UC BERKELEY COLLEGE OF CHEMISTRY

CHEMISTRY C150

INTRODUCTION TO MATERIALS CHEMISTRY

Optical Properties of Quantum Dots

FINAL PAPER

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1 Introduction

Quantum dots are nanocrystals of a semiconductor material that exist in a size regime between single molecules and bulk crystalline solids. They are extraordinary because their minute size produces a physically confined electron cloud, an effect known as quantum confinement. Purely as a result of their spatial properties, they are subject to a variety of interesting and unique optical, electronic, and chemical phenomena that are not found in other materials. The size dependency of these phenomena means that they can be easily controlled by tuning the size distribution of a collection of quantum dots. As more methods to reliably synthesize variable sizes of monodisperse nanocrystals are developed, quantum dots have increasingly cost-effective substrates for optical materials. These unique qualities have made quantum dots an attractive material for a variety of scientific and commercial applications, some of which have recently been realized.

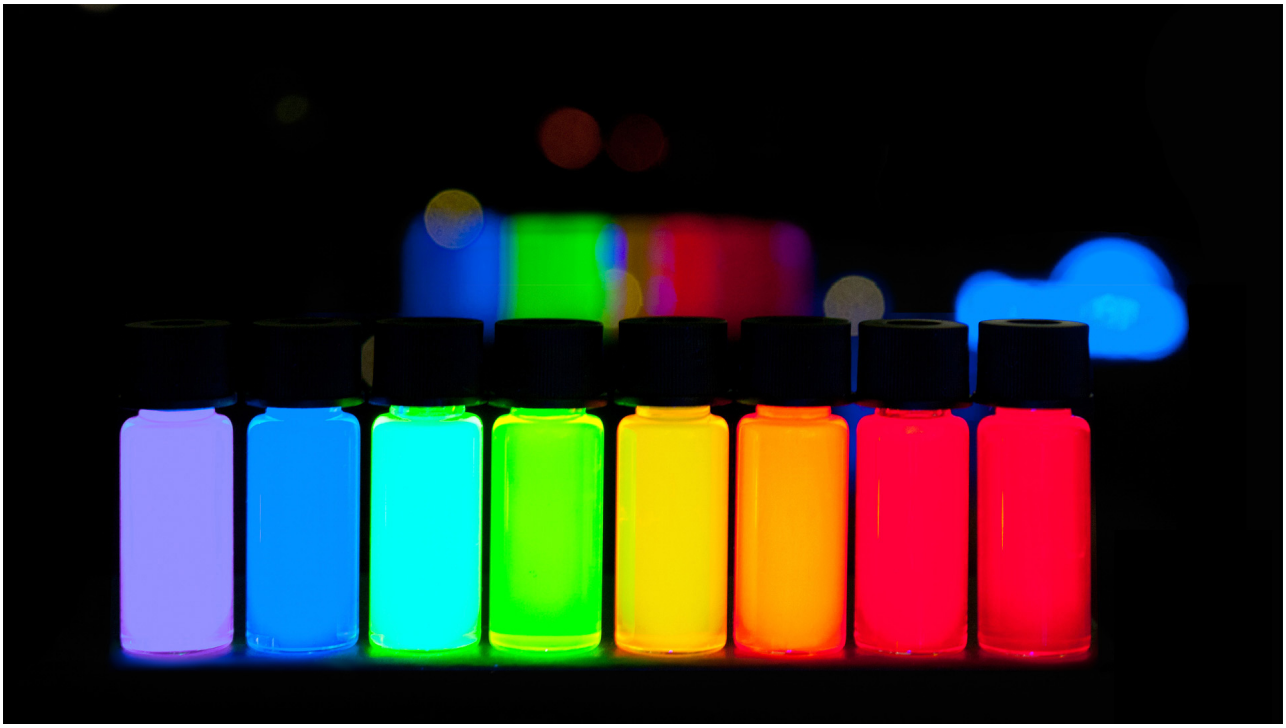

Figure 1: A set of solutions of colloidal quantum dots of increasing size (left to right), fluorescing under UV light.

2 Background

The extraordinary optical and electronic properties of nanocrystalline semiconductors were discovered in 1981 by Alexey Ekimov of the Vasilov State Optical Institute in Russia, who first synthesized nanocrystals embedded in a glass matrix[1]. Four years later, Louis Brus, working at AT&T Bell Labs, synthesized the first colloidal semiconductor nanocrystallite solutions; Mark Reed would go on to coin the phrase "quantum dots" in a 1988 paper, a much more linguistically palatable term than "zero-dimensional semiconductor nanostructures"[2]. However, it was not until a seminal 1993 paper by Murray, Norris, and Bawendi (that has since acquired an astonishing 7,400 citations) detailing a "hot-injection" synthesis for monodisperse colloidal nanocrystals[3] that researchers began to evaluate quantum dots for their potential commercial applications, not just as a curiosity.

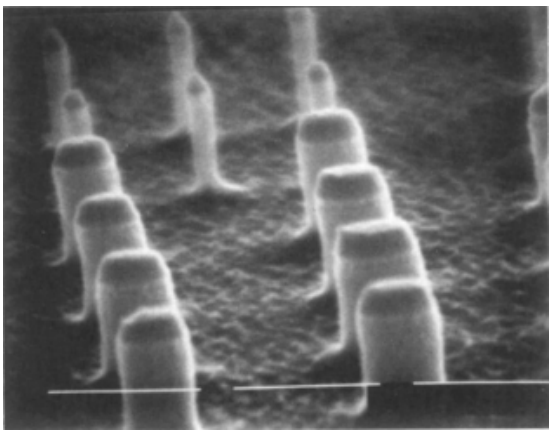

Figure 2: An SEM image of GaAs nanostructures created via electron-beam lithography. Horizontal bars are 0.5 μm.[2]

This drastic shift in tone was largely precipitated by the wealth of possibilities that this new synthesis method presented. Previously, quantum dot syntheses were largely limited to a "top-down" approach – carving a nanocrystallite from a larger bulk material. Such a process generally involved the manipulation of layers bound to a surface, using methods like atomic force microscopy, chemical vapor deposition, electron-beam lithography, and molecular beam epitaxy[4] to whittle down a semiconductor layer into tiny pillars that were small enough to suffer quantum effects (see

Figure 2). Though effective at producing small quantities of quantum dots suitable for quantum confinement and entanglement experimentation, this process was unsuitable for any sort of large-scale application – the cost, in time, resources, and necessary instrumentation, was simply too high to produce bulk samples of quantum dots that could be exploited for commercial use.

Murray, *et. al.* provided an alternative to the costly, inefficient "top-down" syntheses – a "bottom-up" approach, where quantum dots nucleated from individual monomers. If growth rates were consistent and crystallization timepoints controllable, this method could produce macroscopic quantities of monodisperse quantum dots, without the need for expensive instrumentation or labor-intensive lithography. This "bottom-up" synthesis approach proved incredibly effective, and variations of it are used today for commercial syntheses of quantum dots on the kilogram-scale[5] (Figures 3 and 4).

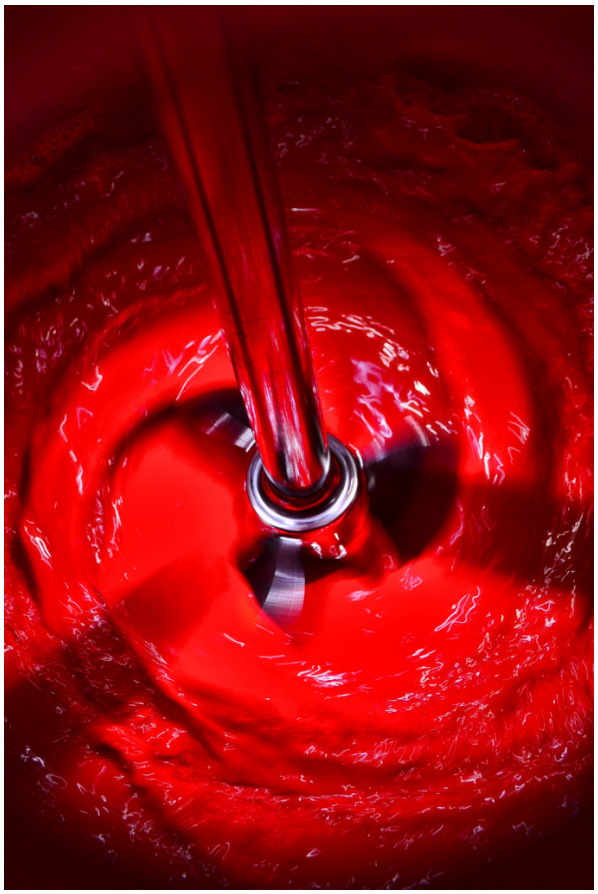

Figure 3: A 70-liter batch reactor of quantum dots, seen under a UV flashlight.

Figure 4: Various batches of quantum dots, synthesized on the kilogram-scale by Nanosys, Inc.

Since this discovery, quantum dots have been studied for a variety of optical applications – as fluorophore alternatives in electronic screens and displays, biodyes for UV tagging, dye sensitizers in dye-sensitized solar cells, and more. Synthesis processes have been optimized and streamlined, and a variety of branching avenues of interest (such as core/shell quantum dots and shaped quantum dots) have been developed. Some applications, such as for molecular catalysis, as qubits for quantum computing, or as biological delivery systems, depend instead on the physical size of quantum dots, but examples of this sort are far less common. Because their unique properties largely stem from their interesting electronic structure, most applications focus on their optical properties.

3 Principles

The unique properties of quantum dots arise almost solely because of size regime in which they exist. As semiconducting materials, they have an intrinsic band gap through which electrons can be bridged by excitation by incident light. However, unlike bulk semiconducting materials, quantum dots too sparse to create the continuous valence and conduction bands typical of macroscopic semiconductors. Instead, quantum dots produce a rarefied electronic structure that is more reminiscent of the discrete electronic states found in single atoms; the larger the quantum dot, the smaller its band gap. The larger a quantum dot becomes, the more continuous its electronic structure and the

closer its band gap becomes to that of the bulk material (see Figure 5). Unlike a single atom, however, this size dependence allows the band gap energy to be modulated by varying the size of the quantum dot, essentially allowing for the synthesis of materials with arbitrary band gap energies.

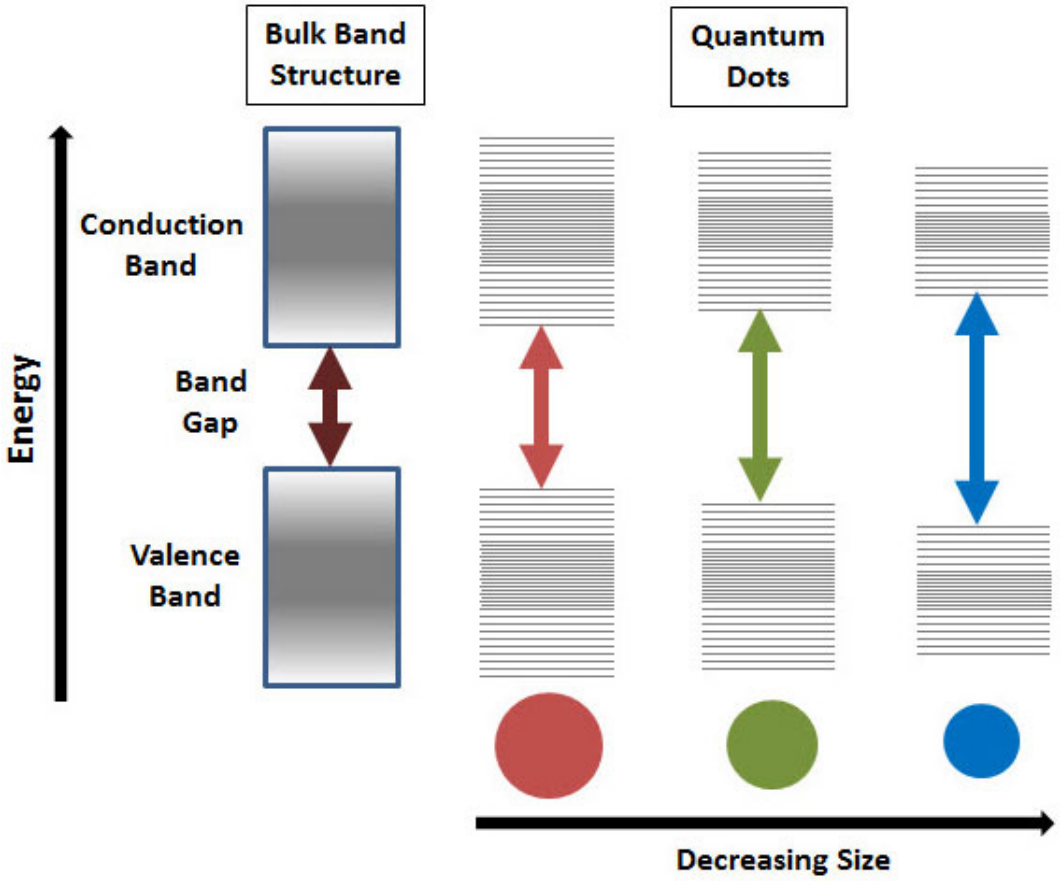

Figure 5: The electronic structure of quantum dots varies with the size of the dot.

The optical properties of quantum dots occur in part due to a unique effect known as quantum confinement. When a photon of sufficient energy (greater than or equal to the band gap) strikes a quantum dot, it can excite an electron from the valence band to the conduction band, leaving a positive hole in its place. Generation of an electron-hole pair (also known as an exciton) is a common phenomenon in semiconducting materials; however, in a quantum dot, the average exciton size (the exciton Bohr radius) is *smaller* than the size of the quantum dot, producing a confinement energy as the exciton is squeezed into the material. The magnitude of this confinement energy can be aptly modeled as a particle in a box, as seen in Equation 1.

$$E_{\text{confinement}} = \frac{\hbar^2 \pi^2}{2a^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) = \frac{\hbar^2 \pi^2}{2\mu a^2}, \tag{1}$$

where m_e is the effective mass of the electron, m_h is the effective mass of the hole, μ is the reduced mass of the exciton system, and a is the radius of the quantum dot.

The effect of changing size on the band gap of the quantum dots depends on the confinement regime that the quantum dot is in regime, which is a function of how the size of the quantum dot compares to the exciton Bohr radius a_b^*, which can be calculated for a specific material by Equation 2 (in practice, this is on the order of 10Å, though it varies by material). If the quantum dot radius is on the same order of magnitude as the exciton Bohr radius, it is said to be in the "weak confinement regime" and is affected by noninsignificant quantum effects. More interesting, however, are quantum dots in the "strong confinement regime", which are smaller than the exciton Bohr radius. In this regime, confinement effects dominate, energy levels do not yet form a continuous spectrum, and the optical and electronic properties can be easily controlled.

$$a_b^* = a_b \varepsilon_r \left(\frac{m}{\mu}\right), \tag{2}$$

where a_b is Bohr exciton radius, a_b is the Bohr radius (about 0.53Å), and ε_r is the dielectric constant of the semiconductor, which varies as a function of size.

There is also an additional energy associated with the Coulombic attraction between the positive hole and negative electron of the exciton, as seen in Equation 3.

$$E_{\text{exciton}} = -\frac{1}{\varepsilon_r^2}\frac{\mu}{m_e} R_y, \tag{3}$$

where ε_r is the size-dependent dielectric constant of the semiconductor, and R_y is the Rydberg energy (approximately 13.6 eV).

Thus, the total energy of a fluorescing photon can be modeled as the sum of the band gap of the quantum dot, the quantum confinement energy, and the bound exciton energy, as seen in Equation 4.

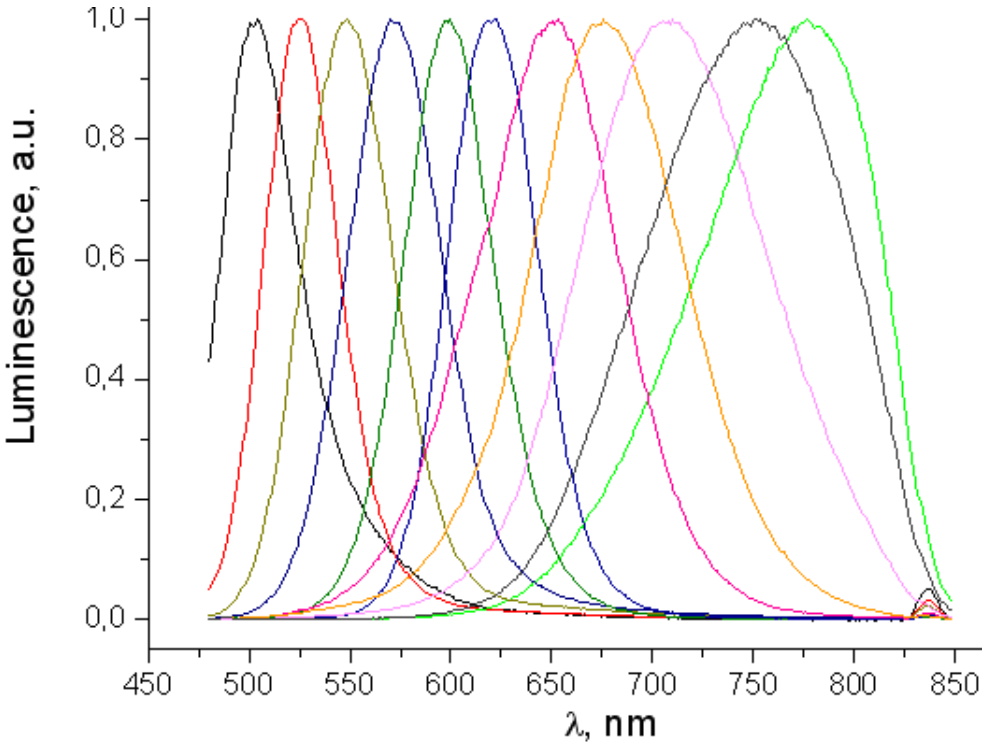

Figure 6: The emission spectras of various CdTe quantum dots, ranging in size from 10 Å to 70 Å (left to right).

$$E_{\text{total}} = E_{\text{bandgap}} + E_{\text{confinement}} + E_{\text{exciton}} = E_{\text{bandgap}} + \frac{\hbar^2 \pi^2}{2\mu a^2} - \frac{1}{\varepsilon_r^2}\frac{\mu}{m_e}R_y \tag{4}$$

The upshot of all of this is that in the size regime less than about 10-100Å, quantum dots have highly tunable absorption and emission spectra, as can be vividly seen in Figures 6 and 7. It is this high degree of control that allows for quantum dots to be optimized for a variety of commercial and scientific applications.

4 Applications and Proven Capabilities

One of the first, and most obvious, applications of quantum dots is in electronic displays. Because of their bright and narrow emission spectra, quantum dots are obvious choices to replace OLED and LCD screens. By exciting various sizes of quantum dots with light from blue GaN (gallium nitride) LEDs, a full spectrum of colors can be produced with high visual fidelity (Figure 8).

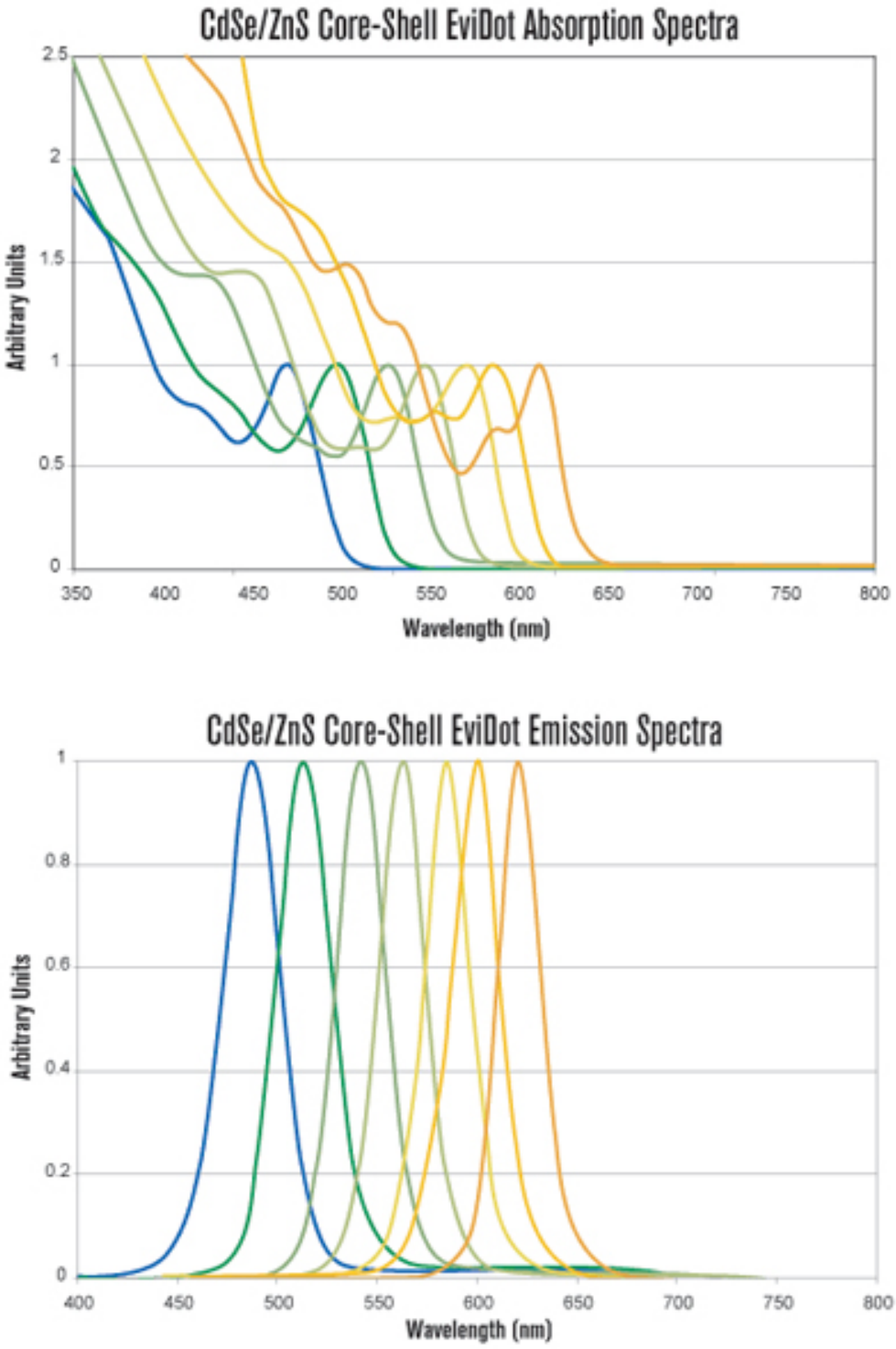

Figure 7: Absorption and emission spectra for CdSe/ZnS core/shell quantum dots.

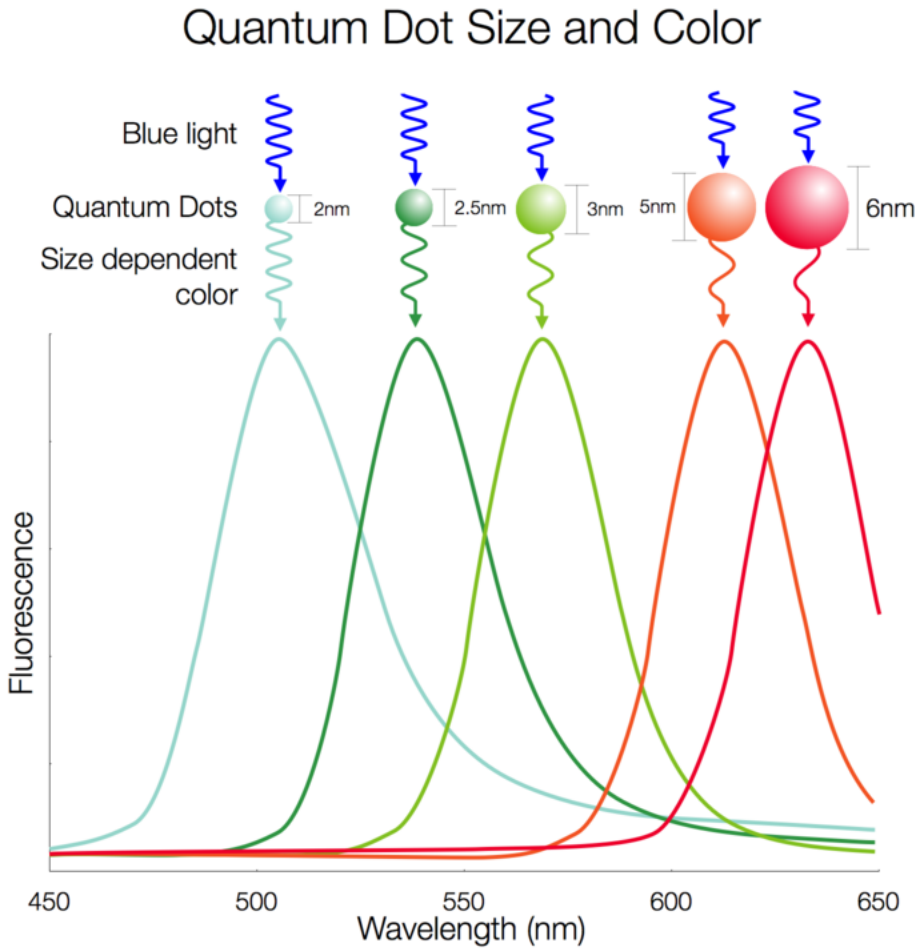

Figure 8: Quantum dots are used in commercial Quantum Dot Enhancement Film (QDEF^{TM}), by Nanosys, Inc.

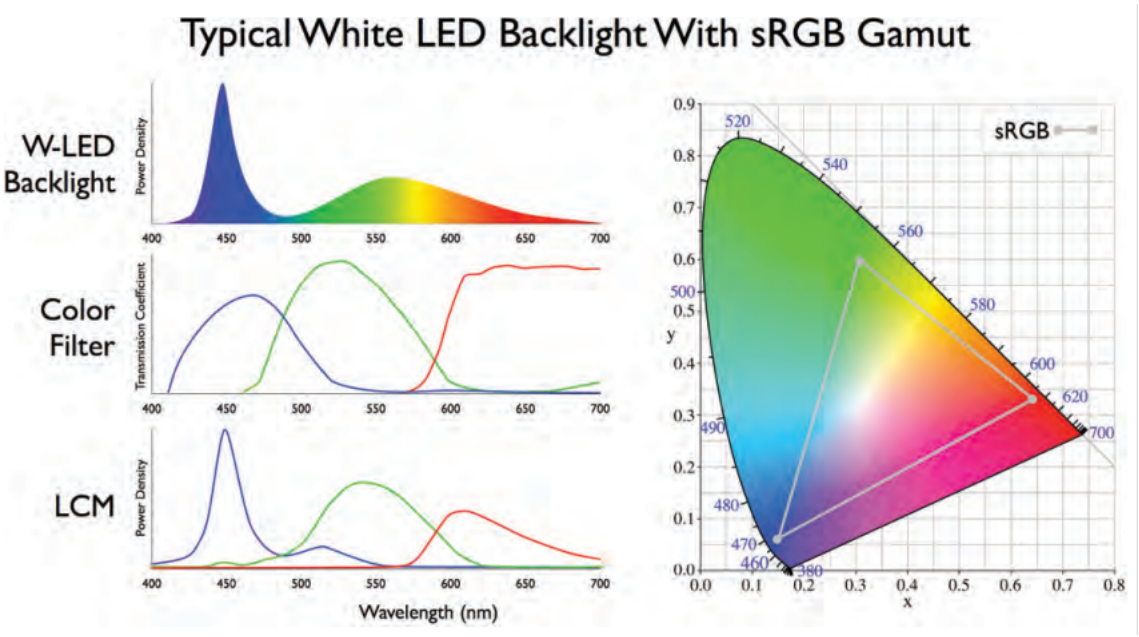

Figure 9: The color gamut of a typical LCD screen is plotted on a CIE 1931 visible-color space. Of note: the resulting gamut only covers about 35% of the human visible chromatic range.

Quantum dots provide a marked improvement on conventional LCD screens, which often utilize a YAG (yttrium aluminum garnet)-based phosphor combined with a GaN or GaInN (gallium indium nitride) LED light source that flows into a liquid crystal module (LCM). This approach produces a spectrum that is rich in blue and yellow, but with a weak green and red component. This can be seen quantitatively in Figure 9 – the white LED backlight does not match well with the RGB color filters, and produces a color gamut that only spans about 35% of the human visible chromatic range (as measured on a CIE 1931 color space, which relates colors by actual electromagnetic wavelength to human physiologically perceived color)[6].

A quantum-dot film, by contrast, produces much greater color fidelity. As seen in Figure 10, a quantum dot backlight produces a much more vivid color gamut that spans a greater portion of the CIE 1931 color space, as well as covering 100% of the Adobe 1998 RGB spectrum (a reference spectrum for ensuring reliable color reproduction from screen to print)[6].

On top of all of this, quantum dot displays have high long-term stability; as seen in Figure 11, quantum dot screens suffer no significant degradation after 30,000 hours of operation (roughly 3.5 years of continuous operation), a value much higher than competing display formats[6].

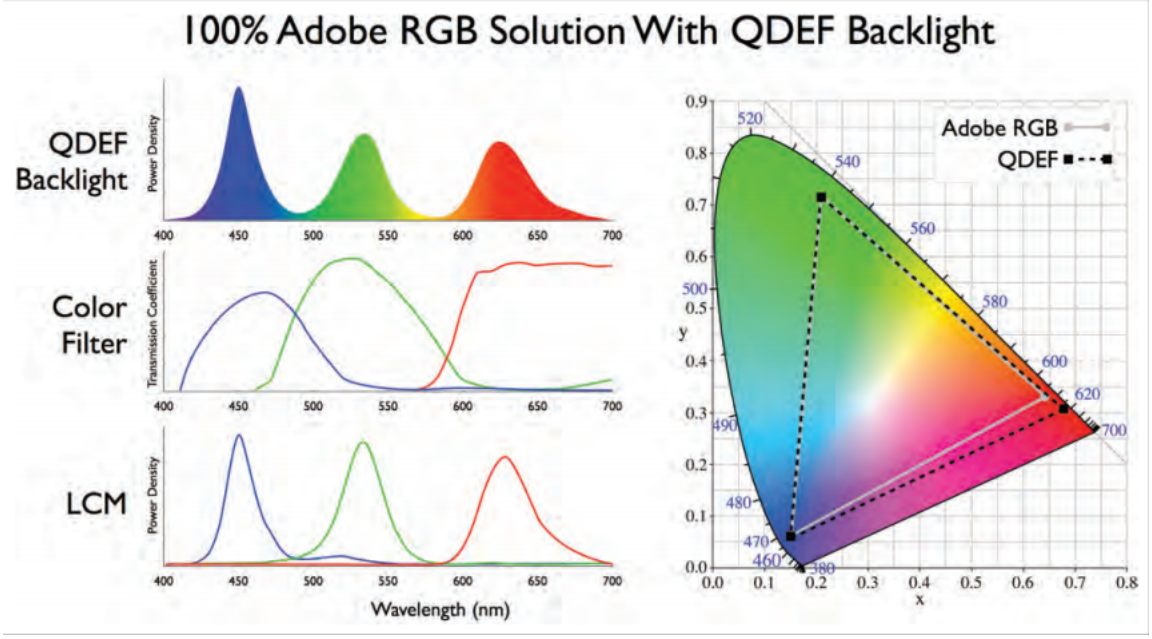

Figure 10: The color gamut of QDEF™ backlight with an off-the-shelf color filter produces markedly better chromaticity, and encompasses 100% of the reference Adobe 1998 RGB reference spectrum.

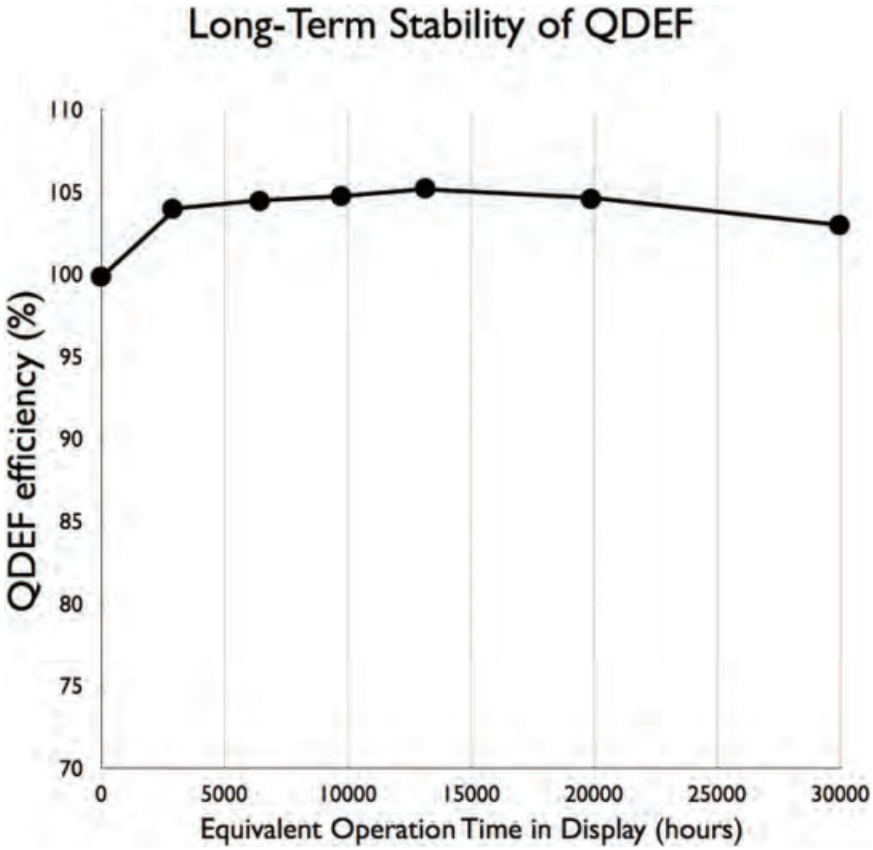

Figure 11: Reliability data shows no significant decrease in screen quality after 30,000 hours of continuous operation.

As a result of these obvious advantages over existing technology, quantum dot displays have begun to make their entrance onto the commercial marketplace. In 2013, the first quantum dot TVs were introduced, and they continue to be sold to this day, despite their rather high pricing (roughly $3000).

5 Future Directions

There is still a plethora of work being performed on quantum dots. Quantum dots are being tested as biological dye alternatives, because they are more fluorescent and more chemically and biologically stable than existing biodyes[7]. They also show great promise in the field of photovoltaics, largely because their tunable sizes allow for the creation of photovoltaic cells with arbitrary band gaps (a feature which is especially useful in multi-junction cells, which layer multiple junctions with different band gaps on top of each other to maximize the efficiency of solar energy capture. Multiple-exciton generation has also been demonstrated in quantum dots, and they have been investigated as alternatives to molecular dyes in dye-sensitized solar cells[8].

Fabrication of quantum dots is another area of intense future research. Core/shell nanocrystals have been developed as a means to add extra synthetic handles to quantum dot synthesis as well as to increase quantum yield by decreasing passivation. The precise topology of a quantum dot is also known to affect its electronic properties, but the exact nature of this relationship is not clear at this time, nor do scientists have ways to control the topology of arbitrary quantum dot syntheses (Figure 12).

6 Conclusion

Quantum dots have a storied history despite their rather recent discovery, and have an abundance of applications in a variety of fields, largely as a result of their interesting and unique electronic structure, which grants researchers an unparalleled level of control of their optical properties. Quantum dot displays present a number of advantages over conventional LCD displays, and quantum dot-

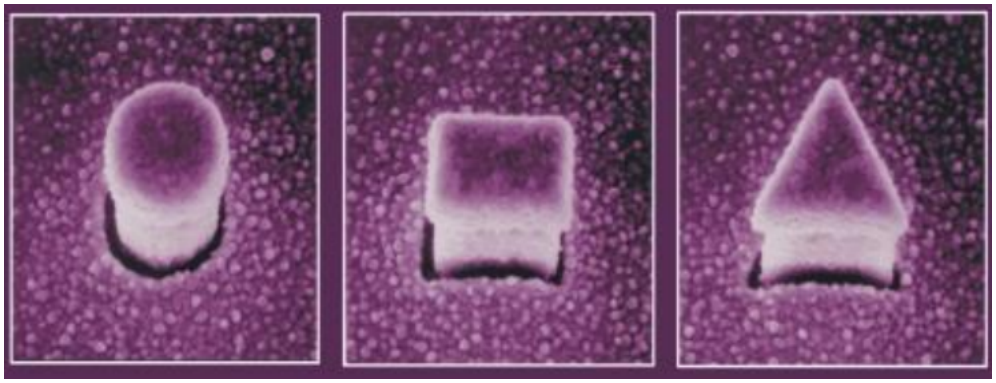

Figure 12: Differently-shaped quantum dots can be synthesized by various epitaxial means, though the precise electronic differences between differing topologies are not known at this time.

based screens have already shown great success in the commercial market. Quantum dots also show promise in photovoltaic cells and as bioimaging agents, though presently these fields remain strictly experimental. Nevertheless, it is evident that quantum dots will continue to revolutionize fields in the near future, as they have for the past several years.

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