Controlled Synthesis of CdS Nanorods by a Novel Route

Yuan-tao Chen, Yun Guo, and Hu-lin Li*
College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P. R. China.

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CdS nanorods were successfully synthesized through CS_2 reacting with $CdCl_2$ and ethylenediamine in tetradecylamine aqueous solution. The as-obtained samples were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The size of CdS nanorods was controlled simply by varying the growth temperature.

In recent years semiconductor nanocrystals are of great interest for both fundamental research and technical applications, due to their strong size dependent properties and excellent chemical processibility.[1–3] As one of the most important II–VI group semiconductors, CdS nanocrystals have critical applications, such as solar cells, nonlinear optical materials, quantum size effect semiconductors, optoelectronic and electronic devices, biological labeling,[4] these applications can be exploited only with relatively monodisperse samples. In fact, control of nanocrystal size distribution is quite difficult, this is because very little is quantitatively known about crystallization in general, regardless of size and shape.

Of late, various methods have been developed for the synthesis the one-dimensional (1D) CdS nanorods, such as template-assisted,[5,6] colloidal micellar,[7] solvothermal synthesis,[8] and molecular assemblies.[9] So far, Alivisatos and his co-workers synthesized high-quality CdTe, CdSe and CdS nanocrystals, controlling their nucleation and growth by two surfactants.[10–12] Furthermore, Cheon reported the controlled synthesis of CdS nanorod by thermal decomposition of a single-source molecular precursor in one surfactant system.[13] Prompted by these studies, we developed a novel chemical route based on one surfactant system but not thermal decomposition of molecular precursor to prepare CdS nanorods through CS_2 reacting with $CdCl_2$ and ethylenediamine in tetradecylamine aqueous solution. The size of CdS nanorods was controlled by reaction temperature. The new scheme is reproducible and thus has potential for industrial production. Here, carbon disulfide was used as the sulfur source and ethylenediamine as not only nucleophilic attacking regent to release S^{2-} but also shape-controlled ligands to form the complex of $[Cd(en)_2]^{2+}$. Carbon disulfide reacts with ethylenediamine as described by the following reaction:[14,15]

$$H_2NCH_2CH_2NH_2 + CS_2 \rightarrow H_2NCH_2CH_2NHCSSH$$

The product will undergo polymerization accompanied by release of gaseous H_2S.

In a typical process, a 60 cm^3 aqueous solution containing ethylenediamine (0.180 g) and cadmium chloride (0.183 g) and tetradecylamine (0.50 g) was heated to 70 °C. Carbon disulfide (0.234 g) was rapidly injected into the hot solution and maintained at this temperature for 1 h. All the reagents were commercially available and analytical grades and used without further purification. The white turbid mixture rapidly changed to bright yellow. All the steps were performed under magnetic stirring. Finally, the bright yellow mixture was treated with warm ethanol; the precipitate was filtered off, washed with distilled water and warm absolute alcohol, and then dried in air for 2 h before characterization. In contrast, we changed the reaction temperature to 100 or 120 °C, while all other conditions kept constant.

The samples were characterized by X-ray diffraction with a Rigaku D/MAX-2400 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å). Figure 1 shows the XRD pattern for CdS sample prepared at 70 °C. All the diffraction peaks have a one-to-one correspondence to those of the bulk hexagonal CdS. (JCPDS card no. 41-1049). As the reaction temperature is increased the crystallinity of the sample was obviously improved. It was noted that the stronger (002) peak in the XRD pattern than expected, which indicated a preferential orientation of [001] in the CdS crystal. We inferred that the CdS crystal growth was oriented and morphologies were 1D rod-like. This inference was confirmed by transmission electron microscopy image (Figure 2A). The CdS crystallites display rod-like morphology with diameters of 10 ± 2 nm and lengths of 100 ± 9 nm. The selected area electron diffraction (SAED) results taken from one of CdS nanorods, indicating that the CdS is polycrystalline, match well with the XRD results. A TEM image was taken with a Hitachi H-800 transmission electron microscope using an accelerating voltage of 100 KV.

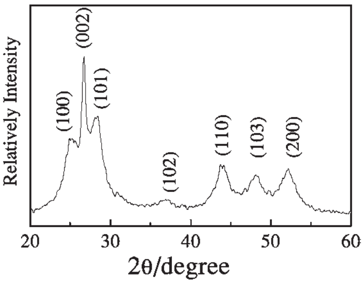
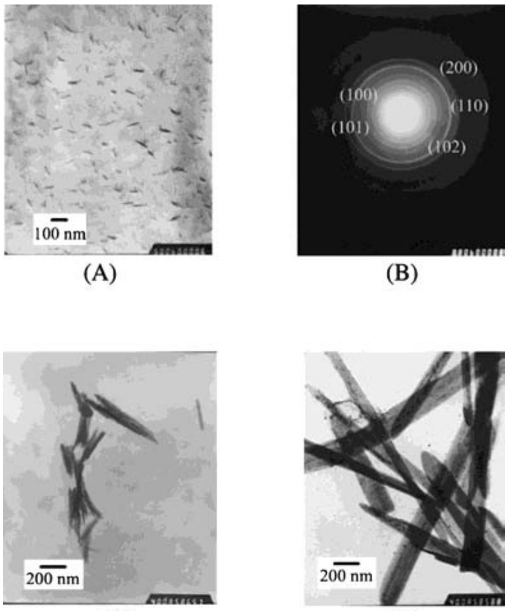


Figure 1. XRD pattern for CdS sample prepared at 70 °C.

As the reaction temperature is raised to 100 or 120 °C, an increase in both the width and length is observed (30 ± 10, 150 ± 40 nm in width and 180 ± 50, more than 600 nm in length). The size distribution of the sample formed at 70 °C is nearly mono-disperse, but it turns to broad as the reaction temperature is raised. We also found there was little change in the width and length if the reaction time was within 5 h.

To illustrate the interesting results just reported, we speculate the growth kinetics of CdS rod grown by this new approach as follows. Ethylenediamine and cadmium ion can form the relatively stable tetradentate ligand complex of $[Cd(en)_2]^{2+}$, which had been confirmed by IR spectroscopy and XRD.[16] Thus there is only one direction for S^{2-} to coordinate facilely to the above complex. That is to say, CdS growth is faster along this



(A) (B) (C) (D)

Figure 2. TEM images and electron diffraction pattern for the CdS samples. (A) Sample prepared at 70 °C; (B) SAED pattern for one of nanorod in A; (C) Sample prepared at 100 °C; (D) Sample prepared at 120 °C.

direction, which may be [001] direction in the hexagonal phase. The anisotropic growth character determines the resulting crystal shape. Under a certain condition, if the overall growth rate is very slow, a nearly spherical shape that minimizes surface area is favored; if the growth rate is increased significantly, the result is rod-like shape. The formation of CdS nanorods is a case of the latter. The tetradecylamine seems to increase the growth rate as hexadecylamine.[13] To further understand the function of tetradecylamine, a similar process was used to prepare CdS without tetradecylamine, CdS crystallites were found to display spherical shape. In tetradecylamine system, the elevated temperature caused rapid release of gaseous H_2S and made more unstable the tetradentate ligand complex of $[Cd(en)_2]^{2+}$, hence it is faster for S^{2-} to coordinate the complex from [001] direction and more facile for S^{2-} to coordinate the complex from other direction, thus higher temperature leads to a significant increase in the width and length. Of course, the exact reaction mechanism will be the subject of our future intensive study.

In summary, a novel route for the control of the size of CdS nanorods has been developed. CdS nanorods were controlled simply by varying the growth temperature. It is reasonable to assume that a similar process could also achieve other chalcogenide nanorods except that only other MCl_n compounds have substituted the reactant $CdCl_2$.

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