Synthesis of CdS Nanocrystals with Different Shapes via a Colloidal Method

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Size- and shape-controlled monodisperse wurtzite structured CdS nanorods have been successfully synthesized using a facile solution-based colloidal method. Depending on the control of injection/growth temperatures and the variation of Cd-to-S molar ratios, the morphology of the CdS nanocrystals (NCs) can be adjusted into bullet-like, rod-like, and dot-like shapes. X-ray diffraction (XRD), transition electron microscopy (TEM), and absorption spectroscopy were used to characterize the structure, morphology, and optical properties of as-synthesized CdS NCs. It was found that uniform CdS nanorods could be successfully synthesized when the injection and growth temperatures were very high (> 360 °C). The aspect ratios of different shaped (bullet-like or rod-like) CdS NCs could be controlled by simply adjusting the molar ratios between Cd and S.

Key Words: CdS nanorods, Colloidal processing, Semiconductors, Wurtzite

Introduction

CdS nanocrystals (NCs), as one of the most important II-VI semiconductor materials, have attracted much attention because of their wide potential applications in many fields, such as solar cells and light-emitting diodes.1-6 As well known, properties of NCs are severely dependent on their size and shape. For example, one-dimensional (1D) nanorods and nanowires have been observed to exhibit optical properties that are different from those of zero-dimensional (0D) quantum dots.7,12 Therefore, systematic tuning of the crystal phase, size, and shape of semiconducting CdS NCs is important because it represents an attractive approach for developing next-generation, low-cost, and high-performance solar cells. A variety of methods have been devised to prepare 1D CdS NCs, such as template method, hot-injection route, polymer controlled growth, and liquid-phase colloidal syntheses.13-21 Among these methods, the hot-injection approach has been proved to be an effective way for the synthesis of high-quality 1D nanostructures.13,15,19 However, few investigations were focused on the synthesis of highly uniform, different rod-shaped CdS NCs via a hot-injection colloidal method.

In this paper, a facile solution-based method was adopted for the synthesis of monodisperse wurtzite structured CdS NCs. Depending on the control of injection/growth temperatures and the variation of Cd-to-S molar ratios, the morphology of the CdS NCs can be controlled in the form of bullet-like, rod-like, and dot-like shapes. And uniform CdS nanorods could be successfully synthesized with high injection/growth temperatures, and the aspect ratios of bullet-like and rod-like CdS NCs could also be tuned by simply adjusting the Cd-to-S molar ratios.

Experimental

Chemicals. Cadmium oxide (CdO, 99.99%), sulfur (S, 99.98%, powder), 1-octadecene (ODE, 90%), n-octadecyl-phosphonic acid (ODPA), tri-n-octylphosphine oxide (TOPO, 90%), and octadecylamine (ODA) were purchased from Aldrich. All reagents were used as received without further experimental purification.

Synthesis of Monodisperse CdS Nanorods. In a typical synthesis, CdO (0.0578 g, 0.45 mmol), ODPA (0.3763 g, 1.125 mmol), ODA (0.1 g), and TOPO (4 g) were loaded into a three-necked flask and degassed at 120 °C for 10 min, then the mixture was heated to 370 °C under nitrogen flow to obtain a colorless clear solution. The mixture was cooled to 370 °C under nitrogen flow to obtain a colorless clear solution. Then, a sulfur precursor solution made by dissolving sulfur powder (0.1152 g, 3.6 mmol) in ODE (2 mL) at 150 °C was quickly injected, and the temperature was lowered to 360 °C for the growth of NCs. The resulted product was separated from the crude solution by precipitating the particles with acetone and centrifuging. To investigate the synthesis conditions for anisotropic CdS nanorods, parallel experiments were also carried out by using different Cd-to-S molar ratios and reaction temperatures.

Characterizations. X-ray diffraction (XRD) studies of CdS NCs were carried out with a Philips X’Pert Pro X-ray diffractometer using Cu Kα radiation (wavelength = 1.54 Å). To get better signal-to-noise ratio, the XRD data were collected at a scan rate of 16 s with 0.2° per step. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) studies were performed using a JEOL-100CX II microscope and JEOL JEM-2010 electron microscope operating at 100 and 200 kV, respectively.
Results and Discussion

Generally, the synthesis of monodisperse NCs could be separated into two steps, nucleation and growth.1,2,22-24 The separation of nucleation and growth provides a good chance to investigate the influence of different transition period on the morphology of eventual NCs. In our synthesis, ODE reacted with sulfur powder at 150 °C to form S-ODE complex with high concentration as S precursor. ODPA acted as coordinating ligand and stabilizer, which can cap Cd²⁺ to form a complex. TOPO was chosen as the solvent to get high reaction temperatures, and a few ODA was used as the co-reagents to activate the Cd precursors. When high concentrated S precursor was injected into the highly reactive Cd precursor solution with high temperatures, CdS NCs were formed quickly with monodisperse size distributions, and the size could be controlled by simply adjusting the nucleation/growth temperatures. Figure 1(a) and 1(b) are the low-and high-magnification TEM images of bullet-like CdS NCs obtained with a Cd-to-S molar ratio of 1:8 at an injection temperature of 370 °C (nucleation temperature), followed by a growth process at 360 °C for 10 min. The dynamic light scattering (DLS) data of the CdS nanorods is shown in Figure 1(a) inset. The average size of the CdS nanorods (in chloroform) is 20.7 nm (PDI = 0.08). HRTEM image of a single CdS nanorod is shown in Figure 1(c), it reveals a high crystallinity with continuous lattice fringes throughout the whole rod. The distance between adjacent lattice fringes is 0.33 nm, which is consistent with the interplanar distance of the (002) planes of wurtzite CdS nanorods.

The effect of Cd-to-S molar ratio on the morphology of CdS NCs was systematically investigated as shown in Figure 1(d)-(f) and it was found that the shape and size of the CdS crystals were very sensitive to the precursor molar ratios. When the Cd-to-S molar ratio was 1:16, irregular dot-like CdS NCs were formed (Fig. 1(d)). It seems that the irregular CdS NCs were tend to form rods, but eventually no rods were formed. This was because the molar ratio of Cd:S was too small. Most of the Cd precursor was consumed in the nucleation stage, residual Cd precursor was too few and could not afford the further growth of CdS nanorods, so only irregular dot-like CdS NCs were formed and regular rod-like NCs could not be synthesized. If the Cd-to-S molar ratio was increased to 1:4 and 1:2, rod-like CdS NCs were synthesized successfully with a diameter of ~10 ± 4 nm and ~11 ± 2 nm, and the length-to-diameter ratios were about 4:1 and 5:1, respectively. It suggests that different shapes (bullet-like and rod-like) of CdS NCs could be obtained by simply adjusting the Cd-to-S molar ratios.

The preparation of anisotropic nanorods is generally explained by two factors: the capping ligand chemistry and the nanorod growth kinetics. For the CdS nanorods we synthesized here, ODPA was preferentially adsorbed onto certain crystal facets, thus inhibiting the growth rate on those facets. For cadmium chalcogenides with wurtzite structure, phosphonic acids preferentially adsorb onto the nonpolar facets, leaving the polar {002} facets more exposed for monomer deposition.25 But the nanorods growth kinetics must be adequately controlled in order to induce preferential deposition on specific crystallographic surfaces. This control is achieved here by appropriate Cd-to-S molar ratio and suitable injection/growth temperatures.

To investigate the structure of as-synthesized CdS nanorods, their crystallographic properties were determined using powder XRD. Figure 2 shows a typical XRD pattern of the CdS nanorods which were prepared with the injection and

![Figure 1](image-url)

**Figure 1.** Low- (a) and high-magnification (b) TEM images of as-synthesized bullet-like CdS NCs prepared under injection/growth temperature of 370 °C/360 °C for 10 min with a Cd-to-S molar ratio of 1:8; (c) HRTEM image of an individual bullet-like CdS NC; TEM images of CdS NCs prepared using different molar ratios: (d) Cd:S = 1:16, (e) Cd:S = 1:4, and (f) Cd:S = 1:2. Inset of (a): DLS data of bullet-like CdS nanorods.
growth temperature of 370 °C and 360 °C, respectively. According to the XRD pattern, the peak positions of the CdS nanorods are in agreement with bulk CdS in wurtzite structure. Seven obvious peaks corresponding to the (100), (002), (101), (102), (110), (103) and (112) planes of wurtzite CdS are clearly distinguishable in the pattern (JCPDS 41-1049). Different from our previous report, high monomer concentration and high reaction temperature favors the formation of wurtzite CdS nanorods. From the XRD pattern, a higher and narrower (002) peak is observed in contrast to other peaks which indicates the extension of crystalline domain along the c-axis. The corresponding selected-area electron diffraction (SAED) pattern shows seven distinct rings and the calculated d-spacings match well with the interplanar distances of wurtzite structured CdS (Figure 2 inset), which also could be indexed to a single hexagonal phase. The intense and sharp diffraction peaks suggest that the as-synthesized products are crystallized well.

To further study the growth process of CdS nanorods, aliquots were taken from the reaction flask at different times and resultant TEM images are shown in Figure 3(a)-(d). After the early stage of the reaction (5 s) with an injection temperature of 370 °C and growth temperature of 360 °C, small nanoparticles with diameter of about 5.6 nm were obtained (Fig. 3(a)). With the reaction prolonged to 30 s, the irregular spherical products are observed in Figure 3(b). When the reaction time was extended to 1 min, the products became short nanorods (Fig. 3(c)). With a reaction time up to 5 min, the aspect ratio of CdS nanorods increased gradually, and the bullet-like CdS nanorods with an average width of 10 nm and length of 15-22 nm were obtained (Fig. 3(d)). With the consumption of the monomer during growth, the aspect ratio gradually increased. Thus, size-controlled CdS nanorods could be obtained by tuning reaction time.

Figure 3 shows the corresponding absorption spectra of CdS NCs samples taken at different time intervals in the above typical synthesis. With the size growth of CdS NCs, the absorption spectra almost show no red shift, which means the growth process of CdS nanorods does not impact the absorbance spectra. This is as expected though, because the Bohr diameter of CdS (~6 nm) is close or even smaller than the average diameter and length of the nanorods, and therefore the optical properties are primarily determined by radial quantum confinement.

It is well-known that the solvothermal temperature plays a crucial role in the formation of CdS NCs with various crystal structures, shapes, and sizes. TEM images of the nanocrystals prepared under different reaction temperatures are shown in Figure 5. It was found that with the decrease of the growth temperature (such as under the same injection temperature of 370 °C but different growth temperatures of 330 °C (Fig. 5(a)), 300 °C (Fig. 5(b))), the shape of as-prepared CdS NCs changed from short rod-like to irregular dot-like accompanying inhomogeneous trigonal ones. This is because the anisotropic growth of NCs needs stronger driving force, which could not be sufficiently provided by the low reaction
temperatures, so the residual monomers could only form irregular dot-like nanoparticles rather than regular prolonged nanorods. When the injection temperature was decreased (such as injected at 350 °C (Fig. 5(c)) and 330 °C (Fig. 5(d))), the rod-shaped CdS NCs almost disappeared and dot-shaped CdS NCs emerged. The results indicate that higher injection/growth temperatures (370/360 °C) are necessary for the formation of uniform bullet-like CdS NCs.

Conclusions

In summary, we have successfully synthesized monodisperse wurtzite structured CdS NCs with different rod-like shapes via a colloidal method. Depending on the adjustment of injection/growth temperatures and molar ratio variation between Cd and S precursors, the morphology of the CdS NCs can be controlled in the form of bullet-like, rod-like, and dot-like. It was found that uniform rod-like CdS NCs could only be successfully synthesized with high injection/growth temperatures, and the aspect ratios of bullet-like and rod-like CdS NCs could also be tuned by simply adjusting the Cd-to-S molar ratios.

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References