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Controlled synthesis of CdS nanowires using diamines

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Abstract. We demonstrate a new, simple, inexpensive process and systemic control over CdS nanowires using sulfur powders and organic diamines without any catalysts, surfactants, and templates under atmospheric benchtop conditions. By changing the kinds of amines and reaction temperatures can result in control of the shape and size of the nanocrystals, which are moderately monodispered with unique forms.

PACS. 61.46.+w Nanoscale materials: clusters, nanoparticles, nanotubes, and nanocrystals

1 Introduction

Recently interest in low-dimensional semiconductor materials has been motivated by the push for miniaturization of electronic and optoelectronic devices and a need to understand the fundamentals of nanoscale chemistry [1–5]. As in such regards, the synthesis of CdS nanowires has been rapidly developed. Control of the size and shape, especially the diameter, is a key factor in the success of nanowire synthesis. To date, various methods have been reported for achieving this purpose [6–14]. Lieber [11] has developed vapor-liquid-solid (VLS) techniques to synthesize CdS nanowires. Qian's group [12] has established some new chemical techniques to synthesize CdS nanowires *via* solvothermal route and polymer-controlled growth. Chen *et al.* [13] has prepared CdS nanowires in a micellar. Cheon *et al.* [14] controlled synthesis of CdS nanowires using monosurfactant system. However, introducing template, catalysts or surfactants to the reaction system means a much more complicated process involving the preparation of catalysts or the selection of templates and surfactants, and may bring about an increase of impurity concentration in the final product. As the most developed system in terms of synthesis [15], high-quality CdSe nanocrystals with nearly monodisperse size and shape are in active industrial development for biological labeling reagents [16]. Our laboratory has made significant progress toward the development of a general synthetic approach to single crystal semiconductor nanowires of CdS.

In this communication, we demonstrate a new, simple, inexpensive process and systemic control over CdS nanowires using sulfur powders and organic diamines without any catalysts, surfactants, and templates under atmospheric benchtop conditions. By changing the kinds of amines and reaction temperatures can result in control of the shape and size of the nanocrystals, which are moderately monodispered with unique forms.

2 Experiments

In a typical procedure, an appropriate amount of $Cd(OAc)_2{\cdot}2H_2O$ and sulfur powders (molar ratio, 1:8) was added into a flask that has been filled with appropriate volume of amine. The reactions were performed at appropriate temperature for 2−3 h, the solution slowly changes to orange-yellow, which were separated by centrifugation. Samples a, b, and c were obtained at room temperature, 60 °C, and 120 °C, respectively. The resulting nanocrystals were obtained as yellow powders, which were washed several times with distilled water and absolute ethanol to remove the excessive amine and other by products. They are dried in a vacuum at 100 °C for 2 h.

The samples obtained were characterized with X-ray powder diffraction (XRD). The XRD patterns were recorded with a Japan Rigaku D/max-2500 rotation anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54178 Å), employing a scanning rate of 0.05° s^{-1} in the 2θ range from 10° to 70°. Transmission electron microscopy (TEM) images and electron diffraction patterns were taken with a Hitachi H-800 TEM operating at 200 keV. The samples for these measurements were dispersed in absolute ethanol by being vibrated in the ultrasonic pool. Then the solutions were dropped onto Cu grids coated with amorphous carbon films. UV-vis spectra were obtained on Hitachi Model U-3010 Spectrophotometer. The Photoluminescence (PL) spectra were taken from a Hitachi F-4500 spectrometer.

3 Results and discussion

In our synthetic system, the resulted CdS nanowires formation indicated that the nucleation and growth were well-controlled. The diamine plays a key role in the controlling nucleation and growth of nanowire. The first step

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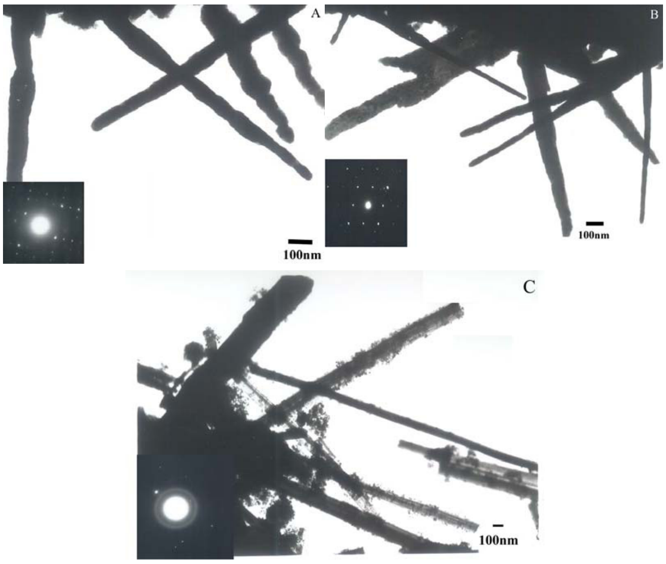

Fig. 1. TEM images of CdS nanowires synthesized in (a) enthylenediamine, (b) 1,4-butanediamine, and (c) 1,6-hexanediamine. Inset corresponding electron diffraction pattern.

of our approach involved the formation of H_2S in solution through the reaction of sulfur powders with excess diamine. Then, the reaction between Cd^{2+} and S^{2-} produce the small amount of CdS nanocrystallinites. Our TEM studies suggested that it was these nanocrystallinites of CdS that served as the seeds for the growth of nanowires in the next step. The samples for all of the measurements shown in this paper are not filtered. Samples a, b, and c were obtained from ethylenediamine at room temperature, 60 °C, and 120 °C, respectively.

$$S_8 + NH_2RNH_2 \longrightarrow H_2S + S_7NHRNHS_7 \qquad (1)$$

$$R = CH_2CH_2, (CH_2)_4, (CH_2)_6$$

$$Cd^{2+} + H_2S \longrightarrow CdS + 2H^+. \qquad (2)$$

The H_2S can be liberated from a mixture solution of sulfur powder and diamines, the product $S_7NHRNHS_7$ molecular has two active NH groups to chelate with Cd^{2+} cation and has a relatively weak intermolecular coordinating interaction, which allows the products to grow in a less confined environment. In the processes of the CdS formation, this bidentate ligand complex could serve as a molecular template in control of the CdS crystal growth.

We have characterized the CdS nanowires using a number of techniques. TEM shows that the wires are single crystals. The CdS obtained from ethylenediamine precursor at 120 °C are wire structures; we observe the width of is in a range of 50−260 nm and 0.37−2.4 μm in the length (Fig. 1a). The energy-dispersive analysis confirms that the elemental composition of CdS is almost 50:50 atomic ratios. Figures 1b and 1c show that the width and length of CdS nanowires obtained from 1,4-butanediamine are in the range of 70−170 nm and 0.44−1.25 μm, respectively, and from 1,6-hexanediamine are in the range of 100−300 nm and 2.2−2.7 μm, respectively. The mean alkyl chain of diamine is increased, the length and width of wire is decreased, and however, the aspect ratio is increased. The yield of CdS nanowires from these diamines is about 30%.

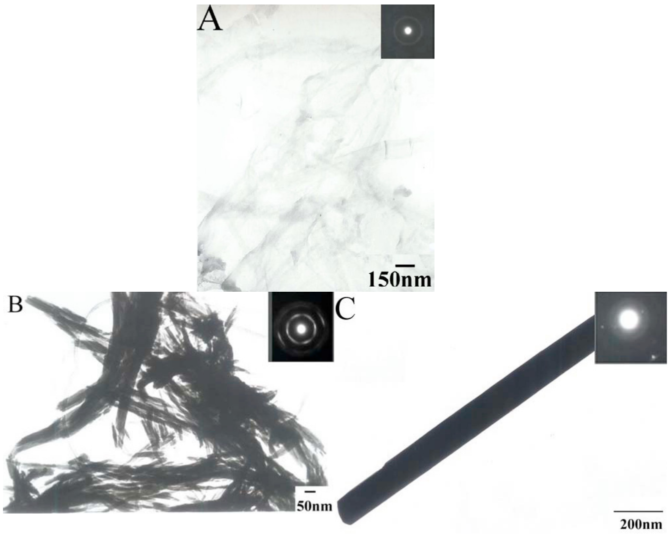

Fig. 2. TEM images of CdS nanowires formation: samples (a) a, (b) b, and (c) c. Inset corresponding electron diffraction pattern.

The contrast varying the growth temperature at a fixed ethylenediamine concentration leads to non-crystalline CdS nanowires. The XRD patterns at the whole process showed that the crystallinites of the samples were continuously improved with the reaction temperature being increased. The XRD pattern of sample a, Figure 2a, showed that the majority of the products were poorly crystallized. With the increased reaction temperature, the crystalline of sample b was obviously improved (Fig. 2b showed the XRD pattern of sample b). Although the diffraction peaks of (002) could not be well distinguished. It was noted that the diffraction peak of (002) was stronger than expected. This unusual diffraction peak of (002) indicated a preferential orientation along the *c*-axis and a wire like shape [17]. The wirelike shape was confirmed by TEM photographs. TEM photographs showed that there was an accordion-like folding process in the morphology evolution of the samples. The sample a displayed a lamellar shapes, as shown in Figure 3a. The SAED pattern (Fig. 3a inset) consisted of several diffused diffraction rings, which indicates that sample a was poorly crystallized. These results were consistent with that from its XRD pattern. TEM photograph (Fig. 3b) of sample b revealed that the lamellar broke into needlelike fragments, which is very critical in the formation process of CdS nanowires. The sample c's higher crystalline lead to form more wide and longer nanowires. It is clear that the width and length are 357 nm and 4.21 μm, respectively.

The absorption spectrum in Figure 4 displays an obvious absorption peak at 504 nm for CdS nanowires synthesized in ethylenediamine at 120 °C, Corresponding to the characteristic absorption band of bulk CdS.

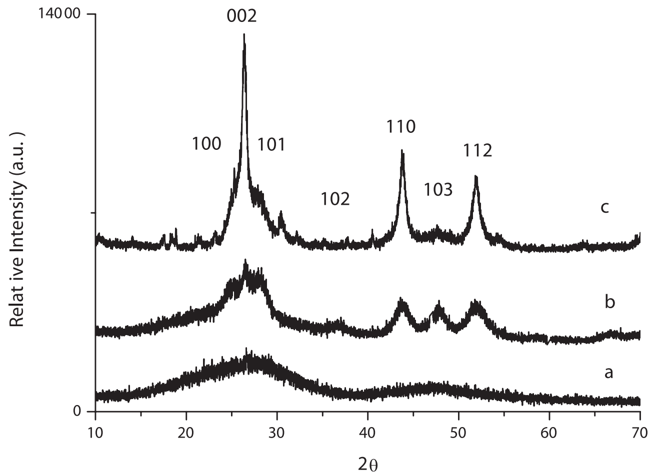

Fig. 3. XRD patterns evolution during CdS nanowires formation: samples (a) a, (b) b, and (c) c.

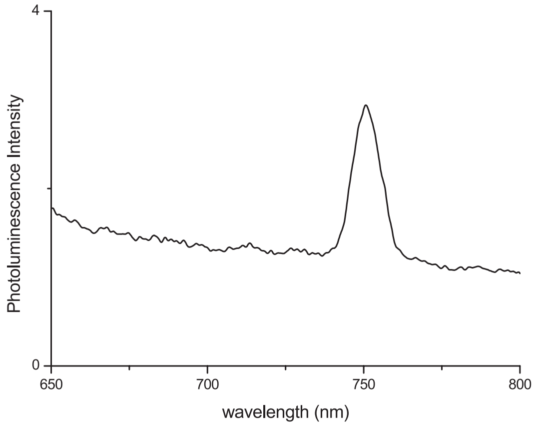

Fig. 4. UV-vis absorption spectra of CdS nanowires synthesized in enthylenediamine at 120 °C.

The room temperature photoluminescence (PL) measurement results of the CdS nanowires obtained from ethylenendiamine at 120 °C are shown in Figure 5. The excited wavelength was 504 nm, a red emission band around 750 nm was observed in the PL spectra patterns of CdS nanowires. Usually, two emissions are observed from semiconductor nanoparticales-excitonic and trapped [18]. The excitonic emission is sharp and located near the absorption edge of the particles, while the trapped emission is broad and stokes-shifted. The luminescence at 750 nm observed from the synthesized CdS used ethylenediamine at 120 °C could be attributed to trapped emission. It is thought that the trap emission is mainly due to excess of sulfur at the interface, which is well-known to quench radiative band gap recombination, and not to the low crystallinity of the particles. In addition, the diameters of our synthesized CdS nanowires are larger than that of exciton Bohr diameter (6 nm). Therefore, the luminescence at 750 nm observed from the CdS nanowires (Fig. 5) is trapped emission. It is therefore reasonable to believe that the red light emission from the CdS nanowires in our work can be attributed to the surface states or core defects of CdS nanowires.

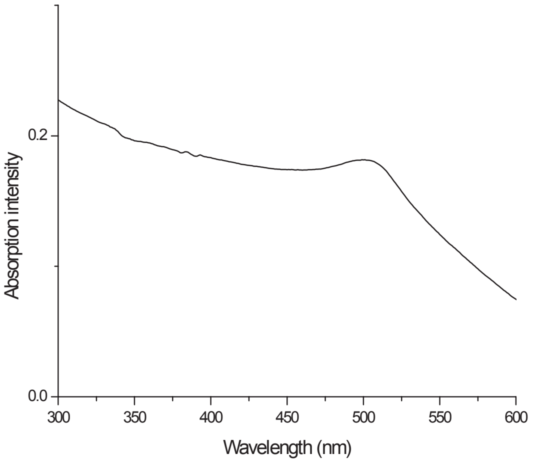

Fig. 5. Photoluminescence spectra at room temperature for the CdS nanowires synthesized in enthylenediamine at 120 °C.

4 Conclusions

In conclusion, we have described a simple chemical process to directly prepare CdS nanowires without any catalysts, surfactants, and template with control on size and shapes of the nanocrystals using sulfur powder and diamine as S^{2-} precursor. Temperature and the kind of diamines provide us with a mechanism by which it is possible to control the various sizes (architectures). The reaction conditions are simple and also can easily be done under atmospheric benchtop condition for large quantity preparations. It is highly possible that this approach can be extended as a general synthetic method for other metal sulfide *e.g.*, PbS, Cu_2S, ZnS, WS_2 etc. We believed that the well-controlled CdS nanowires will be obtained and the yield of nanowires will be increased when the growth conditions by manipulating the composition of the reaction solvent, the stock solution, the reaction temperature, etc. are optimized.

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