energy contained in the microdroplet cavity. In other words, this microdroplet serves
simultaneously as the analyte container and the optical cavity, endowing not only a stronger interaction between light and the analytes but also a larger interaction space compared to the solid counterparts. Based on these potential benefits, we estimated the performance of this optofluidic system for sensing applications.

A key parameter characterizing such a refractive index optical sensor is the sensitivity $S$, which is defined as the shift rate of the resonant wavelength $\lambda$ with the refractive index $n$:

$$S = \frac{d\lambda}{dn}$$

where the shift of the resonant wavelength $\lambda$ of the microdroplet cavity is attributed to the change of the refractive index $n$ of the microdroplet due to the addition of even trace amount of analytes. Figure 4-12 shows a linear dependence of the resonance wavelength on $n$ of the $\theta_A = 161.5^\circ$ microdroplet. A high sensitivity $S \sim 531.8$ nm/RIU can consequently be achieved. Nevertheless, the resonance mode with a sensitivity below 100 nm/RIU (e.g., 30 nm/RIU in silica microsphere-based sensor and 22.8 nm/RIU in a sensor based on Si$_3$N$_4$ microdisk$^{141}$) is due to the typical evanescent wave interaction with the surrounding medium and analytes. Compared to the solid counterparts, the remarkable sensitivity $S$ of the water-based microdroplet cavity results in larger shift in the resonant wavelength for a given index change. The $Q_{\text{total}}$, which is inversely proportional to $\Delta\lambda_{\text{FWHM}}$, is another key parameter of optical sensors. A narrow line width $\Delta\lambda_{\text{FWHM}}$, namely a high $Q$ factor, will result in enhanced detection resolution. The $Q_{\text{total}}$ of this microdroplet cavity with $\theta_A = 161.5^\circ$ and 170.9$^\circ$ can reach above $10^4$, which is superior to that of some conventional optical sensors for biosensing applications (e.g., $Q \sim 6000$ in a slotted photonic crystal cavity with $S \sim 500$ nm/RIU$^{142}$). That is, this microdroplet-based system has potential applications in high-resolution detection of single biomolecules.
Compared to the $Q_{\text{total}}$ of the solid WGM system or the droplet-based WGM system but coupled from the equatorial plane, the $Q_{\text{total}}$ of the meridian WGM system is relatively small. Nevertheless, this $Q_{\text{total}}$ value has less sensitivity to the ambient environment changes such as thermal disturbance. Furthermore, this meridian sensing system based on strip waveguide-droplet coupling is more stable and feasible for practical implementation. Intriguingly, this WGM sensing system can be easily integrated with the EWOD platform\textsuperscript{15,140} so that the microdroplet can be adaptively manipulated to pick up the target analytes, such as biological species or chemical reagents, thereby digital and precise biosensing can be achieved on this lab-on-a-chip system.

4.6 Chapter Summary

WGM sensing in water-based microcavities is highly desired in practice because they are more closely analogous to the biological environment. In this work, we analyzed a fluidic and deformed microdroplet system as an optical cavity, in which WGMs are stimulated by an embedded strip waveguide on a micro/nanostructured superhydrophobic surface. The embedded strip waveguide
beneath the nanopillared surface can not only stabilize the microdroplet at the Cassie state but also enable the WGMs to be generated in the meridian direction, which makes the coupling process more facile and more stable compared to the WGMs coupling along the equatorial plane. As a compromise, the unavoidable deformation in the microdroplet meridian plane weakens the quality factor $Q$. Nonetheless, the nanopillar patterned superhydrophobic surface above the waveguide can mitigate such deformation and have the potential to achieve a high-quality $Q$ factor. In this regard, the microdroplet with $\theta_A = 151.2^\circ$ and $156.3^\circ$ has total $Q$ factor $> 10^3$; and the microdroplet with $\theta_A = 161.5^\circ$ and $170.9^\circ$ has total $Q$ factor $> 10^4$. Besides, in terms of sensing application, making the microdroplet itself serves simultaneously as the trace analyte container and the optical cavity, a high sensitivity $S > 530$ nm/RIU can be achieved, which is more sensitive than the solid counterparts.

On the other hand, a water microdroplet may evaporate very fast when it is directly exposed to the ambient, causing the WGMs to drift during measurement. A prior study$^{143}$ reported that the size stabilization of microdroplets containing no salt can be obtained via an electrically controlled mini humidity and demonstrated that the diameter variation of a 12 $\mu$m water droplet was only $\approx 1$ nm during 82.8 seconds. Even though water evaporation can be effectively mitigated by controlling the humidity inside a chamber, the WGM sensing system can be more easily applied without the enclosure. Currently, to slow down the evaporation process of a water droplet, a proper amount of glycerol was added in to water to form glycerol–water mixture in some WGM studies. In our meridian WGM configuration, owing to the high contact angle ($\theta_A > 160^\circ$) of the glycerol–water mixture on a superhydrophobic surface, fluidic microcavities with the geometry of a truncated sphere minimally distorted by gravity and contact line pinning effects could be generated. For future applications, the stable and feasible waveguide coupling microdroplet system can be integrated with EWOD platform leading to a digital lab-on-a-chip sensor with high throughput and high sensitivity even in a complex sample matrix.
Chapter 5  Leidenfrost Evaporation Assisted Ultrasensitive SERS Detection Using Hierarchical Plasmonic Micro/Nanostructures

5.1 Chapter Introduction

The conventional method of creating superhydrophobic surface-enhanced Raman spectroscopy (SERS) surfaces by conformally coating a hydrophobic layer on structured substrates may deteriorate their SERS performance because the hydrophobic film may partially block hot spots and therefore compromise Raman signals of analytes. In this paper, we report a novel type of high-performance SERS platform that is formed by integrating nanolaminated plasmonic nanostructures on a hierarchical micro/nanostructured surface, i.e., carbon nanotubes (CNTs) decorated on Si micropillar arrays. In comparison with several hours of natural evaporation, well-controlled Leidenfrost evaporation, i.e., heat-assisted evaporation, on the hierarchical plasmonic surfaces can overcome the diffusion limit of dilute analytes contained in a water droplet and thus can quickly concentrate analyte molecules within several minutes on a remarkably reduced footprint for ultrasensitive SERS detection. Here we demonstrate that a Leidenfrost droplet on the hierarchical plasmonic surface can reduce the final deposition footprint of analytes by 3-4 orders of magnitude and enable ultrasensitive SERS detection of nanomolar analytes in an aqueous solution. In particular, this hierarchical plasmonic surface has densely packed intrinsic SERS-active hot spots that give rise to SERS enhancement factors (EFs) exceeding $10^7$. Leidenfrost evaporation-assisted SERS sensing on hierarchical plasmonic micro/nanostructures provides a new avenue for ultrafast
and ultrasensitive biochemical detection without the need for additional surface modifications and chemical treatments.

Most of the results presented in this chapter were covered in Junyeob Song, Weifeng Cheng, Meitong Nie, Xukun He, Wonil Nam, Jiangtao Cheng, and Wei Zhou. "Leidenfrost evaporation assisted ultrasensitive SERS detection using hierarchical plasmonic micro/nanostructures." *ACS Nano*, 2019, under review.

5.2 Design of SERS Hierarchical Micro/Nanostructured Substrate

Hierarchical plasmonic micro/nanostructures used in this work consist of Au/Ag nanolaminated plasmonic nanostructures decorated on top of two-tier Si/CNT micro/nanopillar arrays (Figure 5–1). Figure 5–1A illustrates the key steps to fabricate hierarchical plasmonic micro/nanostructures. As described in our previous work, we created the two-tier Si/CNT micro/nanopillar arrays by the combination of top-down microfabrication and bottom-up chemical synthesis approaches. Briefly, we fabricated square-shaped Si micropillar arrays by photolithography patterning and deep reactive ion etching. Then, a thin layer of nickel was coated on the micro-structured substrate as a catalyst to grow CNTs by plasma-enhanced chemical vapor deposition (PECVD). Finally, we deposited alternating layers of Au (25 nm thick) and Ag (6, 8, and 12 nm thick from the bottom to the top) on the two-tier Si/CNT micro/nanopillar array structures by electron-beam evaporation.
**Figure 5-1.** Hierarchical plasmonic micro/nanostructures. (A) Schematic illustration of the fabrication process to create hierarchical plasmonic micro/nanostructures. (B) Top-view optical image of hierarchical plasmonic micro/nanostructures. (C) Top-view and (D-E) cross-sectional SEM images of hierarchical plasmonic micro/nanostructures.

As shown in the top-view of optical image (Figure 5-1B), hierarchical plasmonic micro/nanostructures have a dark appearance reflecting a broadband absorption in the visible spectrum. From the top-view (Figure 5-1C) and the cross-sectional view (Figures 5-1D-E) of scanning electron microscopy (SEM) images, we can observe a good microscale uniformity of hierarchical plasmonic micro/nanostructures, where the Si micropillar arrays formed by top-down reactive ion etching have a micropillar width of 6 μm, a micropillar height of 6 μm and a periodicity of 9 μm. In contrast, the CNT nanopillars with a 30% solid-liquid fraction have relatively large variations in both the diameters and heights ranging from 50 nm to 600 nm, due to the random CNT growth process in PECVD. The line-of-sight electron-beam deposition of alternating Au and Ag layers on top of CNT nanopillars can generate nanolaminated plasmonic nanostructures as optical nanoantennas with intrinsic hot spots to concentrate light in the nanoscale (Figure 5-1E).
5.3 Fabrication of Hierarchical SERS Substrate

On a 2 cm × 2 cm Si substrate of 500 µm thick, squarely positioned micropillars were formed by deep reactive ion etching. The etched Si substrates were coated with a thin layer of nickel as a catalyst, and CNTs were subsequently grown by plasma-enhanced chemical vapor deposition. The micropillars are 5 µm in width, 6 µm in height, and spaced 9 µm center to center. The CNT nanopillars are approximately 0.4 µm tall with a 25% surface coverage. Lastly, a series of electron beam deposition was performed to stack alternating Au-Ag-Au multilayered nanoantennas (total 7 layers) on the hierarchical Si/CNT structures. The thickness of Au layer is 35 nm. For the Ag layers, 6, 8, and 12 nm were sequentially deposited from bottom to top.

5.4 Optical Property Measurement and Simulation of SERS Substrate

We carried out broadband absorption measurements to examine the optical properties of hierarchical plasmonic micro/nanostructures in comparison with different benchmark or control samples (Figure 5–2A), including bare Si micropillar arrays, Au/Ag-coated Si micropillar arrays, and two-tier Si-CNT micro/nanopillar arrays. In the entire visible and near-infrared wavelength range between 400 nm and 1000 nm, both hierarchical plasmonic micro/nanostructures and Si-CNT micro/nanopillars show flat high absorption spectra over 90%. Despite their similarity in far-field optical spectra, hierarchical plasmonic micro/nanostructures can achieve nanolocalized light concentration and induce optical absorption within an ultrathin skin depth (< 30 nm) of metal layers\(^{145}\) while the Si-CNT micro/nanopillars have a much larger light penetration depth due to their smaller free carrier density. As expected, Au/Ag-coated micropillar arrays and Si micropillar arrays show weaker absorption than the hierarchical plasmonic micro/nanostructures because they lack metal nanostructures to support localized surface plasmon modes.
To understand the microscopic origin of observed optical properties for hierarchical plasmonic micro/nanostructures, we performed 3D finite-difference time-domain (FDTD) calculations using commercial software (FDTD solution, Lumerical Inc.) (See details in Supporting Information). Figure 5-2B depicts the calculated absorption spectra of nanolaminated Au/Ag plasmonic nanostructures sitting on CNT nanopillars with different diameters ($d$). As the nanopillar diameter increases from 100 nm to 150 nm, 200 nm, and 250 nm, a distinct resonant absorption peak redshifts from 595 nm to 645 nm, 670 nm, and 695 nm, respectively, while the absorption feature below 530 nm does not change spectral shape due to the interband electronic transitions in Au. The inset of Figure 5-2B shows the FDTD-calculated near-field distribution map of $|E|^2$ at the resonant wavelength of 670 nm for the nanolaminated Au/Ag plasmonic nanostructures sitting on CNT nanopillars with $d = 200$ nm. The FDTD-calculated mode profile reveals an electric dipole nature for the localized plasmon modes in the nanolaminated Au/Ag plasmonic nanostructures. Since the resonant wavelengths of electric dipolar plasmon modes strongly depend on the diameters of plasmonic nanostructures, hierarchical plasmonic micro/nanostructures composed of various plasmonic nanostructures with different diameters can show a broadband optical absorption due to the inhomogeneous broadening effects.\textsuperscript{90} Besides, near-field optical simulations show that plasmonic nanostructures can enhance the local electric field intensity $|E|^2$ by up to three orders of magnitude, which corresponds to SERS EFs on the order of $\sim 10^6$ according to the $|E|^4$ approximation.\textsuperscript{146} Therefore, our numerical calculations predict that hierarchical plasmonic micro/nanostructures can support SERS hot spots with a broad spectral response.
Figure 5-2. Optical and SERS properties. (A) Measured reflectance spectra of hierarchical plasmonic micro/nanostructures in comparison with those from reference samples. (B) FDTD-calculated reflectance spectra of plasmonic nanostructures with different nanopillar diameters ($d = 100$ nm, 150 nm, 200 nm, and 250 nm). Inset: FDTD-calculated $x$-$z$ distribution map of $|E|^2$ for the plasmonic nanostructure with a nanopillar diameter of 200 nm ($d = 200$ nm) at its resonant wavelength ($\lambda = 670$ nm). (C) Raman spectra of benzenethiol (BZT) from hierarchical plasmonic micro/nanostructures in comparison with control samples. (D) Confocal Raman images for BZT signals at 1079 cm$^{-1}$ from hierarchical plasmonic micro/nanostructures. (E) Histogram of Raman signal intensities and corresponding SERS EFs (1079 cm$^{-1}$) for hierarchical plasmonic micro/nanostructures. (F) SERS EFs (1079 cm$^{-1}$) of the nanolaminated hierarchical SERS substrates at 5 different locations. Boxes were plotted with 1.5 interquartile range (IQR) and lines from top to bottom indicate: Q75 + 1.5 IQR, Q75, Q50, Q25, Q25 – 1.5 IQR.

For numerical optical simulations, we used the 3D finite-difference time-domain (FDTD) method with commercial software (Lumerical Inc, Canada). A uniform mesh size of 2 nm was used in x, y, and z directions. Optical constants of Au and Ag were selected from the literature.\textsuperscript{147} Ag layers
on the pillar were offset in the x-direction (10 nm). We used Bloch boundary condition in the x and y directions with a periodicity of 400 nm and perfectly matched layer (PML) boundary condition in the z-direction. The index of the background in the air was 1 and the substrate (including the pillar) of Si was based on the literature.\textsuperscript{148} Incident light is a linear-polarized plane wave propagating perpendicular to the surface. Table 5-1 summarizes the parameters for the FDTD simulations.

Table 5-1. Simulation parameters used to calculate optical properties

<table>
<thead>
<tr>
<th>Material for the nanoantenna</th>
<th>Au-Ag- Au-Ag- Au-Ag-Au</th>
<th>Diameter of the nanopillar</th>
<th>80 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness of Au layer</td>
<td>25 nm</td>
<td>Diameter of the Au and Ag nanoantenna</td>
<td>80 nm</td>
</tr>
<tr>
<td>Background index</td>
<td>1</td>
<td>Mesh step size</td>
<td>2 nm</td>
</tr>
<tr>
<td>Simulation time</td>
<td>300 fs</td>
<td>Source wavelength</td>
<td>300–1300 nm</td>
</tr>
<tr>
<td>Boundary condition (x, y)</td>
<td>Bloch</td>
<td>Boundary condition (z)</td>
<td>PML</td>
</tr>
</tbody>
</table>

5.5 Methodology of SERS Measurement

In order to measure the SERS signals on the nanolaminated hierarchical SERS substrate, benzenethiol (BZT) (CAS#: 108-98-5, Sigma-Aldrich, USA) was used as a benchmark analyte. To form a self-assembled monolayer (SAM) of BZT on the substrate, we incubated the substrate in 1 mM ethanol solution for 18 hours, cleaned with a stream of ethanol solution, and dried with a gentle nitrogen stream. For Raman measurements, we used a confocal Raman microscopy system (Alpha 300rsa+, WITec, Germany). By using a collimator, beam splitter and long-pass filter for 785 nm, we introduced the incident laser and collected back-scattered signals simultaneously. The
laser power was 1 mW and the integration time was 1 s per pixel. For the Raman measurement of Rhodamine 6G (R6G) (CAS#:989-38-8, Sigma-Aldrich, USA), the laser power was 1.3 mW, and the integration time was 0.1 s per pixel.

5.6 Experimental Characterization of SERS Sensing Performance

By Raman measurements of benzenethiol (BZT) molecules assembled on these substrates, we characterized the SERS performance of hierarchical plasmonic micro/nanostructures in comparison with different benchmark samples (Figure 5-2C), including bare Si micropillar arrays, Au/Ag-coated micropillar arrays and two-tier Si-CNT micro/nanopillar arrays. Figure 5-2C depicts the average BZT Raman spectra from abovementioned samples, which were acquired by measuring 10 × 10 pixels over a 3 μm × 3 μm area using a 100× objective lens (NA:0.9) under the excitation of a 785 nm diode laser with 1 mW power by an integration time of 1 s for each pixel. As expected, hierarchical plasmonic micro/nanostructures exhibit an excellent SERS performance by showing distinct BZT Raman features, while the control samples of bare Si micropillar arrays, Au/Ag-coated micropillar arrays and two-tier Si-CNT micro/nanopillar arrays did not show any BZT Raman signatures due to the lack of plasmonic nanostructures enhancing local optical fields. From hierarchical plasmonic micro/nanostructures, five notable Raman peaks of BZT molecules can be observed corresponding to the CS stretching and CCC ring in-plane deformation vibration (at 427 cm⁻¹), the CCC ring in-plane bending mode (at 1004 cm⁻¹), the CH in-plane bending mode (at 1030 cm⁻¹), the CCC ring in-plane breathing mode with CS stretching mode (at 1079 cm⁻¹), and the CC stretching mode (at 1579 cm⁻¹).⁴⁴⁹

By 2D Raman mapping of the top micropillar regions over multiple positions (Figure 5-2D), we have evaluated the uniformity of the SERS hot spots on hierarchical plasmonic micro/nanostructures. As shown in Figure 5-2E, the histogram of Raman intensities and corresponding SERS EFs at 1079 cm⁻¹ from 5 different regions (500 pixels in total) follows a log-
normal distribution curve, reflecting the major contribution from uniformly distributed hot spots instead of a few of individual ones. We used the following definition for the calculation of SERS EFs: EF = (ISERS/N_{SERS})/(I_{Raman}/N_{Raman}). Figure 5-2F illustrates the measured SERS EFs of the hierarchical plasmonic micro/nanostructures at five different positions with the averaged SERS EFs of $1.45 \times 10^7$, $1.68 \times 10^7$, $1.81 \times 10^7$, $1.67 \times 10^7$, and $1.53 \times 10^7$, respectively. The small variations of SERS EFs on these different positions reflect the uniform SERS performance of the scalable and hierarchical plasmonic nanolaminated surfaces for practical SERS applications.

5.7 Wettability of SERS Substrate Surface

While the optical properties of hierarchical plasmonic micro/nanostructures determine the magnitude of SERS EFs at hot spots, their surface wettability properties also play a vital role in SERS detection performance by influencing the evaporation process of analyte droplets. To investigate their surface wettability properties, we used the optical tensiometer (Attension® Theta, Biolin Scientific, Sweden) to conduct both static and dynamic contact angle (CA) measurements for the samples of hierarchical Si-CNT micro/nanostructures without nanolaminated Au-Ag deposition (Figures 5-3A-B) as well as those with nanolaminated Au-Ag deposition (Figures 5-3C-D). In static CA measurements, we randomly selected 4 positions on each substrate to measure the static CA of water droplets of 20 uL and conducted 40 times measurements at each position for statistical analysis (Figures 5-3A and 5-3C). The dynamic CAs of each substrate were also measured by dripping a water microdroplet on the surface and then gradually tilting the substrate until the droplet started sliding on it. The advancing CA ($\theta_{\text{advancing}}$) and receding CA ($\theta_{\text{receding}}$) on each sample were measured 20 times, respectively (Figures 5-3B and 5-3D). Since the standard deviations of both the static and dynamic CA measurements are less than $0.3^\circ$ according to the statistical analysis (Figures 5-3A-D), both the samples of hierarchical Si-CNT
micro/nanostructures (Figures 5-3A-B) and the hierarchical plasmonic micro/nanostructures (Figures 5-3C-D) exhibit uniform surface wettability properties.

Figure 5-3. Surface wettability by contact angle measurements. (A) Static and (B) dynamic contact angle measurement results for hierarchical CNT-Si micro/nanostructures without the nanolaminated deposition of alternating Au and Ag layers. (C) Static and (D) dynamic contact angle measurement results for hierarchical plasmonic micro/nanostructures with the nanolaminated deposition of alternating Au and Ag layers. The insets of droplets in panels (B) and (D) show the sliding angles of droplets on micro/nanostructured surfaces without and with alternating Au/Ag coatings, respectively.

As shown in Figures 5-3A-B, the hierarchical Si-CNT micro/nanostructures without nanolaminated Au-Ag coating show an average static CA of \(\sim 166^\circ\) (Figure 5-3A) and a contact angle hysteresis (\(\text{CAH} = \theta_{\text{advancing}} - \theta_{\text{receding}}\)) of \(\sim 5^\circ\) (Figure 5-3B). These results reveal that
the hierarchical Si-CNT micro/nanostructures own intrinsic superhydrophobicity with a water droplet on it. In contrast, with nanolaminate Au-Ag deposition, hierarchical plasmonic micro/nanostructures show a reduced static CA of $\sim 134^\circ$ (Figure 5-3C) and a remarkably increased CAH of $\sim 32^\circ$ (Figure 5-3D), which reflects a decreased surface hydrophobicity with the water droplet in the Wenzel state due to the deposition of hydrophilic Au-Ag metal films on top of Si-CNT micro/nanostructures. To accomplish ultrasensitive SERS detection of low-concentration analytes in solutions, we need to minimize the analyte deposition area (footprint) via controlling the analyte droplet evaporation process, during which the circumferential base of the shrinking droplet should be ideally levitated in the Cassie state so that its three-phase contact zone can continuously recede without being pinned on the rough surface. As such, because a water droplet on the hierarchical plasmonic micro/nanostructures is in the Wenzel state as shown in Figures 5-3C-D, during the natural evaporation process; however, the pinning effect along the contact line leads to the final deposition area of similar size ($\sim 1.5$ mm in diameter of 20 uL droplet) to its initial contact area.

5.8 Leidenfrost Evaporation for Minimizing Deposition Area

To significantly reduce the final deposition area of diluted analytes contained in a water droplet, which is initially in the Wenzel state on the hierarchical plasmonic micro/nanostructures, we hence exploited the Leidenfrost effect to partially convert the perimetric base of the analyte droplet into the Cassie state by well-controlled substrate heating as illustrated in Figure 5-4A. Previous studies have found that depending on their surface wettability flat smooth substrates have a pretty high Leidenfrost temperature ranging between 210 °C and 320 °C for water at atmospheric pressure, while micro/nanostructured surfaces of the same materials can lead to a much lower Leidenfrost temperature reduced by over 100 °C. The Leidenfrost effect can induce the transition of a droplet from the Wenzel state to the Cassie state on hierarchical plasmonic
micro/nanostructures in two steps. First, the substrate heating incurs evaporation in the micropillar arrays under the peripheral base of a droplet and converts the peripheral portion of the droplet from the Wenzel state to the Cassie state. Second, the fast-evaporated vapor can gradually lift the droplet and fully transit it to the Cassie state following the continuous receding of three-phase contact line from the peripheral zone towards the center area. By precisely controlling the substrate temperature, it is possible to maintain the droplet in the Cassie-Wenzel hybrid Janus state, which means the circumferential contact zone is levitated to the Cassie state while the central contact base remains pinned in the Wenzel state. Therefore, maintaining a Janus droplet at the Cassie-Wenzel hybrid state can be beneficial for ultrasensitive SERS detection by 1) providing low contact friction for the droplet to recede to a small deposition area due to the marginal Cassie state, and 2) stabilizing the droplet on the SERS active spot due to the central contact region in the Wenzel state.

Figure 5-4. Leidenfrost evaporation of analyte droplets on hierarchical plasmonic micro/nanostructures. (A) Schematic of the experimental procedure for heat-assisted evaporation of liquid droplets containing
R6G molecules. (B) Static contact angle measurements of droplets at different substrate temperatures on hierarchical plasmonic micro/nanostructures. (C) IR camera images showing the droplet footprint evolution during the evaporation process at the substrate temperature of 130 °C.

To investigate the effects of substrate heating on the droplet transition between the Wenzel state and the Cassie state, we measured the contact angles of DI water droplets of 20 uL under various substrate temperatures ranging from 25 °C to 185 °C (Figure 5-4B). According to the measurements, a water droplet on a hot hierarchical plasmonic micro/nanostructured surface can experience three different phases. In the first phase, when the substrate temperature $T$ increases from 25 °C to 75 °C, the droplet stays in the Wenzel state, and its contact angle decreases from ~138° to ~123° due to the reduced surface tension of water. During the second phase, when $T$ increases from 75 °C to 160 °C, the droplet experiences the transition from the Wenzel state to the Cassie-Wenzel hybrid Janus state; thus, the droplet contact angle dramatically increases from ~123° to ~180° with the continuously shrinking contact area due to the levitating force of vapor. During the third phase, when $T$ rises from 160 °C to 185 °C, the droplet is completely levitated with no contact with the substrate due to the Leidenfrost effect. To minimize the deposition footprint size of the analyte molecules, keeping the droplet in the second phase is preferred.

We dripped an analyte droplet of 20 uL on the hierarchical plasmonic micro/nanostructured surface under the room temperature condition ($T_{\text{ambient}} = 20 ^\circ C$). To maintain the droplet in the Cassie-Wenzel hybrid Janus state with a stable evaporation rate, we set the initial substrate temperature at 130 °C and then let it naturally cool down by turning off the hot plate. Figure 5-4C shows the dynamic evolution process of the temperature contour of a droplet in the Cassie-Wenzel hybrid Janus state during evaporation, recorded by an IR camera (A300, FLIR Systems, USA). The whole evaporation process lasted for ~150 s, and the temperature of the droplet center during the evaporation process was maintained below 90 °C according to the IR camera images (Figure 5-4C). Thus, the current heating approach to inducing Leidenfrost evaporation is compatible with
the SERS detection of analyte substances with chemical stability under 90 °C. For Leidenfrost-assisted SERS detection of temperature-sensitive analyte molecules (such as proteins and DNAs), it is essential to reduce further the Leidenfrost temperature, which can be achieved by 1) increasing the filling ratio of air entrapped in the micropillar arrays, 2) reducing the surface energy of micropillars, or 3) reducing the surrounding pressure during the evaporation process.  

The translational state of droplet wetting between Cassie-Baxter state and Wenzel State, what we called partial Leidenfrost state in the main text, was observed during our heat-assisted evaporation process. Here, a simple energy analysis is derived to find the energy state of droplet at the interstate.

Figure 5-5. Diagram of wetting state a) Wenzel State b) Interstate c) Cassie State

The total surface energy of a sessile droplet on a surface is the sum of all the surface energy for creating interface, including the liquid-solid interfacial energy $E_{ls}$, liquid-gas interfacial energy $E_{lg}$, solid-gas interfacial energy $E_{sg}$. Especially on superhydrophobic surface, the total surface energy is dependent of the wetting state of the droplet.

For the droplet at Wenzel state (Figure 5-5(a)), its total surface energy $E_W$ could be calculated as:

$$E_W = N[\gamma_{ls}(d^2 + 4wh)] + \gamma_{lg}S_{cap}^W$$

(5 – 1)

where $\gamma_{ls}$, $\gamma_{sg}$ and $\gamma_{lg}$ denote the surface tension for liquid-solid, solid-gas and liquid-gas interface, respectively. $N$ is the number of micropillars underneath the droplet base. And $d$, $w$ and
are the periodicity, width and height of microstructure, respectively. $S_{\text{cap}}^W$ is the liquid-gas surface area of droplet cap at Wenzel state.

Similarly, the total surface energy $E_C$ of the droplet at Cassie state (Figure 5-5(c)) could be calculated as:

$$E_C = N\left[\gamma_{ls} w^2 + \gamma_{sg} (d^2 - w^2 + 4wh)\right] + \gamma_{lg} S_{\text{cap}}^C \quad (5 - 2)$$

where $S_{\text{cap}}^C$ is liquid-gas surface area of droplet cap at Cassie state.

For the droplet at the interstate between Cassie and Wenzel State (Figure 5-5(b)), its total energy will be more complex but still could be estimated as:

$$E_I = N\left[\gamma_{ls} w^2 + \gamma_{sg} (d^2 - w^2 + 4wh)\right] - N_W\left[(\gamma_{sg} - \gamma_{ls}) (d^2 - w^2 + 4wh)\right]$$

$$+ \gamma_{lg} S_{\text{cap}}^I \quad (5 - 3)$$

where, $N_w$ is the number of pillars are totally wetted (at Wenzel state). $S_{\text{cap}}^I$ is liquid-gas surface area of droplet cap at interstate.

Combined with Young’s equation, $E_I$ could be rearranged in terms of contact angle $\theta_I$:

$$E_I = N\left[\gamma_{ls} w^2 + \gamma_{sg} (d^2 - w^2 + 4wh)\right] - N_W\left[\gamma_{lg} \cos \theta_I (d^2 - w^2 + 4wh)\right]$$

$$+ \gamma_{lg} S_{\text{cap}}^I \quad (5 - 4)$$

Combining the equation 5-1 and 5-2, the energy difference $\Delta E_{IW}$ between interstate and Wenzel state could be calculated as:

$$\Delta E_{IW} = E_I - E_W = (N_W - N)\left[\gamma_{lg} \cos \theta_I (d^2 - w^2 + 4wh)\right] + \gamma_{lg} (S_{\text{cap}}^I - S_{\text{cap}}^W) \quad (5 - 5)$$

While the energy difference $\Delta E_{IW}$ between interstate and Cassie state could be calculated as:

$$\Delta E_{IC} = E_I - E_C = -N_W\left[\gamma_{lg} \cos \theta_I (d^2 - w^2 + 4wh)\right] + \gamma_{lg} (S_{\text{cap}}^I - S_{\text{cap}}^C) \quad (5 - 6)$$
For the droplet on the superhydrophobic surface whose contact angle $\theta_I > 90^\circ$, the first term of equation 5-5 and 5-6 should be larger than 0. And the second term of 5-5 and 5-6 could also be estimated based on the assumption of spherical droplet model.

$$
\gamma_{lg}(S_{cap}^I - S_{cap}^W) = 2\pi R^2 \gamma_{lg} (\cos \theta_W - \cos \theta_I) \quad (5 - 7)
$$

$$
\gamma_{lg}(S_{cap}^I - S_{cap}^C) = 2\pi R^2 \gamma_{lg} (\cos \theta_C - \cos \theta_I) \quad (5 - 8)
$$

Based on our experimental observation, the contact angle of droplet at interstate is almost same as the contact angle at Cassie state and larger than that at Wenzel state($\theta_I = \theta_C > \theta_W$), which means the second term of two equations should be also positive value. Therefore, the total energy of interstate droplet $E_I$ should be larger than the energy at Wenzel state $E_W$ and Cassie state $E_C$.

During the normal diffusive-driven evaporation process of sessile droplet on superhydrophobic surface, it has been experimental validated that the evaporation would drive the droplet at Cassie state into the Wenzel state. It could be explained by the total energy of droplet at Wenzel state $E_W$ become less than $E_C$ once the droplet size beyond a critical size $r_c$.\textsuperscript{165} In our case, the heat-assisted evaporation process would provide a source term for the whole system to drive the droplet beyond energy barrier $\Delta E_{IW}$ and keep at the quasi-stable state, namely partial Leidenfrost state. The existence of partial Leidenfrost state would be postponed and decrease the critical size $r_c$, thus could achieve minimized footprint of the solutions.

### 5.9 IR Camera Calibration

The IR camera FLIR A300 (IR resolution is 320 x 240 pixels, spatial resolution is 1.36 mrad, and FPS is 30 Hz) was calibrated before the temperature measurement of the droplet during the heating and evaporation process. The relationship between the IR camera monitoring temperature and the target surface temperature can be then correlated in the form of a curve fitting to the IR data.
The IR camera calibration is implemented by (1) calibrating the temperature measurement of a large body of bulk water, then by (2) calibrating the temperature measurement of a small droplet since our goal is to measure the temperature distribution in the droplet. The calibration results from step (1) and step (2) should closely match each other.

To calibrate the IR measurement of bulk water, 150 mL water was heated up to the boiling point and the air-liquid (water) interface temperature was measured by a thermal couple. The thermal couple bead was placed as close as to the water interface so that the interface temperature was measured, instead of the water bulk temperature. Then, the IR camera was set to measure the temperature of the water with the water emissivity of 0.995, the ambient temperature $T_{amb} = 20 ^\circ C$ and the relative humidity of 50%. And the monitored cooling process of the bulk water with the temperature ranging from 90 °C to 25 °C is shown in Figure 5-6(a).

![Figure 5-6.](image)

**Figure 5-6.** (a) IR calibration of bulk water temperature; (b) Correlation between the temperature measurements of bulk water by IR camera and thermal couple.

The IR monitoring data and the thermal couple measurements are plotted in Figure 5-6(b), and the linear fitting is:
\[ T_{thermal\ couple} = 3.6 + 0.93 \cdot T_{IR\ camera} \ (°C) \]  

(5 – 9)

After calibrating the IR measurement of bulk water, the IR calibration of a water microdroplet temperature is subsequently conducted by the following steps:

1. Mount the thermocouple through a hole in the substrate such that only the bead is sticking out, as illustrated in Figure S3. *Note:* This way can make the thermocouple measure the temperature of the microdroplet of water, instead of the substrate.

2. Heat up the substrate to ~ 120 °C and heat up the water droplet to ~ 70 °C, respectively. The reason not to keep the droplet at a higher temperature is that the evaporation rate of the droplet becomes faster as the temperature increases. To maintain the droplet in a relatively stable state, the initial temperature of the droplet was set at 70 °C.

3. Add a micro drop of this hot water directly to the bead and allow it to cool down while measuring the temperature through IR camera and thermocouple.

*Figure 5-7.* IR camera calibration for water microdroplet.
Finally, the temperature evaluation of the water droplet was compared with the bulk water calibration, using equation 5-9 as shown in Figure 5-7. The results indicate that the fitting line from the calibration of bulk water fits well with the temperature measurement of water microdroplet, and the standard error between the experimental data and the fitting line is less than 0.3, which shows good reliability of the IR camera calibration.

**Figure 5-8.** Comparison between the temperature measurement of water microdroplet and the IR camera calibration of bulk water.
5.10 SERS Sensing of Ultra-low Concentration Solution

**Figure 5-9.** Leidenfrost evaporation assisted SERS detection of concentrated R6G molecules. (A) Schematic of Leidenfrost evaporation of droplets with substrate heating (top) and natural evaporation of droplets without substrate heating (bottom). (B) Raman spectra, (C) confocal Raman images, (D) bright-field images, and (E) fluorescence images of R6G molecules deposited on hierarchical plasmonic micro/nanostructures via the Leidenfrost droplet evaporation with substrate heating (top) or natural droplet evaporation without substrate heating (bottom).

Compared to natural evaporation, Leidenfrost-assisted evaporation of droplets in the hybrid Janus state can lead to a much smaller analyte deposition area on hierarchical plasmonic micro/nanostructures (Figure 5-9A). To experimentally demonstrate the effectiveness of Leidenfrost evaporation-assisted ultrasensitive SERS detection, we conducted a side-by-side evaluation of Leidenfrost and natural evaporation processes for SERS measurements of Rhodamine 6G (R6G) droplets of 20 µL at a concentration of $10^{-9}$ M. Figure 5-9B depicts the average Raman spectra at the R6G deposition areas on hierarchical plasmonic micro/nanostructures after Leidenforst evaporation (top) and natural evaporation (bottom). We acquired the average Raman spectra by measuring $40 \times 40$ pixels over a $20 \mu m \times 20 \mu m$ area (laser power: 1.3 mW, integration time: 0.1 s/pixel) using 100× objective lens (NA: 0.9) with the focus
on the top surface of the micropillar structures. As shown in Figure 5-9B, Leidenforst evaporation of the R6G droplets in the hybrid Janus state allows direct SERS detection of R6G at a concentration as low as $10^{-9}$ M, while we cannot observe any R6G Raman signatures through the natural evaporation process. Accordingly, the 2D confocal Raman image shows intense R6G SERS spatial distribution patterns at 1507 cm$^{-1}$ on the top plane of hierarchical plasmonic micro/nanostructures from Leidenforst evaporation (Figure 5-9C top) but not from nature evaporation (Figure 5-9C bottom). As expected, strong R6G SERS signals were also detected on the bottom plane of the hierarchical plasmonic micro/nanostructures following Leidenforst evaporation (Figure 5-10), which confirms that the droplet stayed in the hybrid Cassie-Wenzel Janus state with the final analyte deposition footprint formed both on top of the micropillars and in the micropillar cavities of the hierarchical SERS substrate. Figures 5-9D and 5-9E show the bright-field images and the fluorescence images of the R6G deposited areas on hierarchical plasmonic micro/nanostructures following Leidenfrost evaporation and natural evaporation, respectively. By Leidenfrost evaporation, the bright-field image (Figure 5-9D top) clearly shows a red-colored circular-shaped pattern of densely packed R6G molecules with a final R6G deposition area of $\sim 450 \, \mu m^2$, and its shape is in good agreement with the R6G pattern measured by Raman imaging (Figure 5-9C top) and fluorescence imaging (Figure 5-9E top) in the same region of the sample. The excellent shape consistency for the final R6G deposition area between the Raman image, the bright-field image, and the fluorescence image reflects the well-controlled SERS protocols without any contaminants introduced on the SERS surface during the Leidenfrost evaporation of low-concentration R6G droplets.

Figure 5-10 shows SERS 2D confocal mapping of 20 $\mu$L R6G droplet at a concentration of $10^{-9}$ M. A bright and intense R6G spatial distribution patterns at 1507 cm$^{-1}$ is shown on the bottom plane of Si micropillar arrays.
The confocal Raman image of R6G at 1514 cm$^{-1}$ from the footprint of a heating-assisted evaporating droplet with the focus on the bottom plane of Si micropillar arrays.

The fluorescence spectrum of R6G on hierarchical plasmonic micro/nanostructures is shown in Figure 5-11. The fluorescence spectrum is measured by a confocal microscopy system (Alpha 300rsa+, Witec, Germany) with 532 nm laser excitation and a 536 nm long-pass emission filter.
Figure 5-11. The fluorescence spectrum of the deposited R6G droplet residue after heating-assisted evaporation excited by 532 nm laser with a 536 nm long-pass emission filter.

The assignment of Raman peaks we are interested are listed below:

Table 5-2. R6G Raman peak origins.

<table>
<thead>
<tr>
<th>Raman shift (cm⁻¹)</th>
<th>Origin of the peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>1183</td>
<td>in-plane xanthene ring deformations, C-H bend, N-H bend</td>
</tr>
<tr>
<td>1310</td>
<td>in-plane xanthene ring breath, N-H bend, CH2 wag</td>
</tr>
<tr>
<td>1360</td>
<td>xanthene ring stretch, in-plane C-H bend</td>
</tr>
<tr>
<td>1507</td>
<td>xanthene ring stretch, C-N stretch, C-H bend, N-H bend</td>
</tr>
</tbody>
</table>

To explore the origin of the weak Raman signal of R6G footprint after natural evaporation, we conducted the SERS mapping of the bare substrate under the same measurement conditions, (i.e. laser power integration time, objective, spatial resolution, etc.), as shown in Figure 5-12. The
averaged Raman spectrum of naturally evaporated R6G droplet follows the same trend of the bare substrate. The weak Raman profile of naturally evaporated R6G footprint comes from the background of the SERS substrate. The intensity difference is caused by the slight inhomogeneity of different positions on the substrate.

Figure 5-12. Averaged Raman spectra of the bare substrate and $10^{-9}$ M R6G footprint after natural evaporation under the same measurement condition (i.e. laser power, integration time, objective, pixels number, etc).

In contrast to Leidenfrost evaporation, natural evaporation of the same-sized R6G droplets (20 uL, $10^{-9}$ M) on the hierarchical plasmonic micro/nanostructures at room temperature condition took a much longer time (2 hours). It resulted in a much larger final R6G deposition area (~ $2 \times 2$ mm²), as illustrated in the fluorescence image (Figure 5-9E bottom). Therefore, compared to natural
evaporation, Leidenfrost evaporation of analytic droplets can effectively reduce the final analyte deposition area and accordingly increase the density of analytic molecules by a factor of $10^3 \sim 10^4$ in hot spots of hierarchical plasmonic micro/nanostructures without the need for an extra hydrophobic coating. As expected, we cannot detect R6G Raman signals from the hierarchical plasmonic micro/nanostructures after natural evaporation due to the sparse surface density of R6G (Figure 5-9B bottom). The 2D SERS image (Figure 5-9D bottom) shows a few pixels with some weak intensities due to the broad background emission from the substrate instead of Raman scattering from R6G molecules (Figure 5-9B bottom and Figure 5-12). Therefore, Leidenfrost evaporation on hierarchical plasmonic micro/nanostructures can allow fast and ultrasensitive SERS detection of low-concentration analytes in aqueous droplets. By optimizing the hierarchical micro/nanostructures and controlling the substrate heating-cooling dynamics,\textsuperscript{167} it is possible to further decrease the deposition area of low-concentration analytic droplets via Leidenfrost evaporation and therefore achieve even high EFs of SERS detection.

5.11 Chapter Summary

In conclusion, we have demonstrated a new strategy for fast and ultrasensitive SERS detection based on the Leidenfrost evaporation of nanomolar analytic droplets on hierarchical plasmonic micro/nanostructures, which can quickly increase the analytic concentration within a significantly reduced deposition area. Hierarchical plasmonic micro/nanostructures not only support hot spots with SERS EFs as high as $1.8 \times 10^7$, but also allow for Leidenfrost evaporation at decreased temperatures than that on the flat substrates. Compared to natural evaporation, Leidenfrost-assisted droplet evaporation can efficiently facilitate the analytic concentration process from hours to several minutes, reduce the final analytic deposition area (footprint) within hundreds of $\mu\text{m}^2$ and accordingly increase analytic density on hot spots by 3-4 orders of magnitude. Therefore, Leidenfrost-assisted SERS on hierarchical plasmonic micro/nanostructures provides an agile and
facile avenue to overcome the diffusion limit for fast and ultrasensitive detection of low-concentration analyte droplets without the need for extra hydrophobic coating on engineered SERS surfaces.
Chapter 6  Summary and Future Work

6.1 Summary

By taking advantage of the electrowetting phenomenon, the wettability of liquid droplet on micro/nano-structured surfaces and the Leidenfrost effect, this doctoral program focuses on developing high-performance optofluidic sensing systems, including optical beam adaptive steering, whispering gallery mode (WGM) optical sensing, and surface-enhanced Raman spectroscopy (SERS) sensing, respectively.

Beam steering is a widely investigated and used technology in optics, RF/microwave transmission and wireless communications, et al. In recent years, there has been a resurgent interest in this area because of the demanding needs from many critical future photonics applications such as lidar for automated driving and 3D sensing for virtual reality (VR). As such, there have appeared numerous techniques to solve the problems associated with current beam steering schemes based on bulk optics. However, most of these schemes still suffer from limited angular range, low speed and high optical loss, in contrast to the standard bulk-optic solutions that can cover almost all angles with very low loss. In this work, we demonstrate an adaptive optical beam steering system based on the digital operations of an EWOD-driven fluidic rotor. Compared with other liquid-based beam steering devices, the EWOD rotary platform integrated with the 3D printed superlattice hub endows the system with the widest lateral steering range (~360°), the fastest response (~353.5 °/s), the lowest voltage requirement (~40 V), and the lowest power consumption (~10⁻⁵ W). Via the specular reflection mode of beam steering, there is no optical aberration incurred during the beam transmission. Importantly, the full range steering is not constrained by the contact angle saturation effect of EWOD, which generally plays an inextricable role in
conventional EWOD systems. Actually, by integrating EWOD-controlled liquid prism in to the system, the beam can be guided not only laterally but also omnidirectionally.

WGM sensing in water-based microcavities is highly desired in practice because they are more closely analogous to the biological environment. In this work, we analyzed a fluidic and deformed microdroplet system as an optical cavity, in which WGMs are stimulated by an embedded strip waveguide on a micro/nanostructured superhydrophobic surface. The embedded strip waveguide beneath the nanopillared surface can not only stabilize the microdroplet at the Cassie state but also enable the WGMs to be generated in the meridian direction, which makes the coupling process more facile and more stable compared to the WGMs coupling along the equatorial plane. As a compromise, the unavoidable deformation in the microdroplet meridian plane weakens the quality factor $Q$. Nonetheless, the nanopillar patterned superhydrophobic surface above the waveguide can mitigate such deformation and have the potential to achieve a high-quality $Q$ factor. In this regard, the microdroplet with $\theta_A = 151.2^\circ$ and $156.3^\circ$ has total $Q$ factor > $10^3$; and the microdroplet with $\theta_A = 161.5^\circ$ and $170.9^\circ$ has total $Q$ factor > $10^4$. Besides, in terms of sensing application, making the microdroplet itself serves simultaneously as the trace analyte container and the optical cavity, a high sensitivity $S > 530$ nm/RIU can be achieved, which is more sensitive than the solid counterparts. On the other hand, a water microdroplet may evaporate very fast when it is directly exposed to the ambient, causing the WGMs to drift during measurement. A prior study reported that the size stabilization of microdroplets containing no salt can be obtained via an electrically controlled mini humidity and demonstrated that the diameter variation of a 12 μm water droplet was only ~1 nm during 82.8 seconds. Even though water evaporation can be effectively mitigated by controlling the humidity inside a chamber, the WGM sensing system can be more easily applied without the enclosure. Currently, to slow down the evaporation process of a water droplet, a proper amount of glycerol was added in to water to form glycerol–water mixture in some WGM studies. In our meridian WGM configuration, owing to the high contact angle ($\theta_A > 160^\circ$) of the glycerol–
water mixture on a superhydrophobic surface, fluidic microcavities with the geometry of a truncated sphere minimally distorted by gravity and contact line pinning effects could be generated. For future applications, the stable and feasible waveguide coupling microdroplet system can be integrated with EWOD platform leading to a digital lab-on-a-chip sensor with high throughput and high sensitivity even in a complex sample matrix.

Based on the integration of multilayered plasmonic nanostructures on hierarchical micro-nanostructured surfaces, resulting in a hydrophobic surface with high-performance SERS functionality, we have demonstrated a new type of SERS substrates. The intrinsic SERS performance of the hierarchical plasmonic micro/nanostructures achieves EFs of $\sim$1.8 x 10$^7$. Furthermore, the heating-assisted evaporation approach appears to transit the Wenzel droplet to the hybrid Cassie-Wenzel state, and the footprint of the hybrid Cassie-Wenzel state droplet can shrink by three orders of magnitude, leading to a significant increase of the analyte concentration on the SERS active hot spots of hierarchical plasmonic micro/nanostructures. With such densely distributed analytes on the SERS active surface, the SERS signal can be improved by 10 times. Without any surface treatments or adding any lubricants, the proposed heating-assisted evaporation approach can effectively shrink the deposition size down to $\sim$24 μm in diameter ($\sim$450 μm$^2$ in area), which has great potential for achieving even higher concentration detection limit. As a real application, the SERS substrates of hierarchical plasmonic micro/nanostructures are promising to be integrated with an electrowetting-based digital microfluidics system for programmable and reconfigurable bio/chemical sensing applications.

In short, in this doctoral research, a rotary electrowetting-on-dielectric (EWOD) beam steering system was first fabricated and developed with a wide lateral steering range of 360° and a fast steering speed of 353.5°/s, which can be applied in telecommunication systems or lidar systems. Next, the meridian WGM optical sensing system was optically simulated using finite difference time domain (FDTD) method and was numerically validated to achieve a high quality-factor $Q$.
exceeding $10^4$ and a high refractive index sensitivity of 530 nm/RIU, which can be applied to the broad areas of liquid identification or single molecule detection. Lastly, a SERS sensing platform based on a hierarchical micro/nano-structured surface was accomplished to exhibit a decent SERS enhancement factor (EF) of $1.81 \times 10^7$. The contact angle of water droplet on the SERS substrate is $134^\circ$ with contact angle hysteresis of $\sim 32^\circ$. Therefore, by carefully controlling the SERS surface temperature, we employed Leidenfrost evaporation to concentrate the analytes within an extremely small region, enabling the high-resolution detection of analytes with an ultra-low concentration of $\sim 10^{-9}$ M.

6.2 Future Work

This sub-chapter discusses future work based on the knowledge accumulated thus far. Future work should primarily address the following:

- Optimize the design of the rotary EWOD electrode pattern to manipulate the droplet and steer the reflecting membrane with a faster steering speed

- Redesign the rotary EWOD beam steering system with a closed configuration for practical application.

- Fabricate the WGM substrate with the nanostructured surface and the embedded waveguide, and experimentally investigate the performance of the meridian WGM system

- Investigate the methodology to reduce the required temperature of the Leidenfrost-evaporation approach, making it applicable to the temperature-sensitive analytes
References

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