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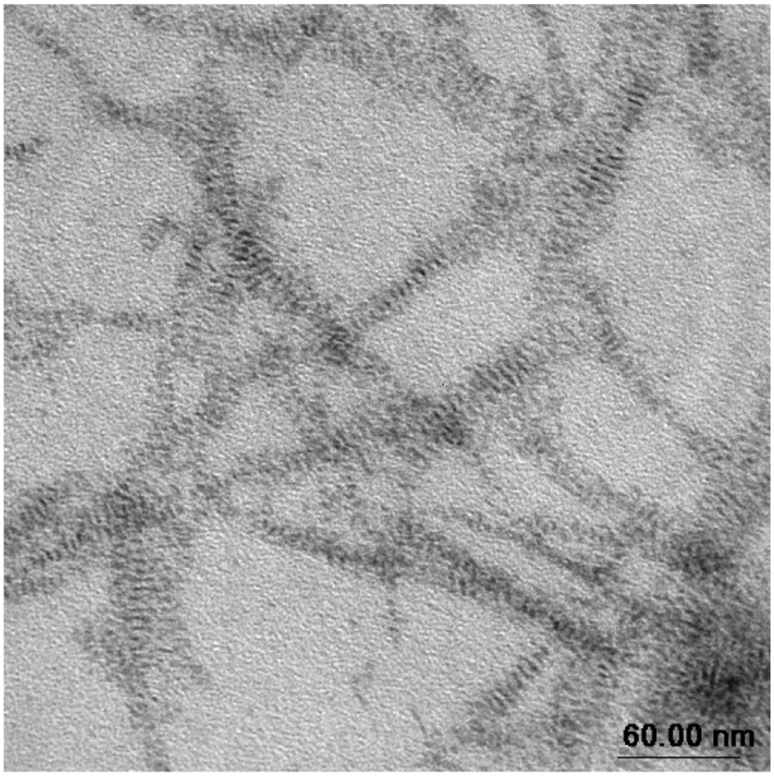

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Synthesis, Optical Properties, and Growth Mechanism of Blue-Emitting CdSe Nanorods

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Abstract: Blue-emitting, cubic phase CdSe nanorods with an approximate diameter of 2.5 nm and lengths up to 12 nm have been synthesized at low temperature (100 °C) in a single surfactant using a single-source molecular precursor. Transmission electron microscopy and dynamic light scattering measurements indicate that the nanorods are formed from self-assembly of isotropic nanoclusters. Anisotropic growth in a single surfactant appears to be favored when growth occurs below the thermal decomposition temperature of the single-source precursor.

Introduction

It is generally accepted that anisotropic growth occurs primarily because the different faces of a growing nanocrystal have varied surface energies which enable different binding strengths with a surfactant. Following adsorption of the surfactant, the crystal "faces" with lower binding energies will grow faster than those with higher binding energies.[1] By using two or more surfactants to facilitate this process, a variety of different shape and size nanoclusters have been grown.[2,3] The conditions necessary for this type of growth are generally stated as (a) an organometallic precursor that decomposes rapidly to monomers at the reaction temperature, (b) two (or more) surfactants that adsorb differentially, and (c) high monomer concentrations and high growth rates.[4,5]

An alternative growth mechanism has also been proposed by Kotov et al.[6,7] In this scheme anisotropic growth proceeds via assembly of isotropic nanoclusters and can be used to assemble micrometer-sized nanowires. The mechanism of self-assembly is attributed to dipole−dipole interactions between the highly charged surfaces of II−VI semiconductor nanoclusters. It was found that partial removal of the stabilizing organic facilitates the self-assembly process as this increases the net charge of the inorganic nanocluster−stabilizing organic composite.

In this study, blue-emitting CdSe nanorods were synthesized using single-source molecular precursors at low temperature, in a single surfactant. The physical, chemical, and optical properties of the resulting material are measured and presented. We discuss the anisotropic growth mechanism with respect to these properties and the synthesis environment.

Synthesis

The single-source precursor, $Li_2[Cd_{10}Se_4(SPh_{16})]$ (Li = lithium, Cd = cadmium, Se = selenium, SPh = phenyl thiolate), was synthesized following the method of Dance et al.[8] and synthesis of the CdSe nanoclusters via that of Strouse et al.[9] Conversion of the single-source precursor to inorganic nanoclusters can be described briefly as follows.

A 36 g amount of hexadecylamine (HDA; Aldrich, 98%) was heated under vacuum to 120 °C and then purged and reevacuated three times with dry nitrogen and allowed to cool to ∼60 °C. While stirring, 0.8 g of single-source precursor was added via airless techniques and the solution temperature raised at a rate of 1 °C/min to 100 °C, where it was held for 72 h. After allowing the solution to cool to 80 °C, 80 mL of toluene was added, followed by an equivalent volume of dry methanol, causing the HDA-stabilized nanoclusters to precipitate. The precipitate was concentrated via centrifugation, the supernatant decanted, and the precipitate redispersed in toluene.

Characterization

Analysis of [Cd] and [Se] concentrations was obtained using a Spectrace (now Thermoelectron) QuantX X-ray fluorescence (XRF) spectrometer. Measurements of the purified samples in dilute solution were compared to NBS Cd in xylene standards and diphenyl selenide in toluene standards prepared in our laboratory at comparable concentrations.

Bright-field transmission electron microscopy (TEM) images were obtained using a JEOL EX at 120 keV with a point-to-point resolution of ∼9 Å. High-resolution TEM (HRTEM) was obtained using a JEOL model 2010 microscope operating at 200 keV and typical magnfications of 400 000−800 000×,

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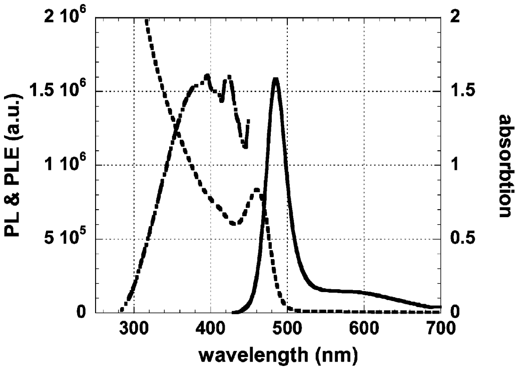

Figure 1. PL (—), PLE (— • —), and absorption (--) of CdSe nanorods.

which allows determination of the atomic lattice fringe spacing. The TEM samples were prepared by evaporating a small amount of dilute nanocluster solution (~3 μL of ~0.01 M CdSe) onto a holey carbon grid, wicking away the excess, and allowing to dry. The samples were analyzed by TEM, HRTEM, and selected area diffraction (SAD). Absorption spectra were obtained in either 2 or 10 mm path length quartz cuvettes (Spectacell) on a double-beam Cary 2300 UV–vis–near-IR absorption spectrometer interfaced to an Apple IIfx computer. Photoluminescence (PL) and photoluminescence excitation (PLE) measurements were obtained using a SPEX Flourolog II double–double grating spectrometer with Xe arc lamp illumination and using a cooled S20-type photomultiplier tube (PMT). All samples were diluted in toluene.

Dynamic light scattering (DLS) measurements were performed using a custom-designed system that measures the autocorrelation function of the scattered light using a Brookhaven instruments BI9000 model logarithmic autocorrelator.[10] The ensemble average translational diffusion constant of the particles obtained from the relaxation of this autocorrelation function was used to compute the effective hydrodynamic diameter, D_h. Since our system exhibited relaxation behavior that is well-described by a double-exponential function, a more detailed analysis was necessary to extract the information and is described below. The data presented here were obtained from a sample of approximately 0.001 M CdSe in toluene, and the data were collected and averaged over a 24 h period.

Results and Discussion

XRF analysis of our HDA-stabilized CdSe nanorods gave a Cd:Se ratio of 1.2:1, and indicated product yields of close to 100%, assuming that only fully reacted species were carried through the precipitation–redispersion process. The PL, PLE, and Aabsorbance data are presented in Figure 1, where it can be seen that the band edge onset is approximately 500 nm. Figure 2 shows a low-resolution TEM image of the nanorods. The nanorods appear fairly uniform with approximate dimensions of 2.5 nm × 12 nm (diameter × length), which is an aspect ratio of ~1:5.

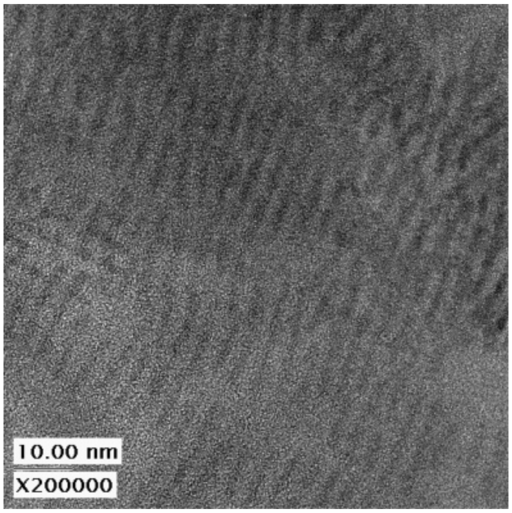

Figure 2. TEM micrograph of CdSe nanorods.

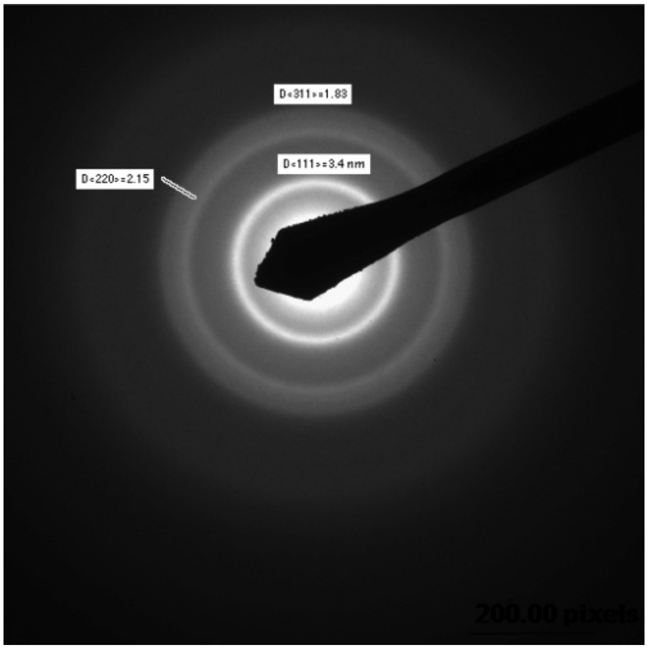

Figure 3. Selected area electron diffraction from a field of 2 nm CdSe clusters and nanorods, showing a cubic, zinc-blende symmetry with the indicated *d* spacing.

From HRTEM images in which the individual lattice planes are visible, we measure a spacing of 3.4 Å. This is similar to that observed in spherical CdSe grown by the same process[9] and is close to that expected for the $d\langle 111\rangle$ reflection of bulk cubic CdSe (3.51 Å). By contrast the $d\langle 100\rangle$ reflection from the bulk Wurtzite structure is 3.72 Å. SAD from a large area of the grid shows three continuous rings with spacings of 3.43, 2.11, and 1.79 Å. Again, these spacings correspond most closely to the bulk cubic symmetry, which has spacings of $d\langle 111\rangle = 3.51$, $d\langle 220\rangle = 2.15$, and $d\langle 311\rangle = 1.83$ Å (see Figure 3). In previous work, (Figure 11 of ref 11), it was noted that the smallest, blue-emitting CdSe clusters, identified as being 1.2 nm in size, showed a qualitative difference in diffraction pattern from that of the larger clusters. The first diffraction peak of the larger clusters closely matched that of the hexagonal, Wurtzite phase, while the first reflection from the 1.2 nm clusters occurred at a larger diffraction angle.[11] Though it was concluded that shape and/or disorder could account for the observed shift, one could also argue that the observed decrease in *d* spacing for the smallest clusters is attributable to cubic symmetry.

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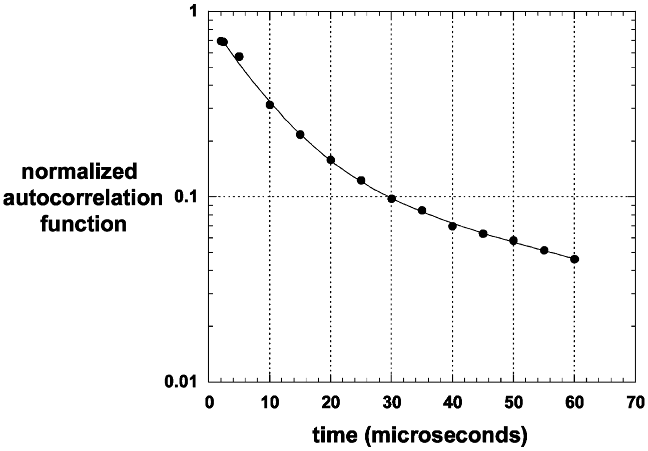

Figure 4. Dynamic light scattering raw data (circles) and double-exponential fit (solid line).

Indeed, other previous work also suggest that 1.7 nm CdSe clusters exist in the cubic phase,[12] and studies on larger CdSe indicate that a disordered cubic or hexagonal structure could occur depending on whether the clusters were annealed at elevated temperature.[13] This work appears to be the first to clearly show using SAD that the cubic symmetry is favored for small sizes.

The approximate diameter of 2.5 nm estimated from the TEM micrographs is consistent with that reported by Strouse et al.[9] of 2.5 nm diameter HDA−CdSe spheres with a band edge onset of ∼500 nm. Furthermore, co-plotting our material with that of Buhro et al.,[14] CdSe ΔE_g vs $1/d^2$ data yields a diameter of approximately 2 nm for nanorods of similar length. However, sizes determined by TEM are subject to overestimation because the stabilizing organic can “blur” the cluster edges. Hence, we suggest that the nanorod diameter is determined by the thermodynamically favored particle size of 1.9 nm (approximately 90 formula units) and that this dimension is responsible for the blue emission.

DLS measurements exhibited a biexponential relaxation. Fitting the autocorrelation function allows the determination of two distinct relaxation times and calculation of the associated translational diffusion coefficients. These data were fit using the equation:

$$Y = M_1 \exp(-M_0/M_2) + M_3 \exp(-M_0/M_4) + M_5$$

where M_2 and M_4 are the relaxation times. The determined values of $M_1 = 0.1501$, $M_2 = 43.4910$, $M_3 = 0.7343$, $M_4 = 7.6687$, and $M_5 = 0.0084$ yield an R of 0.9999. The raw data and fit are presented in Figure 4.

The translational diffusion coefficient (D_t) is related to relaxation time via $D_t = 1/(2\tau q^2)$, where $q = (4\pi n/\lambda)\sin(\theta/2)$. In this case the solvent is toluene and the refractive index $n = 1.496$, the wavelength $\lambda = 633$ nm, and $\theta = 90°$, which yield a value of $q = 2.1 \times 10^5$ cm^{-1}.

Using the values for τ_1 and τ_2 obtained from the double-exponential fit and solving for D_t, we obtain $D_{t1} = 2.61 \times 10^{-7}$ cm^2/s and $D_{t2} = 1.47 \times 10^{-6}$ cm^2/s, respectively. If this system does consist of spherical and rodlike particles, the hydrodynamic radius (R_h) of the spherical particles may be calculated from the relationship $R_h = (kT)/(6\pi\eta D_t)$, where η = viscosity. Substituting D_{t2} we obtain a value for R_h of 2.5 nm. A hydrodynamic diameter of 5 nm is reasonably close to what we would expect for a roughly 2 nm diameter spherical inorganic particle surrounded by a 1−1.5 nm layer of stabilizing hexadecylamine.

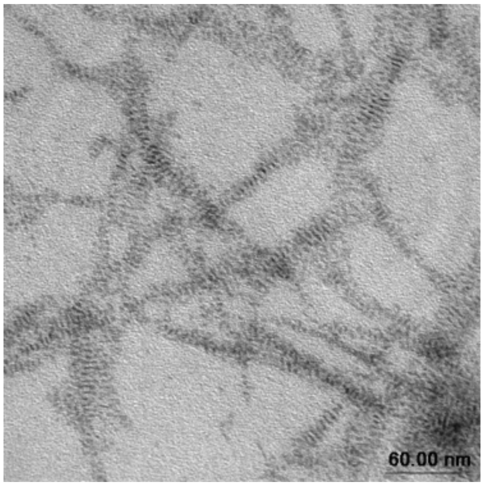

Figure 5. TEM micrograph of CdSe nanorod aggregates.

D_t for Brownian rods may be calculated via[15,16]

$$D_t = [(kT)/(3\pi nL)][\ln(L/d) + 0.312 + 0.565(d/L) + 0.100(d/L)^2]$$

where k is Boltzmann’s constant, T is temperature, n is refractive index, and L and d are rod length and diameter, respectively. Substituting $D_t = 2.61 \times 10^{-7}(D_{t1})$, $d = 5$ nm, and solving for L, we obtain $L_1 = 92.5$ nm. This value is substantially larger than the ∼10−15 nm rod size we observed in Figure 2, but other images (see Figure 5) show much larger structures that appear to be ∼100 nm aggregates of individual 10−15 nm rods. Initially it was assumed that these aggregates were formed via self-assembly during the evaporative TEM sample preparation process, but the DLS-derived length of 92.5 nm suggests that these structures exist in solution.

Further HRTEM analysis of individual rods shows that many of the individual nanorods contain necks (see Figure 6). Elsewhere on the same grid it appears that there are also individual, isotropic particles (see Figure 7). Agglomeration and necking of spherical particles is well-established in colloidal gold systems.[17] These observations in conjunction with the DLS-determined primary particle size of 5 nm (organic−inorganic composite) suggests that the rods are assembled from individual isotropic clusters via a self-assembly mechanism as suggested by Kotov et al., rather than the multiple surfactant-mediated route. It is conceivable that the 2% impurities in the HDA may act as a second surfactant, yet this is far below the weight fractions typically associated with surfactant-mediated anisotropic growth. One might also suggest that the reaction byproduct,

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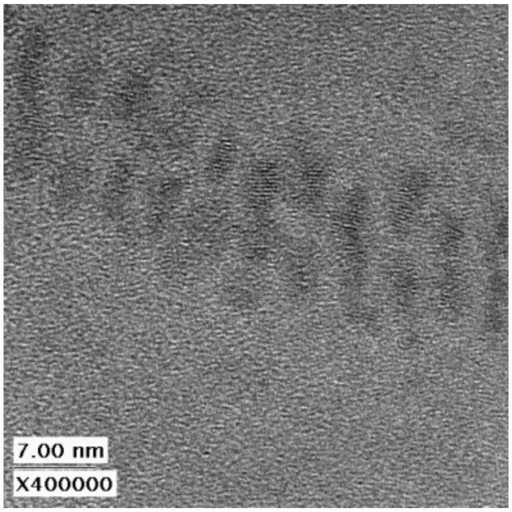

Figure 6. HRTEM micrograph of CdSe nanorods showing necking.

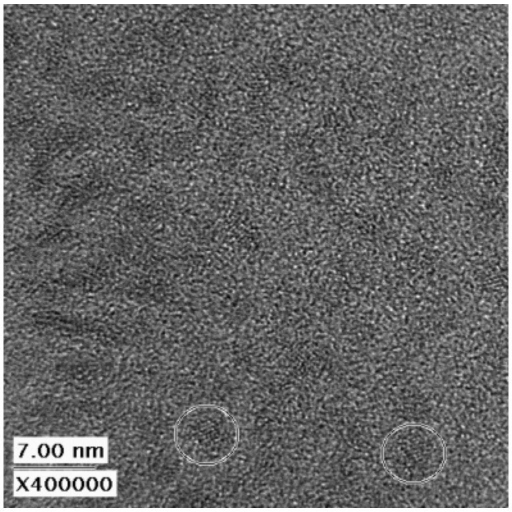

Figure 7. HRTEM micrograph of CdSe nanorod solution containing isotropic nanoclusters. Two such clusters are circled.

thiophenol, might act as a second surfactant. Although it has recently been shown that thiophenol does indeed coadsorb with HDA, it does not however do so in a face-selective fashion.[18] Further, we have also performed this synthesis using a 90/10 wt % HDA/TOPSe mixture and obtained very similar results.

If the anisotropic growth mechanism is via assembly of isotropic nanoclusters, then the question remains, how does this occur in *single* surfactant? Strouse et al.[9] suggest that growth from these single-source precursors in HDA proceeds via formation of Cd_{20} and Cd_{32} clusters (from the original Cd_{10}) which serve as nuclei for monodisperse cluster growth, though they indicate that the onset of further growth requires temperatures in excess of 180 °C. They also note that although the Cd_{10} single-source precursor (same as used here) has a cubic lattice, their high-temperature synthesis yields a hexagonal product.

O'Brien et al.[19] have also reported moderately anisotropic particle formation from single-source precursors when using lower temperatures (150 °C), while, at higher temperatures (240 °C), spherical particles are formed. Because the decomposition temperature of the precursor lies between the two reaction temperatures, it was suggested that at temperatures below the precursor decomposition temperature nucleation and growth occur as competing processes, which perhaps contribute to the anisotropy. Note that they used the hot-injection method (as opposed to adding the precursor prior to heating as was done here) and also used a different single-source precursor and surfactant, a dithiobiurea−cadmium complex and TOPO, respectively. It was shown using both XRD and SAD that their CdS materials crystallized in the hexagonal phase.

The concentration of single-source precursor used in this study was intermediate to that used by Strouse et al.[9] and O'Brien et al.,[19] meaning that concentration differences alone are not likely the source of anisotropic growth. Taken as a whole, these observations suggest that growth of anisotropic nanoclusters in a single surfactant is most strongly dependent on the choice of precursor as well as the synthetic procedure. Although the surfactant must surely play a critical role in the growth process, in this system the presence of 10 wt % of a second stabilizing organic does not alter the reaction product.

Synthesis temperatures below the precursor decomposition temperature seem to favor anisotropy, perhaps merely by enabling thermodynamically stable configurations not possible at higher energies. For instance, although the cubic phase is likely favored for smaller cluster sizes, it is possible that the lower synthesis temperature allows maintenance of the cubic phase directly from the single-source precursor. Growth occurs along the *c*-axis presumably because cojoining along the $\langle 111 \rangle$ plane maximizes the number of bonds formed, which is thermodynamically favorable. The same lattice spacing of ∼3.4 Å is observed in both the spherical and rodlike clusters, further supporting that the growth mechanism is via assembly of originally isotropic particles.

Conclusions

Blue-emitting, cubic phase CdSe nanorods can be synthesized at low temperature in a single surfactant via decomposition of single-source precursors. Anisotropic growth appears to occur via the assembly of originally isotropic clusters. The presence of both isotropic and anisotropic particles was verified by DLS and TEM. In this system, cluster growth is influenced more by the choice of precursor and reaction conditions than the choice of surfactant. Anisotropic growth seems favored by lower reaction temperatures that enable stabilization of structures not possible at higher temperatures.

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