

Chapter 1: Applications of CdSe Quantum Dots

Summary

The photoluminescence (PL) and electroluminescence emission from colloidal cadmium selenide (CdSe) quantum dots (QDs) can be tuned within the visible spectrum from wavelengths of 450 nm to 650 nm by controlling nanocrystal size.¹ This versatility opens up a variety of potential applications for CdSe quantum dots in photonic devices, such as the following:

- emitters for color displays²
- color modifiers for light emitting diodes (LEDs)³
- optical fiber amplifiers^{4,5}
- low threshold lasers⁶
- self-assembled photonic sphere arrays⁷
- polymer-based photovoltaic cells⁸
- optical temperature probes⁹
- chemical sensors⁸
- high-speed signal-processing filters.¹⁰

CdSe quantum dots are also commercially available to fill a growing demand in the field of biomedical imaging.¹¹ Conjugation of QDs with antibodies yields biomarkers that compete with traditional organic fluorescent tags in terms of biocompatibility, excitation and filtering simplicity, and photo-stability.^{12,13}

All these applications—whether photonic or biomedical—prefer photoluminescence emission peaks that are narrow and bright.¹⁴ Under optical excitation, quantum dots' capacity for bright emission is quantified by the photoluminescence quantum yield (PLQY), defined as the ratio of photons emitted to photons absorbed. Under electrical excitation, quantum dots are evaluated based on their internal quantum efficiency (QE), defined as the number of photons emitted per electron injected into the active region. It is quite a challenge to synthesize quantum dots with PLQYs or QEs that can compete with those of traditional organic fluorescent dyes or mature semiconductor emitters. However, quantum dots can currently surpass these mature materials in terms of tunable narrow emission, based on careful control of nanocrystal growth.

By controlling the average nanocrystal size, the band gap of quantum dots can be tailored continuously over a wider energy range than is possible in bulk semiconductors by changing the semiconductor alloy composition. In fact, bandgaps even smaller than those of the bulk semiconductor counterpart have been achieved in QD-polymer composites, perhaps due to bandgap narrowing that occurs due to high local electric fields between closely spaced quantum dots.

Combining the unique optical properties of quantum dots with the electrical properties of conductive polymers produces quantum dot polymer composites for alternative photonic devices. Generally the cost and efficiency of these polymer-based devices can be significantly lower than their semiconductor counterparts, because economical high-volume manufacturing techniques for polymer films can be employed.

This makes polymer quantum dot composites potentially suitable for large area devices, such as animated billboards, photo-detectors, and gas sensors.⁸

Light Sources with Spontaneous Emission

Capitalizing on the narrow emission width possible from quantum dots, researchers are developing new emitters for applications that require carefully controlled color. One such application is the animated billboards on buildings and in sports arenas. Presently, these large color displays contain millions of light emitting diodes (LEDs); the intensities of red, green, and blue LEDs are adjusted to produce a color image, much like the elements of a color television. The cost of such displays could potentially be reduced if discrete LEDs could be replaced by polymer films containing quantum dots with different emission wavelengths. Such composites have demonstrated PLQYs as high as 22% for red emission at 426 nm, and 40% for green emission at 514 nm.³

CdSe quantum dots have been combined with conductive polymers such as polyvinylcarbazole to form active regions sandwiched between aluminum and transparent indium-tin oxide (ITO) electrodes. Applying a voltage across these electrodes excites the quantum dots, producing an electroluminescence spectrum that has a slightly wider emission peak but otherwise closely follows the photoluminescence spectrum of the quantum dots without the polymer.² One benefit of this approach is that the electrical and optical components of the color display could be economically defined using lithography, rather than assembling millions of discrete LEDs. In addition to controlling the emission intensity, different applied voltages can also change the emission color, because the primary location for electroluminescent recombination is shifted between the

interface of the quantum dot and the polymer matrix, and because the polymer may also exhibit electroluminescence.⁸

The absorbance and photoluminescence spectra of quantum dots also allow them to act as wavelength conversion materials for light emitting diodes. Quantum dot emission is typically narrower than that of inorganic phosphorus currently used as wavelength conversion materials.³ Quantum dots absorb light from wavelengths shorter than their absorbance edge and then emit light at their luminescence peak wavelength. For example, commercially available gallium nitride (GaN, $\lambda=425$ nm) blue LEDs provide a convenient excitation source that can be converted to any wavelength in the visible spectrum using appropriately designed CdSe quantum dots.

Researchers are presently considering using the wavelength conversion properties of quantum dots for solid-state white lighting. Here the goal is to produce color-balanced white light with the highest possible energy efficiency and the lowest possible cost. One approach is to surround a blue LED with a quantum dot polymer composite that converts some of the blue light to yellow light so that the human eye perceives the emission as white light.³ Although color mixing is possible with quantum dots, this approach is not energy-efficient enough to replace fluorescent lights. The energy efficiency for yellow emission, for example, is the product of PLQY, the Stokes shift energy conversion efficiency, and the wall plug efficiency of the excitation LED. The efficiency of the quantum dot wavelength conversion also significantly decreases with elevated temperatures produced by the blue LED. It is probably more energy-efficient to develop improved yellow or green semiconductor LEDs to work in concert with high-efficiency blue and red LEDs.¹⁵

Optical Amplifiers

Theoretically, quantum dot lasers offer the potential of better performance than bulk semiconductor lasers or quantum well lasers. This potential arises from tighter confinement of carriers. “In small, strongly confined dots, the separation between energy states is greater than the thermal carrier energies, inhibiting thermal depopulation of the lowest, ‘emitting’ transition and resulting in a low, temperature-insensitive optical-gain threshold, a narrow emission line, and a high-temperature stability.” To realize this dream, quantum dots must have a high PLQY, a narrow size distribution, and a close packing density.⁶

For amplification, the electrons and holes in quantum dots could be excited by pumping at the absorption peak or shorter wavelengths, so that light propagating near the quantum dots' peak emission wavelength would stimulate coherent emission that amplifies the propagating signal. To use quantum dots as the gain media of a laser, a cavity must be formed, which multiplies the stimulated emission within a narrow wavelength band. Some of the techniques for creating laser cavities using optical fiber include feedback rings, etched Bragg gratings, splices, and whispering gallery modes.

Meissner and Holton⁵ demonstrated that CdSe quantum dots capped with ZnS can be inserted by capillary action into holey fibers, after they are drawn. Visible light propagating through the modified fiber coupled strongly with the quantum dots, showing the potential use of quantum dots in fiber-based filters, optical amplifiers, and lasers.⁵ For laser applications, quantum dots have a wide stoke shift between absorption and emission, which can reduce self absorption losses in the active layer.⁸

For telecommunication applications, infrared amplifiers are needed for selected low-loss wavelength bands that propagate long distances through silica fibers. Kershaw *et al.* tested a prototype infrared laser based on HgTe quantum dots as the gain media. Optical gain was demonstrated for wavelengths from 1000 nm to 1600 nm, using a conventional stripe laser design. The maximum gain of 6.9 cm^{-1} greatly exceeds that of conventional erbium-doped silica fiber amplifiers.⁴

One strategy for producing low threshold lasers is to use a microsphere, with a refractive index higher than the surrounding material, to provide the wave-guide action analogous to that found in standard optical fibers. Including quantum dots in the microsphere essentially provides optical gain within the laser cavity. This has been demonstrated using emulsion polymerization of a methylmethacrylate solution containing CdSe quantum dots, yielding spheres of PMMA about 12 microns in diameter with embedded quantum dots. The standard Gaussian distribution of photoluminescence from the quantum dots is modulated by periodic variations caused by self interference. As a photon travels around the inside of a sphere, it interferes with itself to create standing waves, or so-called whispering gallery modes.¹⁶ To form a laser in this system, the CdSe quantum dots would be optically excited by shorter wavelengths until one of the preferred whispering modes was amplified by stimulated emission at a net gain that was larger than the net optical loss of the photon in that mode.

Narrow energy state distributions from quantum dots offers the potential of stable high gain in lasers. Whereas a bulk semiconductor has a nearly continuous distribution of energy states above its bandgap, quantum dots theoretically have discrete energy levels like atoms do, and the spacing between the electron and hole energy levels

increases as the quantum dots are made smaller. Realistically the distribution of energy states in a collection of quantum dots is primarily determined by the size distribution of the quantum dots.

For stimulated emission in a laser, the density of occupied excited states at a particular energy must exceed the density of electrons in their ground state. Only with this population inversion is it possible to emit more photons at the emission energy than are being reabsorbed at that same energy. At the threshold for lasing, the gain at a particular photon energy must equal the magnitude of the net loss in the cavity. The gain scales with the occupation of allowed excited states at each energy. A wider distribution of allowed excited states means that more electrons will have to be excited before the maximum gain reaches the threshold level.¹⁷ Using the water analogy for electrons, it takes more water to fill a wider pot to a target level. In lasers, the target level is the threshold carrier density. Therefore, narrow size distributions in quantum dots are critical to achieving low threshold currents. In the photonics industry, low threshold lasers are like a “holy grail”, because of their potential high energy efficiency and low waste heat dissipation.

Narrow quantum dot size distributions also help stabilize the laser output wavelength.¹⁷ Free carriers may be generated by an injection current density or by an optical pump intensity. The resulting excited electrons will fill the lowest available energy states first, with some randomness due to their thermal energy. In a bulk semiconductor, the electrons are like fans filling a football stadium from the bottom, where the *position* of seats with the highest occupancy levels moves upwards with increasing attendance. So, if the distribution of allowed energy states is wide, the excited

states with the highest degree of population inversion will be at progressively higher energies as the number of electrons is increased. The following undesirable result occurs: the wavelength of peak gain for the laser will blue-shift at higher power levels. In a narrow distribution of quantum dots, the electrons behave more like spectators on bleachers in a small gym, because the random thermal energy can scatter them across the narrow range of allowed energies. Then as the density of electrons increases, the excited energy with the highest population (*i.e.* the photon energy of peak gain) does not change very much. Therefore, for stable laser output color independent of brightness or temperature, quantum dots with a narrow size distribution are desirable as the gain media.¹⁷

Malko⁶ demonstrated the CdSe quantum dots could form the gain media of a laser. CdSe quantum dots suspended in hexane were drawn into glass microcapillary tubes, with an internal diameter of 80 microns. As the hexane was evaporated, the quantum dots packed into a dense gain region close to the whispering gallery modes, where light could propagate around the axis of these tubes. As the optical pump intensity increased above a threshold value, both radial and longitudinal photoluminescence increased dramatically. At these high pump levels, there were periodic amplitude variations with emission wavelength, as expected for lasing along whispering gallery modes. To measure the magnitude of optical gain, CdSe quantum dot films were prepared on glass slides by evaporating the hexane solvent, leaving behind closely packed, self-assembled quantum dot layers. As the length of an optically excited stripe was increased linearly, the magnitude of amplified spontaneous emission increased exponentially, characterized by a modal gain of 130 cm^{-1} .⁶

In the quest for low threshold lasers, Rogach has proposed putting quantum dots into periodic structures called photonic crystals, which could be used as a novel gain media.⁷

Periodic Arrays in Photonic Crystals

When light travels through a media, if the periodicity of the electromagnetic wave matches the periodicity of the refractive index, then the photonic crystal would rather emit or scatter that light instead of transmitting light at that wavelength. The position of this stop-band wavelength, λ_c , can be tailored by adjusting the size or the refractive index of periodic structures.⁷ Refractive index in a nanocrystal-polymer composite can be adjusted by controlling the quantum dot concentration.⁸

When spheres are made with tightly controlled diameters, they can be self assembled into regular arrays with special optical properties. Although polystyrene is transparent in the visible wavelengths, a closely packed periodic array of polystyrene spheres shows anomalous fluctuations in transmission spectrum and even develops a photoluminescence peak at λ_c . In general the stop-band wavelength is given by Equation (1-1), where n_{eff} is the effective refractive index of the whole structure given by (1-2), n_s is the refractive index of the spheres, n_{air} is the refractive index of the air between the spheres, where f is the volume fraction of spheres, and d is the distance between (111) planes, given by (1-3), where D is the diameter of spheres.⁷

$$\lambda_c = 2 n_{eff} d \quad (1-1)$$

$$n_{eff}^2 = n_s^2 f + n_{air}^2 (1-f) \quad (1-2)$$

$$d = D \sqrt{2/3} \quad (1-3)$$

For added freedom in adjusting the effective refractive index, quantum dots can be bound to the surface of the spheres. For glass spheres, the refractive index has been increased from 1.45 for pure silica to 2.6 for glass beads impregnated with CdTe quantum dots. Alternatively polystyrene beads have been coated with a polymer quantum dot composite film using electrostatic self-assembly (ESA) techniques to increase their net refractive index.⁷

Although still in its infancy, this process “might provide a basis for low threshold lasers and novel nonlinear optical phenomena.”⁷

Filters with Unique Optical Properties

The absorbance spectra of quantum dots naturally provide the optical behavior of a long pass filter. Quantum dots absorb light propagating at wavelengths equal to or shorter than their first absorption peak, while transmitting light at longer wavelengths.

The inclusion of quantum dots can also yield unique and unexpected properties. For example, Corning 2-61 and 2-59 glass filters contain CdSe crystals as a result of their thermal processing. These filters act as fast optical shutters, which block some wavelengths only during a visible pulse. After some debate in the literature, regarding the mechanism, it was demonstrated that a pulse of incident radiation at 585 nm (matching the first absorbance peak of the CdSe quantum dots) excited electrons from the ground state to the 1S level, which in turn allowed these excited electrons to make a transition to the 1P level by absorbing infrared light at 3.8 microns. The high speed of this effect and a large magnitude of induced infrared absorbance mean that these filters are useful for signal processing and possibly optical computing.¹⁰

Optical, Thermal and Chemical Sensors

Photovoltaic devices can be formed with an active layer of n-type CdSe quantum dots in p-type polyaniline. Incident light passes through a glass substrate and an indium-tin oxide transparent electrode. Absorption of a photon by a CdSe quantum dot produces an electron hole pair. Holes preferentially conduct through polyaniline to the anode, while electrons percolate through connected quantum dots to the aluminum cathode layer. When the composite contains 90 weight % CdSe in polyaniline, the quantum efficiency (QE) is maximized at about 12%—that is, twelve electrons collected per 100 photons absorbed at a wavelength of 514 nm. The power efficiency (electrical energy out per optical energy in) is only 0.1% under solar radiation.⁸ When quantum dots are used in solar cells, surface defects represent unwanted traps that lead to non-radiative recombination of electron hole pairs.⁸ This is one of the causes of the low efficiencies of nanocrystal-polymer composites, which might be used for special light detectors, but not for serious power generation.

Optical temperature probes have been made using CdSe quantum dots in a poly(lauryl)methacrylate matrix. The photoluminescence intensity decreases with increasing temperature from 100 to 300 K. The decrease in PL intensity is linear near room temperature. There is also a redshift in the emission peak with increasing temperature.⁹

Other sensors are envisioned for nanocrystal-polymer composites, based on the sensitivity of their electrical properties to their environment. The conductivity of these composites increases dramatically when the quantum dot volume fraction reaches a percolation threshold. This conductivity along chains of connected quantum dots can be

used to make gas sensors. If specific solvents cause the polymer to swell after a few minutes, the distance between quantum dots increases as conductivity decreases.

Moisture sensors rely on a more rapid change in polymer dielectric properties in the presence of polar water molecules.⁸

Photoluminescence Markers for Medical Diagnostics

A wide array of potential biomedical applications are increasingly motivating research on quantum dots. Many pathogens can be identified by characteristic proteins. Furthermore, antibodies have been developed that bind to many of these target proteins. With recent advances in immunohistochemistry, these antibodies can be joined to quantum dots to form new luminescent tags. As a medical tool for diagnosis, luminescent tags can help detect the presence of selected diseased tissues or illuminate the structure of diseased areas.

Quantum dots can help read DNA sequences. By attaching quantum dots and antibodies to polymer microspheres, the prevalence of targeted DNA sequences can be read by a standard flow cytometer. The surface of each sphere would also be covered with specific antibodies that would bind to specific protein sequences.¹⁸ This method is being compared to immuno-assay fluorescence arrays.

One of the keys to successful cancer treatment is accurate identification. To diagnose a specific type of cancer, slides are traditionally made from tumor tissue samples, and selective chemical stains can highlight one specific feature at a time, such as nuclei or aster cells. Quantum dots can enhance the capability of simultaneously marking

numerous features with different colors, thus rapidly providing oncologists with a wealth of accurate and valuable information.

In the past, oncologists hoped to find universal cancer indicators, but now researchers recognize that cancer is a complex disease, requiring a wide vocabulary of tests for adequate characterization. Compared to healthy cells, cancer cells tend to have less specific structure and function.¹⁹ Cancer tissue is also less homogeneous than normal tissue. Increasing the optical bandwidth available to pathologists facilitates the recognition of spatial correlations between different cellular features for better cancer detection.²⁰

To meet this need, quantum dots with narrow emission peaks are available in the visible spectrum. Narrower emission peaks allow a larger number of fluorescent tags to be distinguished simultaneously.

Quantum dots have been used to guide cancer surgery. The intensity of scattered luminescence can guide a surgeon to selectively excise only tagged diseased tissue beyond the primary tumor. This is especially important in brain surgery, where cutting out the tumor plus a generous border thickness "just to be sure its does not recur" can reduce the patient's quality of life after surgery.²⁰ Traditionally, a radioactive blue dye is sometimes used to track the flow of cancer cells through the lymph system. However, ionizing radiation is inherently hazardous to both the patient and the medical caregivers. As a potentially safer alternative, near-infrared ($\lambda \sim 850$ nm) quantum dots have been successfully used by Bawendi's group at MIT to mark cancerous lymph nodes for surgical removal from mice and pigs.²¹ Since CdSe quantum dots have the highest known efficiency for two-photon microscopy, mouse capillaries labeled with CdSe

quantum dots can be imaged through more than 0.1 mm of skin.²² However, the well-known toxicity of Cd and Se to cells is just one of the reasons that *in vivo* use of CdSe quantum dots are not being emphasized here.

The visible emission from CdSe quantum dots favors *in vitro* biomedical applications, such as laboratory blood tests, urine analysis, tissue slide staining, cell culture monitoring, etc. The strong scattering of visible light by tissue limits transmission and decreases image clarity. Scattering decreases for longer wavelengths, leading to research on type II quantum dots and HgTe quantum dots, which is relegated to the appendix. Despite these limitations, dilute aqueous biological solutions and thin tissue samples will generally transmit plenty of visible light for quantitative imaging and chemical analysis using CdSe quantum dots.

Quantum Dots vs. Organic Dyes in Biomedical Imaging

For visible imaging, quantum dots have several potential advantages over organic dyes. First, traditional organic dyes have narrow absorption peaks which are very close to their photoluminescence peak. Therefore each dye requires its own expensive, carefully-tuned, sharp-cutoff filter to block the excitation background from the imaging camera. In contrast, quantum dots have a broad absorption tail over wavelengths shorter than the peak emission wavelength. So a single common long pass filter and a single excitation source can pump quantum dots that emit in several distinct wavelength ranges. Although the PLQY of some common visible dyes, such as rhodamine 6G and fluorescein, can be higher than 90% in plain dye-solvent solutions, conjugation to antibodies is required to form luminescent protein tags. Proximity to other molecules

often degrades the PLQY of organic dyes (*e.g.* the PLQY of fluorescein may be cut in half when bound to antibodies).²³ Quenching of this magnitude can be avoided with quantum dots. Additionally the luminescence from organic dyes decreases rapidly with exposure time, which leads to the use of more expensive pulsed excitation sources and detectors. This "bleaching" problem is reduced by using quantum dots.¹²