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On Ultrasmall Nanocrystals

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Abstract

Ultrasmall nanocrystals are a growing sub-class of traditional nanocrystals that exhibit new properties at diameters typically below 2 nm. In this review, we define what constitutes an ultrasmall nanoparticle while distinguishing between ultrasmall and magic-size nanoparticles. After a brief overview of ultrasmall nanoparticles, including ultrasmall gold clusters, our recent work is presented covering the optical properties, structure, and application of ultrasmall CdSe nanocrystals. This unique material has potential application in solid state lighting due to its balanced white emission. This section is followed by a discussion on the blurring boundary between what can be considered a nanoparticle and a molecule.

1. Introduction

Over the last few decades, the field of nanotechnology has grown from a laboratory novelty into a burgeoning industry. This is a direct result of the new phenomena that are exhibited as conventional materials are confined to dimensions less than a few hundred nanometers. Properties such as ballistic charge transport in carbon nanotubes or enhanced surface plasmonic resonance emission from gold nanoparticles occur due their nanoscale dimensions.^{1–4}

Quantum confinement is another unique property that exists only in the nanoscale size regime. Quantum confinement occurs in semiconductors when their size is restricted to dimensions less than or equal to the bulk Bohr diameter of an exciton (a bound electron and hole pair) in that material.^{5,6} When a photon with energy equal to or greater than the band gap energy is absorbed by a semiconductor nanocrystal, the resultant photogenerated electron and hole pair are confined within the crystal lattice at a distance less than the thermodynamic equilibrium distance in the same bulk semiconductor, which can be approximated by the exciton bulk Bohr diameter. Much like the ‘particle in a box’ approximation, as a nanocrystal’s diameter decreases the band gap energy increases due to

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the increased confinement.⁷ This energetic size dependence allows the tuning of the band gap related absorption and emission simply by changing the diameter of the nanocrystal. CdSe semiconductor nanocrystals are the most studied, primarily due to the ability to tune the band gap over the entire visible spectrum, exhibiting size tunable absorption and emission that can be utilized in photovoltaics, light emitting diodes and as alternatives to fluorescent dyes for biological imaging.^{8–17} The main advantages of nanocrystals over organic dyes in these roles are their higher molar absorptivity, continuum absorption that allows for exciting multiple sizes of nanocrystals with one high energy wavelength of light, narrow emission spectra, and a high photostability that can be enhanced by surface passivation.

As synthetic strategies become better understood, nanoparticles are being synthesized with ever-decreasing dimensions to obtain the desired size dependent physical/optical properties and, in some cases, for bio-clearance.^{18–21} However, it has become apparent that new properties arise for nanoparticles with diameters 2 nm or less. At this ultrasmall size, the majority of the atoms of the nanoparticle are at the surface, leading to the surface structures and the local chemical environment enhancing or dominating the physical/optical properties. Any surface passivating ligands now comprise a significant portion of the particle's total atoms. The environment around the particle also becomes significant as a small change in pressure due to lattice strain or a change in solvent at the surface may directly affect its physical properties. The following sections provide an overview of recent work on ultrasmall nanoparticles, with emphasis on white-light emitting CdSe nanocrystals.

1.1 Magic-size Verses Ultrasmall

Magic-size nanocrystals can be categorized as a special case of ultrasmall nanoparticles. The term 'magic-size' is used to describe extremely stable 'sizes' of nanocrystals that are observed during growth.^{22–24} They are believed to have a different thermodynamically stable structure^{25,26}, exhibit an extremely narrow size distribution, and are resistant to growth. This resistance to growth leads to quantized growth, where larger structures form incrementally instead of one structure continually growing in length or diameter. There are currently a growing variety of magic-size nanoparticles being discovered under varied synthetic conditions. A common theme, however, is the appearance very narrow absorption features at specific wavelengths as well as the formation of rods consisting of the individual magic size clustered/chained together. Their growth behavior and the appearance of these organized structures may be a direct result of a unique structure or ligand coverage. The unique absorption spectra for magic-sized CdSe and subsequent theory support the possibility of a 'nanoscale only' crystalline phase. The experimental determination of their structure remains challenge due to their extremely small size and sensitivity to ligand displacement.

1.2 Ultrasmall Metal Nanoparticles

Of metal nanoparticles, gold nanoparticles are by far the most studied and utilized. Nanogold and other noble metal nanoparticles have size dependent surface plasmons that absorb in the visible spectrum.^{3,27} However, Alvarez *et al.* noted that this plasmon band became unrecognizable for diameters less than 2 nm and their absorption spectrum could not be explained by Mie theory.²⁸ Electrochemically, the transition from traditional monolayer protected gold clusters (MPCs) to ultrasmall (2 nm or less) MPCs can be described as the domination of bonding interactions on the cluster capacitance over electrostatic processes.²⁹ Furthermore, it has been demonstrated, utilizing ultrafast transient absorption spectroscopy, that there is an abrupt formation of a band gap for gold with a diameter of 2.2 nm. This was verified by the appearance of a 450 fs periodic oscillation in the transient absorption decay.³⁰ Although a new crystal structure may explain the abrupt change optical properties for

MPCs of 2.2 nm or less, no conclusive determination has been made.³¹ A complete review on ultrasmall gold was recently written by Jin *et al.*³²

Other metal nanoparticles, which have been synthesized in the ultrasmall regime, have also shown divergent properties. Ultrasmall Fe nanoparticles synthesized under stringent air free conditions demonstrated an order of magnitude increase in the effective anisotropy constant compared to the bulk value.³³ Face-centered tetragonal (fct) FePt are of great interest for their magnetocrystalline anisotropy. Although ~2.8 nm diameter FePt nanocrystals show a high coercivity (2.47 kOe) at room temperature, ultrasmall (~1.9 nm diameter) FePt appear primarily superparamagnetic, likely a direct result of their distinctive size.³⁴

2. Ultrasmall White Light-emitting CdSe Nanocrystals

In 2005, we discovered that, under unique synthetic conditions, sub-2 nm CdSe nanocrystals exhibit a very balanced white-light emission.³⁵ This has been followed by research efforts to determine the feasibility of this material for solid state lighting and even biological applications.^{26, 36–38} A portion of the broad emission is similar to deep trap emission observed for conventional, tri-n-octylphosphine oxide (TOPO) capped nanocrystals. As the diameter of the nanocrystal is reduced, this deep trap emission becomes more prevalent and can eventually dominate the emission spectrum. El-Sayed explored this phenomenon by studying the emission characteristics of small CdSe nanocrystals, which included the size range of our white-light emitting nanocrystals.³⁹ The nanocrystals studied exhibited a strongly Stoke-shifted, band-edge emission feature followed by deep trap emission which grew with decreasing nanocrystal diameter. He attributed this effect to the increasing surface-to-volume ratio of the nanocrystals. Nearly 70% of the atoms are on the surface for sub-2 nm nanocrystals, compared to 22% for 4 nm nanocrystals.

2.1 Optical Properties

Ultrasmall CdSe nanocrystals synthesized with a surfactant mixture of dodecylphosphonic acid, hexadecylamine and tri-n-octylphosphine oxide have an additional emission feature residing between a strongly Stoke-shifted first emission peak (not believed to be band-edge) and the broad deep trap emission.^{35, 40, 41} Figure 1 shows a typical absorption and emission spectrum of ultrasmall CdSe, which produces a balanced white-light emission with Commission internationale de l'éclairage (C.I.E.) coordinates of (0.322, 0.365). The narrow band-edge absorption feature suggests that the material synthesized is monodisperse, indicating the white emission is the result of multiple of emitting states, rather than mixture of nanocrystal sizes. The quantum yield for this material has been measured as high as 9%.⁴¹

Ultrafast fluorescence upconversion spectroscopy provides a 'real-time' window to the electronic processes in molecules and semiconductor nanocrystals with the ability to preferentially probe the excited state without interference from other processes such as excited-state absorption or ground-state recovery.⁴² There have been numerous studies of the ultrafast exciton dynamics in CdSe nanocrystals;^{43–49} however, the emission mechanism of sub-2 nm CdSe nanocrystals has not been interrogated with as much detail using this technique.³⁹

Data were collected at five wavelengths within the broad emission spectrum of the nanocrystals corresponding to emission at 459 nm, 488 nm, 535 nm, 552 nm, and 585 nm (Figure 2). The significant result of this work is that all three visible peaks are the result of trap state recombination, with band-edge emission completely suppressed. The emission from the 488 peak with a 2.5 ps decay rate is likely due to recombination at a surface

selenium atom, which is supported the observation of the peaks insensitivity to ligand exchanges of the Cd-binding ligands.

2.2 Pinning and Ligand Effects

The complete suppression of the band-edge emission is consistent with a size-independent emission spectrum for sizes below 2 nm. This ‘pinning’ phenomenon is observed only for CdSe nanocrystals with diameters less than 2 nm. Regardless of the band-edge absorption wavelength, the entire emission spectrum remains unchanged. To demonstrate this effect, CdSe nanocrystals were synthesized with band absorption features as blue as 370 nm, corresponding to diameters near 1.3 nm. Figure 3 shows a distinct break in the size dependent trend of the bluest emission feature once the nanocrystal diameter reaches near or below 2 nm. It is hypothesized that as the band gap widens, inherent surface trap states begin to fall within it becoming the dominant emission mechanism. The trap states are believed to be surface related due to the emission sensitivity to the replacement of the phosphonic acid ligand.⁴⁰

In order to probe the importance of the phosphonic acid surface ligand on the white-light emission, several phosphonic acids with varied chain lengths or structures were synthesized. Ultrasmall CdSe was synthesized utilizing these phosphonic acids in place of the dodecylphosphonic acid used in the original work to avoid any artifacts due that may arise due to a post synthesis ligand exchange process.⁴¹ Surprisingly, the wavelength of the first emission peak exhibited chain length dependence for straight chain phosphonic acids.

Figure 4 shows the same trend seen previously for dodecylphosphonic acid; however, in the ultrasmall region the data diverges with shorter alkyl chains, yielding higher energy first emission features. Even more surprising, the position of the first emission feature in eV correlates with the electronegativity of the phosphonic acid. We have proposed that the electronegativity of the ligand affects the electron density of the surface cadmium atoms. Since the emission process for the most blue emission feature is linked to the surface cadmium atoms, this shift in wavelength is logical.

A strong dependence between the nanocrystal quantum yield and the carbon chain length of the phosphonic acid was also observed. Figure 5 shows that the longer chain length of the phosphonic acid yielded nanocrystals with higher quantum yields, for both ultrasmall and traditionally sized nanocrystals. This effect was independent of purification, suggesting that improved surface passivation was achieved with longer chain surface ligands. A parallel study utilizing carboxylic acids will help clarify the origin of this effect, determining whether it is the result of head group reactivity or an insulating effect of the alkyl chain.

3. Structure

As is evidenced by the multitude of proposed structures for ultrasmall CdSe, an experimentally determined structure is a critical step towards understanding the origin of their unique emission. Specifically, an accurate understanding of the atomic arrangement can be used as a starting point for theoretical treatments to identify the physical nature of the emissive trap states. In the past, conventional high-resolution transmission electron microscopy has been the primary method for structure characterization of nanoparticles. For ultrasmall nanocrystals, the amount of contrast that arises from the amorphous carbon support film is on the order to that obtained from the nanoparticles. As a result, it is incredibly difficult to determine their size, shape, or crystal structure. Aberration-corrected atomic number contrast scanning transmission electron microscopy (Z-STEM) was used to obtain the first lattice resolved images of a sub-2 nm nanocrystal. Using a high angle annular dark field detector in conjunction with spherical aberration correction allows for sub-

angstrom resolution imaging of single atoms and has already been applied to obtain a detailed picture of the crystal structure of larger semiconductor nanocrystals.^{50,51} This dark field technique essentially eliminates the signal from the carbon support film, allowing for improved imaging of low-contrast samples.

The inset in the Z-STEM image (Figure 6) shows a pair of sub-2 nm nanocrystals. To the best of our knowledge, this was the first published lattice-resolved image of a nanocrystal in this size regime. The nanocrystals appear ovoid with reasonably defined lattice planes and an approximate diameter of 1.5 nm. Non-uniform lattice spacing and slightly disordered atomic dumbbell appearance suggests the presence of point defects (vacancies or interstitial atoms) and makes a definite assignment of the crystal structure (wurtzite or zinc blende) difficult. However, the strongly binding phosphonic acids used in the synthesis typically yield wurtzite nanocrystals, likely the case for sub-2 nm nanocrystals.⁵² A wurtzite CdSe ball and stick model is shown in Figure 6 with the approximate size and shape as those in the STEM image.

Challenges clearly still remain in determining the structure. Their small size increases the difficulty of separation from excess precursors as well as an increased tendency for them to aggregate. Although no beam damage has been observed in larger nanocrystals under the same imaging conditions, it may be a possibility for nanocrystals of this size. Utilizing a lower voltage STEM would reduce the amount of knock-on damage that can occur. Additionally, since there are very few atoms to begin with, it becomes difficult to identify the crystal structure without modeling, since a simple stacking fault common to CdSe nanocrystals would account for a considerable portion of the overall crystal structure. Image simulation is likely necessary for unambiguous image interpretation.

4. Application – White-light Source

Beyond the fundamental scientific interest of ultrasmall nanocrystals, the practical application of the white-light emission has also been investigated. Due to rising energy costs, alternative lighting technologies including compact fluorescence and emerging solid-state light emitting diodes (LEDs) have gained considerable attention. LED technology promises the ultimate in power savings and longevity. However, one of the primary deficiencies is producing a palatable white-light emission that will appeal to consumers. The majority of white LEDs use a mixture of phosphors to achieve the appearance of white-light, often yielding an unbalanced or harsh blue light. Ultrasmall CdSe is the first single material to naturally emit a balanced white-light emission. White-light devices based on ultrasmall CdSe were developed utilizing fluorescence and direct electronic excitation.

4.1 Phosphor Conversion for White Light

The simplest approach involves utilizing a UV-LED to excite the white-light nanocrystals. The primary challenge of this approach was determining an appropriate polymer encapsulant. The encapsulant should provide a mechanically stable environment and protect the nanocrystals from thermal damage and photo-oxidation. More importantly, the encapsulant must not adversely affect the color quality of the nanocrystals.

Figure 7 shows the emission from ultrasmall CdSe nanocrystals mixed with a variety of encapsulants. Some of the encapsulants destroyed the nanocrystals out-right, as they required the addition of hardener to cure. The hardener often reacted with the nanocrystals yielding a brown solid. Other encapsulants proved to be too polar for the non-polar capped nanocrystals, resulting in aggregation or phase segregation. This is clearly illustrated in Figure 8, which is a compilation of fluorescence (top) and bright field differential contrast (bottom) microscope images.

Of the polymers tested, biphenylperfluorocyclobutyl (NDM) from Tetramer Technologies proved to be the most compatible with the ultrasmall nanocrystals. The non-polar backbone prevented any serious nanocrystal aggregation and did not modify the nanocrystal luminescence (Figure 8C).

Figure 9 shows the absorption and emission of the same nanocrystals in solution and encapsulated in NDM. Both the absorption and emission overlap very well, with only the addition of a scattering artifact at 730 nm. The inset shown in Figure 9 is a true color image of the final device. The device emission exhibited CIE chromaticity coordinates of (0.324, 0.322) and a color rendering index (CRI) of 93.⁵³

There are several drawbacks, however, to the phosphor down-conversion approach. Fundamentally, there will always be a Stokes-loss that will limit the maximum efficiency. This is a result of the energy difference between the excitation source (the UV-LED) and white light-emission. The final device efficiency is also directly limited by the efficiency of the UV-LED, and not just the nanocrystals. Lastly, bleed-through from the UV-LED, often called the halo effect, will lower the aesthetic appearance of the light source.

4.2 White-light Electroluminescence

The alternative approach is to use the nanocrystals as the active layer in an LED. In this design, the nanocrystals are directly excited by electron and hole injection. This results in a device limited only by the efficiency of the charge injection and the emission efficiency of the nanoparticles. Little is known, however, on how direct charge injection would affect the quality of the white light-emission. As a proof of concept, a simple layered LED design was employed to measure the electroluminescence (EL) from ultrasmall CdSe nanocrystals.

Figure 10 shows an illustration of the device architecture and the current-voltage and luminance voltage behavior. The device was fabricated by spin coating a thin layer of (~ 20 nm) of PEDOT:PSS, followed by spin coating a 5 mg/ml mixture of a hole transport polymer, *N,N'*-diphenyl-*N,N'*bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine (TPD) and ultrasmall nanocrystals (10 mg/ml) in chloroform. This method results in a top layer of nanocrystals phase segregated from the TPD. The final step was to evaporate a 100 nm thick silver electrode on top of the nanocrystals.

Figure 11 shows the normalized EL from an ultrasmall nanocrystal-based LEDs with increasing applied voltage. The EL from the nanocrystal LEDs was slightly broader than the photoluminescence of the same nanocrystals in chloroform. The Ag electrode and the surrounding TPD may be contributing to this, as well as the simple liquid to solid-state change which modified the wavelengths at which the Se and ligand trap states emit. Additionally, local heating of the LED from the current flow may contribute to the observed broadening. At large voltages the blue/green portion of the emission spectrum became quenched, while the deep trap emission remained strong. The effect is similar to that seen when the ligands are displaced from the nanocrystal surface. The high voltage/heat could be disrupting the ligand coverage, quenching the ligand-mediated emission.

This device yielded a perfect white CIE coordinates of (0.333, 0.333) and a CRI of 96.6. Unfortunately, the device had a measured efficiency of 4.83×10^{-5} lumen/watt and external quantum efficiency of 0.00013% at 18.9V. This low efficiency is largely the result of an un-optimized device design and the low quantum efficiency of the nanocrystals.

5. Molecule or Nanocrystal?

In 2001, Mostafa El-Sayed published a paper entitled ‘On the Nanocrystal to Molecular Size Transition: Fluorescence Quenching Studies’ describing the differences between a traditional (greater than 100 atoms) and ultrasmall (20–100 atoms) nanocrystal.³⁹ One of the major differences, between these two size regimes, is that it becomes difficult to differentiate between a surface and an internal atom for the ultrasmall case. For ultrasmall CdSe, nearly 80% of the atoms are on the surface, leaving only two unit cells that can be considered core atoms. The lack of core atoms necessarily means that there is very little organized lattice to form a continuum of atomic states. Since each atom essentially exists in a unique spatial environment, one can describe an ultrasmall nanocrystal as entirely composed of defects. Alternatively, El-Sayed described these defect-ridden nanoparticles as ‘large molecules with exact atomic configurations.’ Just like for molecules, one can envision modifying the nanoparticle’s properties simply by modifying the structure at single atom increments. For example, removing a single atom could quench the photoluminescence or introduce an emitting trap state. Treating white light-emitting CdSe as a molecule lends support to the possibility that the broad emission could arise from the summation of the ensemble emission – meaning some nanocrystals emit red while others blue or green, even though the absorption spectrum indicates a narrow (5–10%) size distribution. It may no longer be adequate to describe an ultrasmall nanocrystal by its diameter, but by its specific atomic arrangement, analogous to a molecular isomer.

Almost as important as the atomic order of the nanocrystal core, the surrounding ligand sphere contributes significantly to the optical and electronic properties. In 2009, Kilina *et al.* published a detailed theoretical work on the physical and electronic interactions between surface ligands and ultrasmall nanocrystals or nanoclusters.⁵⁴ At the surface, significant changes in geometry occur, with and without ligands, including CdSe bond shrinkage. Due to the small size and this surface reconstruction, there are very few equivalent nanocrystal surface–ligand interactions. As a result, a trap state introduced by the absence of a ligand may be dark or semi-bright depending on its position on the nanocrystal surface. Matching well with our observations of the white-light emission dependence with phosphonic acid chain length, the authors reported pure ligand states situated deep inside the valence band of the CdSe nanocluster, with the appearance of hybridized states with electron density delocalized over both the nanocluster and the ligand atoms. The electron density overlap could lead to relaxation pathways dependent on surface ligand structure and electron-phonon interactions, implying that the ligand structure can be used as another means to tune the ultrasmall nanocrystal optical properties. Our phosphonic acid work seems to confirm these assertions. Maintaining the molecule analogy, the surface ligands can be thought of as functional groups that impart different properties to the core molecule.

6. Conclusion and Future Directions

The ability to produce ultrasmall nanocrystals offers scientists both a glimpse into how matter organizes into crystals and access to new material properties that arise due to the domination of surface states and the surrounding matter. Ultrasmall CdSe best embodies this new area of study, exhibiting unique luminescence that is intimately coupled to the electronic nature of the capping ligands. As improved understanding of the underlying mechanisms behind the emission and construction of these ultrasmall nanocrystals is achieved, new synthetic strategies and properties will arise. Synthetic methods for ultrasmall nanoparticles will require atomic precision as nearly every atom directly contributes to the desired property. Paralleling synthetic advances, improved atomic characterization techniques will be needed to accurately describe the entire particle and its ligand shell. Including aberration-corrected STEM, techniques such as pair distribution function (PDF)

analysis, liquid and solid-state NMR may also play a critical role.^{55–58} Ultrasmall nanoparticles will likely move from a simple laboratory curiosity towards practical application, mirroring the development cycle of other nanomaterials.

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Biographies

James McBride majored in Chemistry and obtained his Bachelor of Science degree from Florida Southern College in 1999. In 2005, he obtained his Ph.D. in Chemistry at Vanderbilt University under Sandra J. Rosenthal. His thesis work involved atomic level characterization of CdSe nanocrystals and core/shell nanocrystals with aberration-corrected scanning transmission electron microscopy and Rutherford backscattering spectroscopy. In 2006, his co-discovery of white light-emitting CdSe nanocrystals with Michael J. Bowers earned him a Popular Mechanics Breakthrough award. Currently, he is a Research Assistant Professor at Vanderbilt University utilizing Z-STEM to guide the development ultrasmall core/shell nanocrystals.

Albert Dukes studied Chemistry at Clemson University and received his bachelors of science in 2005. He is beginning his sixth year as a chemistry graduate student at Vanderbilt University. His research focuses on the synthesis, ultrafast carrier dynamics, and optical properties of ultrasmall CdSe nanocrystals. Currently, he is constructing an instrument to optically trap and interrogate individual ultrasmall nanocrystals. In 2009 he was awarded a Science Teaching Fellowship to work with 8th grade science teachers on improving the science curriculum of inner city schools in Nashville, TN. He hopes to pursue a career in academics after graduation.

Michael Schreuder studied Chemistry at Northwestern College in Orange City, Iowa graduating in 2005 with a B.A. He then studied under Sandra J. Rosenthal at Vanderbilt University earning a PhD in 2010. His dissertation was entitled “Ultrasmall, White-light CdSe Nanocrystals: Ligand Effects and Incorporation into Solid-State Lighting.” Michael now works for Sharp Laboratories of Europe in Oxford, England. He is currently researching nitride nanocrystals for the purpose of displays and lighting.

Sandra J. Rosenthal is Professor of Chemistry, Physics, Pharmacology, Chemical and Biomolecular Engineering and the Director of the Vanderbilt Institute of Nanoscale Science and Engineering at Vanderbilt University. Rosenthal completed her undergraduate degree at Valparaiso University in 1987. She earned her Ph.D. in 1993 in Physical Chemistry at the University of Chicago followed by a NSF Postdoctoral Fellowship at UC Berkeley. Rosenthal joined the faculty at Vanderbilt in 1996 researching the synthesis, structure, and ultrafast carrier dynamics of nanocrystals. Rosenthal has been recognized with honors, including the Madison-Sarratt Prize for Excellence in Undergraduate Teaching and a Popular Mechanics Breakthrough Award.

Fig. 1. Absorption (dotted line) and emission (solid line) of ultrasmall CdSe nanocrystals.³⁵
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Fig. 2.

Ultrafast upconversion summary. (A) Absorption and emission of the sample probed, exhibiting a narrow band-edge absorption (light-grey line) and white emission (black line). The colored arrows indicate the wavelengths probed during the ultrafast experiment. (B–F) ultrafast data traces acquired at 459 nm (B), 488 nm (C), 535 nm (D), 552 nm (E) and 585 nm (F). (G) A comparison of early time dynamics at 459 nm and 552 nm. The fast decay at 459 nm (blue circles) coincides with the rise occurring at 552 nm (red triangles) indicating that the state emitting at 585 nm is being populated by the state emitting at peak 459 nm.⁵⁹ Reproduced by permission of The American Chemical Society (ACS)

Fig. 3.

The position of the first emission feature is plotted against the position of the first absorption feature for CdSe nanocrystals passivated with (a) octylphosphonic acid, (b) dodecylphosphonic acid, and (c) hexadecylphosphonic acid. In all cases, when the band-edge absorption wavelength is below 420 nm, corresponding to nanocrystals less than 1.72 nm in diameter⁶⁰, the first emission feature is pinned at approximately 440 nm. The line on each graph represents the trend of blue shifting emission with a blue shift in the absorption. The emission spectrum remains broad and unchanged at nanocrystal sizes below 2 nm.⁴⁰ Reproduced by permission of The American Institute of Physics (AIP)

Fig. 4.

First emission feature λ versus band-edge absorption feature λ . (A) Traditional and pinned nanocrystal sizes. The boxed area is the pinned region. (B) Enlarged area from panel A shows the pinned emission features. Note the slope change from traditional to ultrasmall nanocrystals.⁴¹ Reproduced by permission of The American Chemical Society (ACS)

Fig. 5. Quantum yield of dirty and clean nanocrystals: (top) ultrasmall size and (bottom) traditional size regime. Clean and dirty refer to nanocrystals before and after a centrifugation cleaning process.⁴¹ Reproduced by permission of The American Chemical Society (ACS)

Fig. 6. Z-STEM image of white-light emitting CdSe nanocrystals with a primary absorption peak at 417 nm. Although the majority of nanocrystals appear to be aggregated, a pair of well defined nanocrystals is circled in the inset image. The nanocrystals appear to be crystalline with visible rows of atoms. They are approximately 1.5 nm in diameter and are likely wurtzite. These nanocrystals may resemble the wurtzite ball and stick model in the lower right.⁵⁹ Reproduced by permission of The American Chemical Society (ACS)

Fig. 7.

The emission from ultrasmall single-sized nanocrystals in various encapsulants. The samples were all $50 \pm 3 \mu\text{m}$ thick films and at 9% w/w nanocrystal to polymer loading.⁵³

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Fig. 8. Representative white-light fluorescence (top) and bright field differential interference contrast (bottom) micrographs of encapsulated nanocrystals at 5% w/w loading in: a) siloxane b) epoxy c) BP-PFCB. All images were acquired with an exposure time of 5 ms, displayed with equivalent thresholds, and at the same thickness ($\sim 2 \mu\text{m}$). The scale bars represent $10 \mu\text{m}$ on all the images. The uniform fluorescence illustrated in c) is representative of disperse nanocrystal fluorescence in BP-PFCB and is not an artifact due to overexposure of the image.⁵³ Reproduced by permission of The Royal Society of Chemistry (RSC)

Fig. 9.

Absorbance and emission of CdSe white-light nanocrystals. The dashed lines are absorbance spectra, while the continuous lines show the emission of the nanocrystals. The red spectra are nanocrystals solvated in toluene; the blue spectra are 12% w/w nanocrystals in biphenylperfluorocyclobutyl polymer (NDM). The feature at 400 nm (blue solid line) is an artifact due to the tail of the excitation source's emission, and the emission feature at 730 nm is a 2nd order diffraction peak introduced by the detection setup. The inset is a true color photograph of a 365 nm LED coated with encapsulated nanocrystals.⁵³ Reproduced by permission of The Royal Society of Chemistry (RSC)

Fig. 10. Current-voltage and luminance-voltage behavior. The device structure of the white CdSe nanocrystal devices is shown in the inset.⁶¹ Reproduced by permission of The American Chemical Society (ACS)

Fig. 11.

Comparison of nanocrystal EL at 15.9 V (lightest shade) with the PL of TPD and nanocrystals in solution excited at 365 nm. The PL from ultrasmall nanocrystals is the darkest spectra; the TPD only emission is the middle shade (centered at 410 nm). The broad EL emission has CIE coordinates of (0.333, 0.333), a CRI of 96.6, a CCT of ~5500 K, and is white to eye.⁶¹ Reproduced by permission of The American Chemical Society (ACS)