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Band Gap Variation of Size- and Shape-Controlled Colloidal CdSe Quantum Rods

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ABSTRACT

We report the band gaps of rodlike CdSe quantum dots with diameter varying from 3.0 to 6.5 nm and length from 7.5 to 40 nm. A qualitative explanation for the dependence of band gap on width and length is presented.

Semiconductor nanocrystals, also known as "quantum dots", have been intensely investigated because of their size-dependent optical and electrical properties.[1−4] The confinement of photogenerated electrons and holes in the nanocrystals can be tuned by adjusting the shape and height of the potential. Extensive work has been devoted to detailed comparison of theory of quantum-confined electronic states in these nanocrystals with experiments in which the diameter of spherical dots is varied.[5−13] Early phenomenological models are based on the effective mass approximation;[7−10] later developments include tight-binding models[11,12] and empirical pseudo-potential calculations.[13] Each of these models can provide an adequate description of the band-gap variation vs diameter for spherical or nearly spherical dots, and they also provide varying levels of success in describing higher electronic excited states. The advent of new methods to precisely control the diameter and length of rodlike CdSe nanocrystals provides a new set of experimental data against which the theories can be tested.[14−16] Here we report initial measurements of the band gap (photoluminescence energy) of CdSe quantum rods vs their diameter and length.

CdSe quantum rods are synthesized via pyrolysis of dimethylcadmium and Se/tributylphosphine solution in a hot mixture of trioctylphosphine oxide, hexylphosphonic acid, and tetradecylphosphonic acid under inert gases.[16] Figure 1 shows transmission electron micrographs of several CdSe rod samples. The size distribution is typically 5% in diameter and 10% in length.

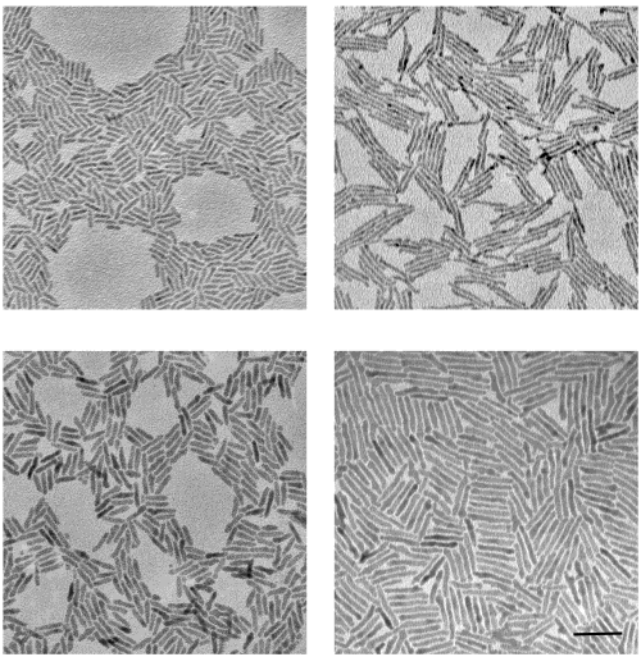

Figure 1. TEM images of four CdSe rod samples. The scale bar is 50 nm.

To understand the relationship between the band gap and the dimensions of these quantum rods, we measured photoluminescence spectra of CdSe rod samples with different widths and lengths. Samples were dispersed in toluene, and their photoluminescence spectra were measured on a commercial Spex 1682 0.22 m fluorometer at room temperature. All the samples were excited at wavelengths far shorter than

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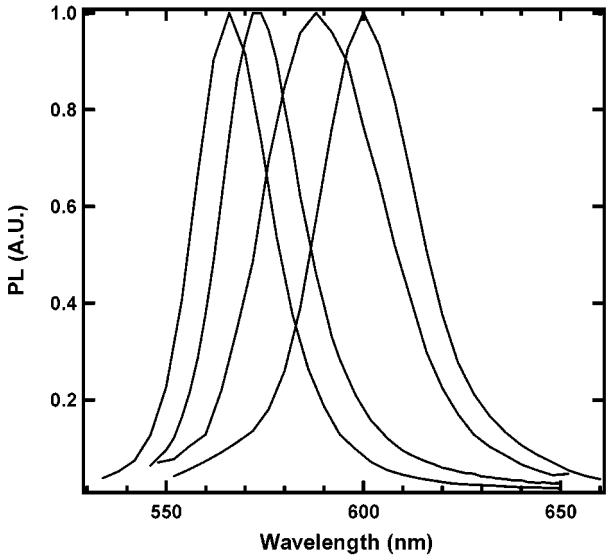

Figure 2. Photoluminescence spectra of 3.7 (±0.2) nm wide CdSe quantum rods with lengths of 9.2, 11.5, 28.0, and 37.2 nm, respectively (from left to right), excited at 450 nm.

their absorption edges to avoid spectral size selection, and the spectral resolution for the photoluminescence spectra is 4 nm. The room temperature quantum efficiency of the rods is typically 5−10%. Figure 2 shows the emission spectra of 3.7 nm wide rod samples with four different lengths. By only changing the length of CdSe quantum rods, we can tune the wavelength of their emission over the same range as in CdSe spherical dots, while the emission from each individual quantum rod is highly linearly polarized,[16] in contrast to the plane-polarized emission from spherical dots.

Although the electronic structures of both zero-dimensional and one-dimensional quantum-confined systems[17,18] have been well described by current models, little work has been done on the size regime intermediate between them, i.e., quantum rods with large aspect ratio. Quantum rods provide an opportunity to study the evolution of properties from quantum dots to quantum wires. In Figure 3, we show the band gap variation vs width and length for quantum rod samples at room temperature, with the aspect ratio ranging from 1 to 12. The original data are also given in Table 1. As expected from quantum confinement considerations, the general tendency is that the emission shifts to lower energy with an increase in either width or length. The data are fit with a polynomial in 1/length (1/*L*), 1/width (1/*W*), and aspect ratio (*L*/*W*). The surface of best fit obtained is 1.8563 −

Table 1. Band Gap Energy of CdSe Quantum Rods with Different Widths and Lengths at 295 and 7 K[a]

length (nm)	width (nm)	PL (eV) 295 K	PL (eV) 7 K	length (nm)	width (nm)	PL (eV) 295 K	PL (eV) 7 K
11.0 (±0.7)	3.2	2.20		8.7 (±0.9)	4.3	2.07	
37.8 (±3.0)	3.3	2.08		16.4 (±2.0)	4.3	2.08	
43.1 (±3.2)	3.4	2.03		8.6 (±1.0)	4.4	2.10	
28.0 (±2.2)	3.5	2.11		31.5 (±3.3)	4.4	1.98	
38.5 (±4.4)	3.5	2.05		15.3 (±0.8)	4.5	2.10	
11.5 (±0.8)	3.6	2.17	2.20	19.8 (±2.0)	4.6	2.02	
22.1 (±1.8)	3.6	2.16		19.8 (±1.2)	4.6	1.97	
7.6 (±0.8)	3.7	2.16		12.4 (±1.3)	4.8	2.03	
9.2 (±0.7)	3.7	2.19		19.4 (±1.4)	4.8	2.03	
26.1 (±3.2)	3.7	2.12	2.17	40.4 (±3.7)	4.8	1.93	
28.8 (±4.8)	3.7	2.12		18.4 (±2.0)	4.9	2.06	
8.6 (±0.8)	3.8	2.12		18.9 (±2.1)	4.9	2.06	2.09
37.2 (±4.0)	3.9	2.07	2.10	12.0 (±1.4)	5.1	1.99	
44.3 (±4.0)	3.9	2.06	2.10	11.4 (±1.2)	5.2	2.00	
9.7 (±0.7)	4.0	2.12		22.2 (±2.2)	5.2	2.00	
11.6 (±1.0)	4.0	2.18	2.23	40.8 (±4.2)	5.3	1.90	
41.3 (±6.8)	4.0	2.02		18.2 (±1.5)	5.4	2.00	
12.7 (±1.0)	4.1	2.15		8.5 (±1.0)	5.5	1.95	
13.4 (±1.1)	4.1	2.13		18.4 (±1.8)	5.5	1.96	2.02
16.9 (±2.3)	4.1	2.04		23.6 (±2.9)	5.5	1.97	
40.2 (±4.0)	4.1	2.00		14.0 (±1.2)	6.2	1.94	
16.5 (±2.4)	4.2	2.06		17.6 (±1.0)	6.4	1.93	
20.2 (±2.0)	4.2	2.02	2.05				

[a] The numbers in parentheses are standard deviations. For rod width the standard deviation is 0.2−0.3 nm.

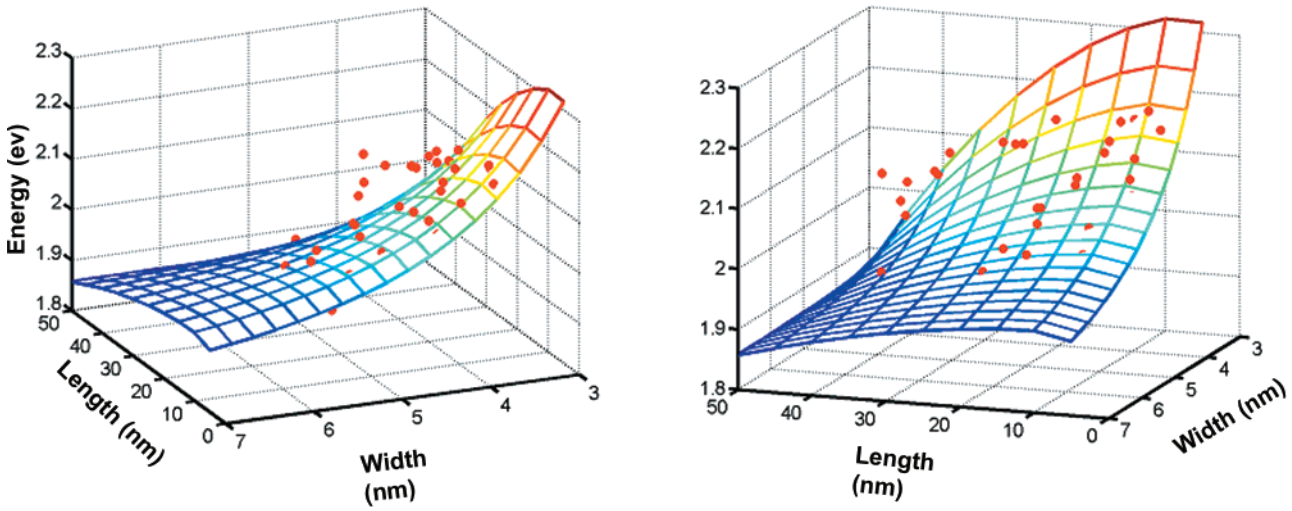

Figure 3. Band gap of CdSe quantum rods vs length and width viewed from two different angles. The mesh is the best fit described in the text.

Ⓦ A three-dimensional graph in wrl format is available.

$2.0835/L^2 + 4.5507/W^2 - 0.0018(L/W)^2 + 0.0001(L/W)^3 + 10.5824/L^3 - 0.3833/W^3$. The standard deviation of this fit is ~30 meV, which is only slightly greater than the thermal energy at room temperature. The polynomial fit is provided for the convenience of the reader but has no direct physical signifinance. In the surface we see a slight increase in band gap (<20 meV) for rods shorte than 10 nm. This is due to uncertainty in both the experiments and the fitting and cannot be extrapolated to disklike nanocrystals.

Recently, we reported an empirical pseudopotential calculation performed on CdSe quantum dot nanorods.[16] The results revealed a level crossing of the two highest occupied electronic states with increasing aspect ratio, which successfully explains the polarization of the emission. A quantitative description of band gap variation for CdSe quantum rods, however, is still unavailable, though we can qualitatively understand it using the concepts of quantum confinement and "band-mixing"[10] in CdSe nanocrystals. From the fitting surface, we see that for all the widths and lengths of quantum rods we have studied here, the emission peak positions depend more sensitively on width than on length, as indicated by the slopes (Figure 3). This suggests that the band gap is mainly determined by the lateral confinement, which plays an important role even when rods are very long. This can be further justified by the fact that the slope of the peak position with respect to width is almost the same for the rods when the widths are the same, even though the lengths may be very different.

It is well-known that the mixing of the valence bands in spherical CdSe nanocrystals is a very important factor controlling their optical properties.[10] For example, the coupling of the "heavy hole", "light hole", and the "split-off" bands under confinement determines the oscillator strength and polarization of optical transitions. In CdSe quantum rods, the symmetry breaking caused by the elongation modifies the band-mixing in such a way that each eigenstate has a definite component of total angular momentum along the long axis.[16] As shown for 3.0 nm wide rods, for example, when the aspect ratio is greater than 1.3, the hole eigenstates with the lowest energy have the greatest absolute value of translational momentum along the long axis of the crystal. Because the translational momentum projected onto the long axis depends on the length of the quantum rods, changing length will affect the band gap. Especially when the width of the rods is much smaller than the exciton Bohr radius, i.e., 5.6 nm in bulk CdSe, the confinement on the carriers in radial directions are in the "strong confinement regime".[10] The band mixing is substantial so that the band gap very sensitively depends on the length. For rods with width greater than ~5.6 nm, however, where band mixing is less significant, increasing the length only slightly lowers the band gap. The modification of band mixing due to the elongation changes the transition selection rules and oscillator strengths as well.

The geometric anisotropy of the rods facilitates their alignment, so that the polarized emission with tunable wavelength could possibly be used on a macroscopic scale. We hope that the measurements provided here will be of use to theorists interested in testing the models for quantum-confined structures. Future work will include studying of the dependence of higher excited states on the rod width and length.

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