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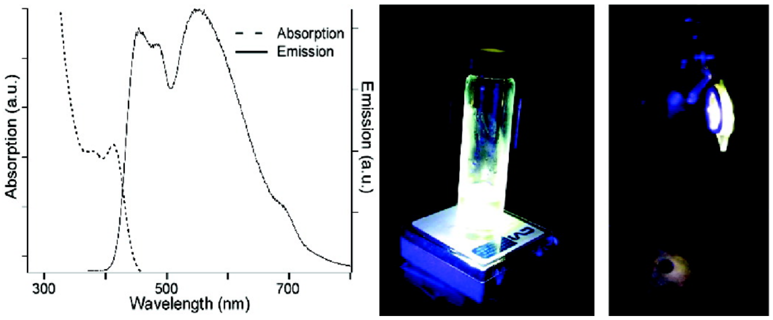

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White-Light Emission from Magic-Sized Cadmium Selenide Nanocrystals

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In response to ever-increasing energy demands and subsequent costs, a tremendous emphasis is being placed on energy saving, solid state lighting devices in the form of light emitting diodes, or LED's.[1,2] Specifically, a need exists for pure white-light LED's as a more efficient replacement for conventional lighting sources. Switching to solid state lighting would reduce global electricity use by 50% and reduce power consumption by 760 GW in the United States alone over a 20 year period.[1,2] The complications associated with design and fabrication of such devices have generated great interest in developing white-light phosphors that do not depend on complex doping schemes or combinations of materials. One proposed solution is to use a mixture of semiconductor nanocrystals as the intrinsic emitting layer for an LED device.[3,4] Semiconductor nanocrystals exhibit high fluorescence quantum efficiencies and large molar absorptivities.[5,6] However, they still suffer from the problem that simply mixing the traditional red, green, and blue colors to achieve white light results in a loss in total device efficiency due to self absorption for a device of more than a few monolayers.[4] In this communication, we demonstrate white-light emission from ultra-small cadmium selenide (CdSe) nanocrystals. This raises the intriguing possibility of using these nanocrystals as a white-light phosphor. These ultra-small nanocrystals exhibit broadband emission (420−710 nm) throughout most of the visible light spectrum while not suffering from self absorption. This is the direct result of the extremely narrow size distribution and an unusually large (40−50 nm) Stokes shift (Figure 1), making them ideal materials for devices currently under development[3] and also an ideal platform to study the molecule-to-nanocrystal transition.

Figure 1 shows the absorption and emission properties of a sample of magic-sized CdSe nanocrystals prepared by the methods of Peng et al.[7] with modifications (see Supporting Information).[8] The first absorption feature is at 414 nm, which has been assigned as a thermodynamically determined "magic size", on the order of 15 Å, for CdSe.[9,10] The emission spectrum shows a band edge emission followed by two features attributed to emission from energetically different midgap states. Although the fluorescence quantum yield for this material thus far is on the order of 2−3%, with a calculated extinction coefficient of 22311 per mole of nanocrystals.[6] Additionally, this material has demonstrated good photostability. Thin films of magic-sized CdSe (neat on a glass slide) were able to maintain their optical properties after 10 days of exposure to intense UV light from a 1000 μW, 370 nm LED (LEDtronics) under ambient conditions (air at room temperature).

Many synthetic schemes have produced magic-sized nanocrystals by growing larger nanocrystals, then etching them with various chemical etchants.[10,11] Magic-sized nanocrystals grown into the magic size, while reported, are relatively rare.[9,12] There are also inverse micellular methods and low temperature organometallic preparations that yield magic-sized nanocrystals,[13] but none of these methods produce nanocrystals with comparable optical properties to the high temperature pyrolytically synthesized nanocrystals.[14]

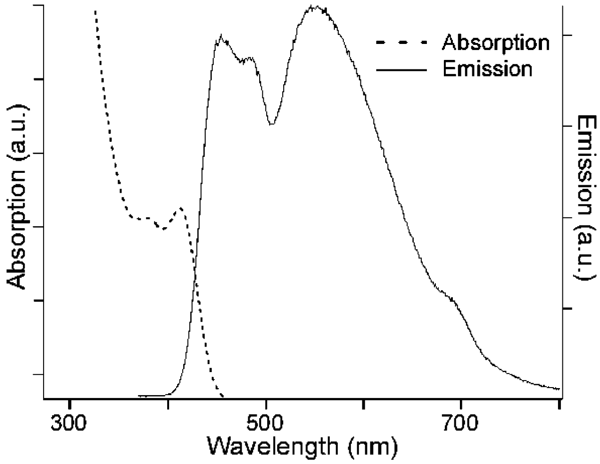

Figure 1. Absorption and emission spectra of magic-sized CdSe. Static absorption and emission spectra were obtained using a Cary Bio 50 UV−visible spectrometer and an ISS photon counting fluorescence spectrometer ($\lambda_{ex} = 367$ nm), respectively.

Our pyrolytically grown magic-sized nanocrystals do not typically exhibit the strong band edge emission feature that is observed in CdSe nanocrystals, but do exhibit strong band edge absorption features indicative of high quality CdSe nanocrystals. We attribute the broad emission to charge recombination from surface midgap states that arise from the presence of noncoordinated surface selenium sites.[15] While band edge emission occurs by direct recombination of the electron and hole within the nanocrystal, deep trap emission occurs when a photogenerated hole, trapped in a midgap state, encounters an electron before it can relax nonradiatively to the ground state.[16]

This phenomenon of hole trapping to the selenium surface sites has been studied by ultrafast fluorescence upconversion spectroscopy.[16] These studies indicate that as nanocrystal size decreases, the amount of hole trapping increases. This is due not only to the reduced physical distance the hole must travel to reach the surface but also to an increased surface-to-volume ratio resulting in more available surface sites. It is not unreasonable to infer that as the nanocrystal size continues to decrease, an even larger population of photoexcited excitons would be funneled toward the hole-trapping decay pathway, ultimately making it the dominant mode of radiative relaxation. Magic-sized nanocrystals are so small that the electron wave function has significant overlap with the selenium surface sites.[17,18] Therefore, any hole trapped on the surface would likely encounter the electron before nonradiatively relaxing to the ground state.[16] Compounding this situation, the nanocrystal growth time is so short (10−20 s normally) that surface reconstruction and high temperature annealing have little time to occur. This results in a surface that is likely defect-ridden. Furthermore, unlike larger nanocrystals, the diameter of the magic-sized nanocrystal and the length of the ligand are quite comparable. Coupling of vibrational modes of the ligand to surface atoms, as well as collisional

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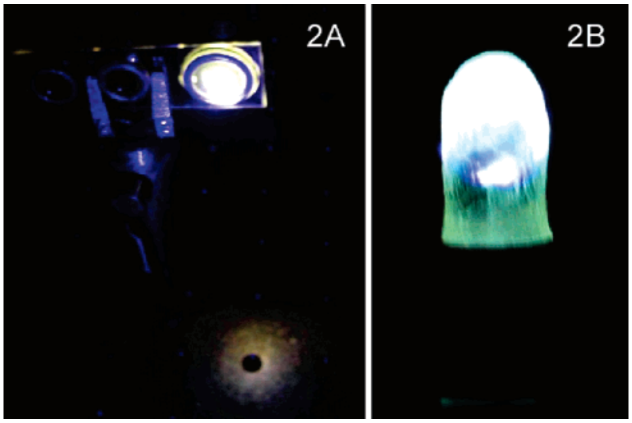

Figure 2. White-light emission from magic-sized CdSe. (a) Thin film of magic-sized CdSe in polyurethane excited by a frequency doubled titanium: sapphire laser (400 nm) with white light clearly seen reflecting off the table surface. (b) A 5 mm commercial UV LED (400 nm) illuminating a thin coating of magic-sized CdSe in polyurethane.

relaxation, could provide other avenues for energy dissipation, providing more effective trap sites and potentially contributing to the broad log-normal emission line shape.

While deep trap emission is quite common in small (<30 Å) nanocrystals, it is usually accompanied by a large band edge emission feature.[19,20] The presence of a strong band edge feature would bias the white-light emission toward a particular color, reducing the quality of the white light produced. The band edge emission feature of our material is greatly diminished, providing a more balanced white-light emission with chromaticity coordinates of 0.322, 0.365, which fall well within the white region of the 1931 CIE diagram.[21] Examples of the white-light emission are shown in Figure 2.

As suggested above, the unique optical properties of these ultra-small nanocrystals make them an ideal material for incorporation into solid state lighting applications in the form of LED's. LED's are made by incorporating an intrinsic emitting layer into a p−n junction device. When under forward bias, electrons and holes are injected into the intrinsic layer, where they recombine to emit light.[22] The wavelength of the emitted photon is determined by the intrinsic layer or phosphor. Typically, phosphors are limited to monochromatic emission, requiring a mixture of phosphors or a complex doping scheme to achieve white light.[23]

An ideal material for a white-light emitting intrinsic layer would be robust, emit over the entire visible spectrum, have high quantum efficiency, not suffer from self absorption, be easy to produce on a large scale, and not waste energy producing wavelengths beyond the visible spectrum (e.g., tungsten, see Supporting Information). Taking into consideration these properties, semiconductor nanocrystals are attractive candidate materials for applications in solid state lighting. Unlike commercial phosphors, their emission colors can be tuned by simply controlling the nanocrystal size. Nanocrystal-based LED's have been demonstrated showing colored-light emission. One example developed by Klimov et al. utilizes core/shell nanocrystals deposited onto an InGaN quantum well. The quantum well is pumped by laser emission, generating electrons and holes which, through energy transfer, cause the nanocrystals to emit light at their fundamental band edge energy.[3] While intuitive, simply mixing several colors of nanocrystals together to achieve white light would result in an overall reduction of device efficiency through self-absorption between the various sizes of nanocrystals. This would be especially detrimental for device designs requiring more than several monolayers.[4] The large Stokes shift and narrow size distribution of these ultra-small nanocrystals, along with the broad emission spectrum, would alleviate any efficiency loss attributed to self absorption from mixing nanocrystal sizes.

In this work, we have shown the potential usefulness of pyrolytically grown magic-sized CdSe nanocrystals as a white-light phosphor. These ultra-small nanocrystals exhibit a strong Stokes shift and broad emission covering the entire visible spectrum. These properties are the direct result of the extreme surface-to-volume ratio forcing the electron and hole to predominately interact at the nanocrystal surface. Consequently, these magic-sized nanocrystals provide the ideal platform to study the nanocrystal−molecule transition. Further, the combination of their intrinsic properties makes them an ideal material for solid state lighting applications. Study of the fundamental properties of this material could lead to the development of more economical and environmentally friendly materials with similar properties, eventually leading to the next generation of solid state lighting technologies.

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Supporting Information Available: A comparison of magic-sized CdSe nanocrystal emission to conventional light sources as well as a complete author list for ref 13, and the synthetic scheme used in this work is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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