Simple Solution-Phase Synthesis of Soluble CdS and CdSe Nanorods

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Semiconductor one-dimensional structures, i.e., nanorods and nanowires, are known to have many interesting physical properties and great potential applications in optoelectronic devices, for example, nanowire light-emitting devices with extremely low power consumption.[1] Of recent, various methods have been used for the preparation of nanorods or nanowires, such as solution−liquid−solid growth, laser ablation, carbon nanotube-confined reaction, electrochemical fabrication, and nonaqueous solution synthesis.[2−7] However, to our knowledge, no effective method has been reported so far for the synthesis of colloidal semiconductor nanorods with a narrow distribution of aspect ratio (length/diameter).

Simple chemical reactions such as electrochemical reduction and arrested precipitation from aqueous ions in a micellar or reversed micellar solution have shown to be useful in the syntheses of colloidal semiconductor or metal nanocrystals with a spherical shape.[8] In these reactions, the size control of the resulting nanoparticles was usually achieved by adjusting the ratio of [H_2O]/[micelles]. From a microscopic point of view, such adjustments may induce change in the size of spherical micelles, and subsequently affect the size of the resulting micelle-encapsulated nanocrystals. The equilibrium shapes of micelles are usually spherical in general, but the shape transitions may occur from spherical to rodlike or to disclike in some micellar solutions with the addition of solubilizate molecules, ions or surfactant additives.[9−13] Recent studies have shown that metal nanorods can be synthesized via electrochemical reduction in micellar solutions.[14] The formation of the metal nanorods could be mainly attributed to the control of the micelles in a rodlike shape by adding different amounts of hydrocarbon molecules into the solution. In this paper, we reported a simple method for the preparation of crystalline and water-soluble CdS and CdSe nanorods via arrested precipitation from their respective inorganic ions in a micellar solution. Various aspect ratios of the nanorods were obtained as different concentrations of cyclohexane were added into the micellar solution.

All reactions were performed under ambient conditions. A typical synthetic condition was described as follows: a micellar solution was prepared by dissolving 2.91 g CTAB (>99%, Merck) into 100 mL of deionizied water (0.08 M). Cadmium chloride (0.035 g, 99.995%, Prochem Inc.) and sodium sulfide (0.034 g, >95%, Sterm) were dissolved in the micellar solutions of 8 and 18 mL to make solutions **A** and **B**, respectively. [Na_2Se (0.054 g, 99.8%, Alfa) instead of Na_2S was used for the synthesis of CdSe samples.] The solution **A** (1 mL) and the solution **B** (1 mL) were then each added to cyclohexane (0−100 μL, see below) and sonicated for 10 min to obtain solutions **A′** and **B′**, respectively. The solution **B′** was injected slowly (20 μL per injection) into the solution **A′**, which was sonicated continuously at 30−40 °C. During the injection, the solution **A′** exhibited a significant color change from cloudy white to yellow or orange (for CdSe samples, an orange or dark red color appeared instead). After the injection was completed, the resulting solution **C** was sonicated for 10 more minutes, and centrifuged at 6500−12000 rpm two to four times. The nanorod solution was obtained from the lower part of the solution **C**. The solution exhibited optically clear colors ranging from yellow to orange (for CdS samples) or orange to dark red (for CdSe samples).

The resulting CdS and CdSe nanorods were structurally characterized using transmission electron microscopy (TEM; Zeiss 10C at 80 kV or Hitachi Fe-200 at 200 kV). The nanorods were deposited from the solution onto an amorphous carbon film or a porous carbon film on a Cu grid. Typical TEM images of CdSe and CdS nanorods (Figure 1) revealed that these materials have a relatively straight rodlike shape. The rodlike shape was

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(15) Different synthetic conditions have been tested in the synthesis of CdS and CdSe samples. In general, the overall morphologies of the resulting nanosized crystals can be affected by the amount of cyclohexane (0−100 μL) added in the synthetic steps described above. The mean aspect ratios of resulting nanorods increased with the increasing amount of cyclohexane. The ratios in most samples were in the range of ~3−10. However, spherical and irregular-shaped nanoparticles were found in the TEM images, and the mean aspect ratios of some samples did not systematically change with the amount of cyclohexane. At this stage, we are making efforts on finding factors other than cyclohexane concentration to achieve a fine control on the aspect ratios of resulting nanorods in the experiment.

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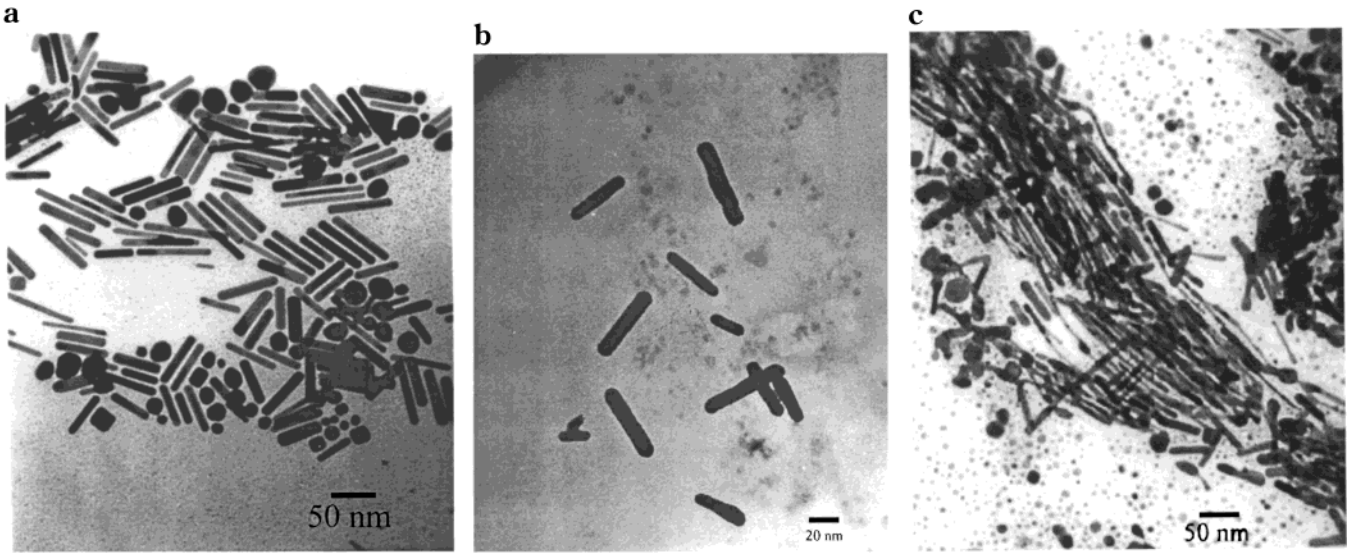

Figure 1. The TEM images taken in bright field of CdSe and CdS nanrods on an amorphous carbon substrate. The average diameters and mean aspect ratios of these samples were obtained from averaging more than 100 individual nanorods shown in TEM images (notice that here we define "nanorods" as those with the mean aspect ratio larger than 2). (a) The CdSe sample was prepared with the addition of 50 μL cyclohexane into the solutions **A** and **B** according to the synthetic steps described above. (b) The CdS sample was prepared with the addition of 50 μL of cyclohexane. Both samples in parts a and b have the mean aspect ratios of ~6. (c) The CdS sample was prepared with the additions of 100 μL of cyclohexane. The CdS nanorods in part c have larger mean aspect ratios than those in part b.

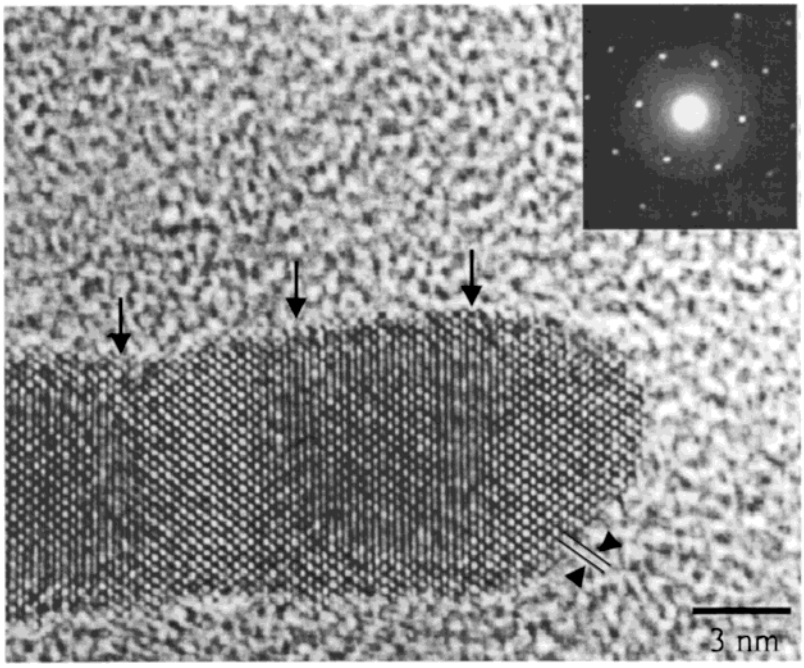

Figure 2. (a) The high-resolution TEM image of a single CdS nanorod showing lattice planes. The largest space of ~0.32 nm between arrowheads corresponds to the distance between two (101) planes. The changes in contrast indicated by the arrows bar could be caused by the variation in diameters of the nanorod. (b) The selected area of electron diffraction pattern (inset) of a wurtzite CdS nanorod from [1,$\bar{1}$,1] direction.

clearly distinguishable from the spherical or irregular shape as also found in the images. The images of parts a and b in Figure 1 indicated that different mean aspect ratios of CdS nanorods have been obtained. The nanorods in parts b and c of Figure 1 were prepared with different amounts of cyclohexane in the micellar solution.[15] These results suggest that cyclohexane plays an important role in the formation of nanorods.

A high-resolution TEM image (HRTEM) recorded on individual nanorods provided further insight into their structures. The HRTEM images of both CdS and CdSe nanorod samples exhibited good crystalline and clear lattice fringes. A bright-field image of CdS nanorods showed a linear segment with an average diameter of ~9 nm (Figure 2a). This image showed clear lattice planes as indicated in the figure. The spaces of lattice planes are close to those obtained from bulk CdS crystals.[16] Faceted structures on the tip of this crystal indicated that the crystal growth was terminated at

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certain stable planes. A selected-area electron diffraction pattern recorded from the direction normal to nanorod long axis confirmed single crystalline of these materials, and the diffraction pattern indexed to the reflection of a wurtzite structure (Figure 2b). The hexagonal lattice has cell constants $a = 4.13$ Å and $c = 6.71$ Å that are close to the reported data.[16] In addition to the structural characterization, the selected-area energy-dispersive X-ray analyses confirmed that the image in the Figure 2a contained both cadmium and sulfur atoms (Cd:S $\approx$ 1:1). However, electron diffraction patterns of CdSe nanorods in our experiment showed that the nanorods exhibited a zinc-blende structure. It has been reported that zinc-blende phases of CdSe nanorods and wurtzite phases of CdS nanorods can be obtained in ethylenediamine nonaqueous solvent systems with cadmium powder and sulfur under pressure in an autoclave.[7]

The effects on the micellar morphologies with the addition of some aliphatic hydrocarbons in CTAB solutions have been investigated previously in a number of studies employing various techniques.[17] Their results indicated that the shape transition of CTAB micelles may occur from rod to sphere (or vice versa) depending on the aliphatic hydrocarbons added. On the basis of previous studies, the formation of the cylindrical nanorods in our experiment may result from the formation of rodlike micelles due to the presence of cyclohexane. However, bilayer vesicles may form under vigorous sonication,[18,19] which was employed in our experiments. Therefore, it is also possible that the formation of inorganic nanorods in a microemulsion may be attributed to the formation of rodlike bilayer vesicles. In this case, cyclohexane molecules may incorporate into bilayers and subsequently induce the morphologic changes of bilayer vesicles.

We are currently testing a large range of parameters that can be easily manipulated in our reactions, including different hydrocarbon molecules, reactant concentration, and temperatures, etc., to narrow the distribution of the aspect ratios of CdS and CdSe nanorods. In addition, we are making efforts to obtain monodispersed nanorods using HPLC and to measure aspect ratio dependency of optical properties of the nanorods.

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