

Formation of CdSe Nanorod-assembled Microtubes in an Ethanolamine-PEG Solution

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A large number of CdSe nanorod-assembled microtubes are prepared via a hydrothermal method in an ethanolamine-PEG solution. The tubes with inner diameters of 900 nm and lengths of 5–50 μm are composed of well-aligned nanorods around 300-nm long. It was found that both the solvent ethanolamine and surfactant PEG-20000 play a key role in the formation of nanorod-assembled microtubes. Ethanolamine as a mild reducing agent was used to reduce SeO_2 to produce Se^{2-} . The optimal conditions to produce CdSe microtubes are that the volume ratio of ethanolamine to water is 1:4 and that the quantity of PEG is 3.0 g. The possible formation mechanism of CdSe microtubes is also discussed.

In recent years, tubular structure materials have been found to be important in potential applications in the syntheses of designed catalysts, photonic band gap materials, and chemical separations media and as selective sorbents.^{1–3} CdSe has been extensively investigated because of its novel optical and electrical properties, which are of special interest for its broad application of photovoltaic devices, electroluminescence (EL), and bio-attachment.⁴ CdSe nanotubes have been reported. Rao et al.⁵ prepared CdSe nanotubes constructed of nanoparticles using NaBH_4 as reductant and Triton 100-X as surfactant. Xia et al.⁶ prepared CdSe nanotubes consisted of nanoparticles by reacting cadmium salts with Se nanowires.

Herein, we report on the preparation of CdSe nanorod-assembled microtubes in an ethanolamine-PEG solution using ethanolamine as a mild reductant and a complexing agent and PEG-20000 as surfactant under hydrothermal conditions. Ethanolamine as a mild reducing agent was used to produce Se^{2-} .

In a typical procedure, 0.50 g of selenium dioxide and 1.50 g of $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ were put into a beaker together. Then, a suitable volume of deionized water was added into the beaker so as to make powders completely dissolved by continuously stirring. Subsequently, about 10 mL of ethanolamine and a mass of 3.0 g of polyethylene glycol (PEG-20000) dissolved in a volume of water were added into the above solution. At last the final solution was transferred into a 60-mL Teflon-lined stainless steel autoclave, which was filled with distilled water up to 80% of total volume. The autoclave was sealed and maintained at 180 °C for 16 h and then allowed to cool to room temperature. The final product was filtered off and washed with absolute ethanol and distilled water several times, respectively, and dried in vacuum at 50 °C for 4 h.

The XRD pattern in Figure 1 shows that all the diffraction peaks can be readily indexed to wurtzite CdSe with calculated lattice parameters $a = 4.272$, $c = 6.992$ Å, which is in consistency with the literature values (JCPDS card No. 8-459). A gen-

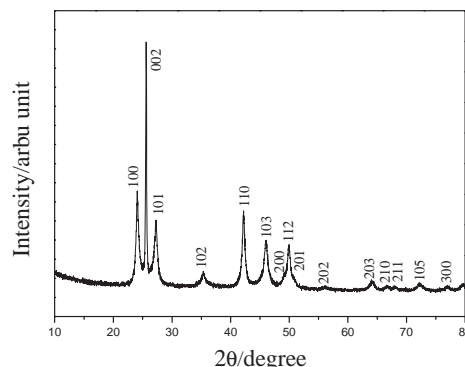


Figure 1. XRD pattern of the as-prepared CdSe nanorod-assembled microtubes.

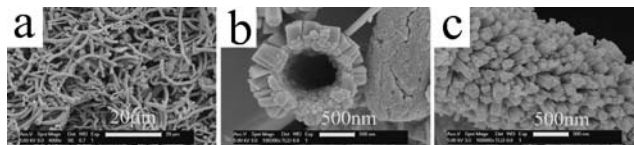


Figure 2. FESEM images of the nanorod-assembled microtubes: (a) Low-magnification image, (b) Side-view of one nanorod-assembled microtube, (c) Cross section of one nanorod-assembled microtube.

eral overview FESEM image in Figure 2a shows that the product is composed of wormlike microtubes with typical lengths from 5 to 50 μm . Figure 2b is the side view of one nanorod-assembled microtube. It can be clearly seen that the microtube is composed of densely well-aligned nanorods with an average diameter of about 100 nm and length of about 300 nm. Figure 2c shows a high magnification of the cross section of one CdSe tube with the inner diameter of about 900 nm while the wall thickness is about 300 nm. It is worth to note that the wall is composed of two layers, the thin inner layer consists of CdSe nanoparticles, while the outer layer growing out from the nanoparticles layer is made up of nanorods as revealed in Figure 2b.

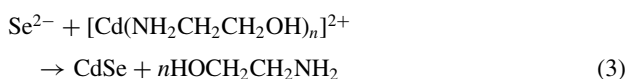
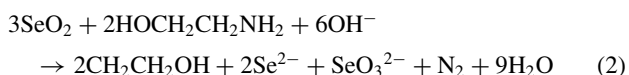
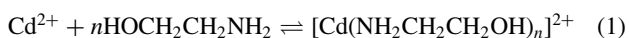
The XPS spectra were measured to identify the surface compositions of the CdSe microtubes. XPS measurements indicated that Se_{3d} and $\text{Cd}_{3d5/2}$ binding energies of the obtained sample are 54.00 and 405.05 eV, respectively, which are close to the reported values⁷ (Figure S1).¹²

Experiments revealed that the addition of ethanolamine and PEG played a crucial role in the formation of the CdSe microtubes. A series of experiments were performed in the present study (in Tables 1 and 2)¹² using a procedure similar to that mentioned in the experimental section. It was found that the volume ratio of ethanolamine to water in the reaction solution imposed a

great influence on the formation of CdSe microtubes. When the volume ratio of ethanolamine to water is 1:4, microtubes can be obtained. However, the amount of the tubes will gradually decrease with the increase of the volume ratio (Figure S2).¹² The amount of the microtubes in the product can also be controlled by the quantity of the added PEG. With the addition of the PEG, the amount of the microtubes increased correspondingly, while only nanowire-assembled microspheres can be obtained in the product without PEG (Figure S3).¹² When the amount of PEG is up to 3.0 g, almost all of the products are microtubes, and the yield of the microtubes is over 90%. So the optimal conditions to produce CdSe microtubes are that the volume ratio of ethanolamine to water is 1:4 and that the concentration of PEG is 3.0×10^{-3} mol/L.

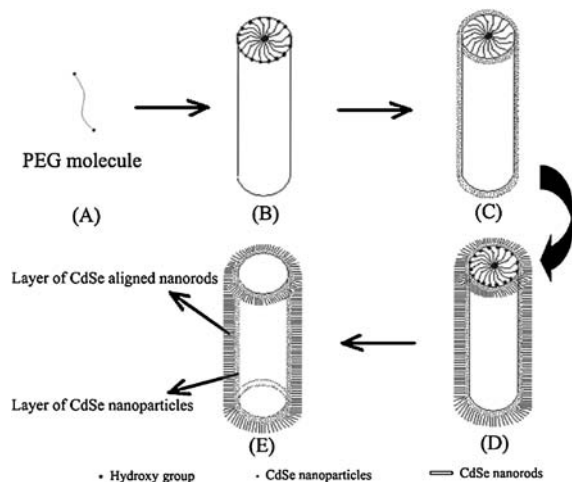
The reaction temperature has little effect on the morphology of the microtubes; however, the reaction time can have an important influence on the morphology of the final products. Only CdSe nanoparticles were obtained after reaction for 3 h (Figure S4).¹² When the reaction time is 6 h (Figure S5),¹² microtubes composed of nanoparticles began to come into being.

From the above experimental results, the reaction that occurred under the present hydrothermal conditions can be illustrated as follows:



As we all know, the strong basicity of ethanolamine would induce the Cd^{2+} to become $\text{Cd}(\text{OH})_2$, then ethanolamine as a good complexing agent would react with $\text{Cd}(\text{OH})_2$ to form $[\text{Cd}(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_n]^{2+}$ complex,^{8,9} which is in accordance with our observation that the solution first became cloudy and then immediately got clear with the addition of the ethanolamine. On the other hand, SeO_2 could be reduced by ethanolamine according to eq 2.

Under the hydrothermal conditions, the PEG molecules could spontaneously organize into rod-like micelles with the hydrophilic group exposed to the aqueous solution especially when their concentration is much higher than the critical micelle concentration.^{10,11} For the amphiphilic action between the hydroxy group of ethanolamine and PEG, $[\text{Cd}(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_n]^{2+}$ complexes would be adsorbed onto the surface of the rod-like micelles and react in situ with Se^{2-} anions reduced by ethanolamine to form CdSe nuclei. These newly produced CdSe nuclei would assemble into nanoparticle layers at the initial stage owing to the high concentration of reactants. The produced CdSe nuclei could grow directed by ethanolamine and further enlarged into nanorods perpendicular to the preformed layers. This is similar to what mentioned by Yang et al.,⁸ in which they reported that one amidogen in a ligand is necessary and sufficient for the formation of 1D nanocrystals. Therefore, well-aligned CdSe nanorod layer would be formed outward from the surface of the nanoparticles layer. Thus, nanorod-assembled CdSe microtubes would be obtained after the micelles were removed by absolute ethanol and distilled water. Noted that most of microtubes are bended, we believed that it



Scheme 1. Illustration of the formation of CdSe nanorod-assembled microtubes: (A) A single PEG molecule, (B) The formation of PEG rod-like micelles, (C) CdSe nanoparticles formed on the surface of the rod-like micelles, (D) Compacted CdSe nanorod arrays formed on the surface of the rod-like micelles, (E) Nanorod-assembled CdSe microtubes.

is attributed to the soft template of the rod-shaped micelles. The growth procedure of the microtubes is depicted in Scheme 1.

In summary, we have demonstrated a large-scale synthesis of flexible wormlike CdSe nanorod-assembled microtubes in an ethanolamine–PEG solution. In this approach, the surfactant PEG as a good soft template plays a key role in the formation of the nanorod-assembled microtubes, while the solvent ethanolamine as a mild reducing agent and a good complexing agent is essential for the formation of the products. These special structures can be expected to have wide potential applications in the future, and this simple method may be applied to synthesize other more interesting self-assembled crystals. Further work is in progress.

This work was supported by National Science Foundation of China and the 973 Project of China (No. 2005CB623601).

References and Notes

- G. A. Ozin, *Adv. Mater.* **1992**, *4*, 612.
- S. J. Mann, *Chem. Mater.* **1997**, *9*, 2300.
- O. M. Yaghi, H. Li, C. Davis, D. Richardson, T. Groy, *Acc. Chem. Res.* **1998**, *31*, 474.
- F. Koberling, A. Mews, T. Basche, *Adv. Mater.* **2001**, *13*, 672.
- C. N. R. Rao, A. G. Govindaraj, F. L. Deepak, N. A. Gunari, M. Nath, *Appl. Phys. Lett.* **2001**, *78*, 1853.
- X. C. Jiang, B. Mayers, T. Herrick, Y. N. Xia, *Adv. Mater.* **2003**, *15*, 1740.
- XI-SpecMaster system (Database)*, XPS International, **1998**.
- J. Yang, C. Xue, S. H. Yu, J. H. Zeng, Y. T. Qian, *Angew. Chem., Int. Ed.* **2002**, *41*, 4697.
- M. N. Wu, Y. C. Zhu, H. G. Zheng, Y. T. Qian, *Inorg. Chem. Commun.* **2002**, *5*, 971.
- Y. N. Xia, P. D. Yang, Y. G. Sun, Y. Y. Wu, B. Mayers, B. Gates, Y. D. Yin, F. Kim, H. Q. Yan, *Adv. Mater.* **2003**, *15*, 353.
- H. Ringsdorf, B. Schlarb, J. Venzmer, *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 113.
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