A Solid-State Reaction for the Synthesis of CdS Nanowires

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

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CdS nanowires have been successfully prepared by solid-state reaction of $Cd(Ac)_2 \cdot 2.5H_2O$ and $Na_2S \cdot 9H_2O$ in the presence of PEG 400 at room temperature.

Solid-state chemistry is a fast-developing science, enhanced by its numerous applications in the high-technology industries.[1] Over the past few decades, solid-state reactions have been used to prepare considerable materials.[2–4] For instance, Wang and co-workers have synthesized ZnS nanoparticles by a solid-state reaction of zinc acetate and thioacetamide.[2] Though the reaction temperature was low, no reaction occurred at room temperature. Ye and his research group reported an effective approach based on solid-state metathesis reaction of hydrated metal salts to produce nanocrystals of sulfides.[3] Prompted by this study, we developed a simple solid-state reaction of $Cd(Ac)_2 \cdot 2.5H_2O$ and $Na_2S \cdot 9H_2O$ in the presence of polyethylene glycol (PEG) 400 to synthesize CdS nanowires. The advantage of this method presented here is that the reaction was performed at room temperature; the reaction time is also very short. The motivation behind this work comes from the critical application of CdS,[5,6] such as solar cells, non-linear optical, quantum size effect semiconductors, and optoelectronic and electronic devices. To the best of our knowledge, it is first time to prepare CdS nanowires by solid-state reaction.

All the reagents are commercially available and analytical grades and used without further purification. The procedure employed by us for preparing CdS nanowires is as follows. In a typical synthesis, 5.330 g of $Cd(Ac)_2 \cdot 2.5H_2O$ (Ac = acetate) and 5 ml of PEG 400, 4.803 g of $Na_2S \cdot 9H_2O$ and 5 ml of PEG 400, were ground for 5 min each, and then mixed. After 30 min of grinding, the yellow product was washed in an ultrasonic bath several times with distilled water and then absolute ethanol to remove the PEG 400. Finally, the resultant was dried in air at room temperature for 5 h before further characterization.

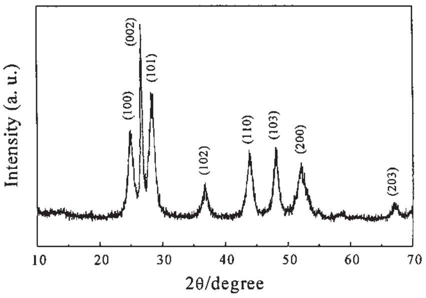

Figure 1. XRD pattern for as-obtained sample.

The crystal structure of the product was analyzed by X-ray diffraction (XRD) on a Japan Rigaku D/MAX-2400 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54178$ Å), at a scanning rate of $0.02\,^\circ s^{-1}$ in the 2θ range of 10° to 70°. Figure 1 shows the XRD pattern for as-prepared sample. The peaks at 2θ values of 25.300, 26.860, 28.540, 37.040, 44.180, 48.680 and 52.400 correspond to the crystal planes of 100, 002, 101, 102, 110, 103 and 200 of the hexagonal CdS respectively. It should be noted that the stronger (002) peak in the XRD pattern than expected, which indicated a preferential orientation of [001] in the CdS crystal. Thus the morphologies of the obtained CdS may be rod-like. The morphology and size were characterized by transmission electron microscopy (TEM) with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 100 KV. The CdS crystallites display rod-like morphology with diameters of ca. 10 nm and lengths of up to 300 nm. The selected area electron diffraction (SAED) results taken from one of CdS nanowires, indicating that the CdS is polycrystalline, match well with the XRD results. The dark field confirmed that the obtained CdS nanocrystals had well-defined crystallinity. IR spectroscopy was carried out to examine the purity of the as-prepared sample; the result indicated the absence of PEG 400, suggesting a high degree of purity. The purity was further analyzed by X-ray photoelectron spectrum (XPS) on an ESCA LAB-220I-XL X-ray photoelectron spectrometer, using a Mg Kα (1253.6 eV) excitation source. It was found that the XPS for the as-prepared sample were typical of CdS reported by other worker,[7] the presence of C and O absorbed from the gaseous molecules; and the two strong peaks at 161.57 and 405.3 eV correspond to S(2p) and Cd(3d) binding energies for CdS, respectively.

In this communication, the formation of CdS nanowires is speculated from the following reasons. First, The presence of coordinated water in $Cd(Ac)_2 \cdot 2.5H_2O$ and $Na_2S \cdot 9H_2O$ may help lower the activation energy and the reaction temperature.[3] It is well-known that most hydrated metal salts have structures with point defects and relatively lower lattice energies. Secondly, Na(Ac) produced in the reaction may form the physical and spacious obstacle and surround the CdS particles to prevent them from aggregating to larger particles, as PEG 400 do. Thirdly, PEG 400 plays critical role in the formation of CdS nanowires. PEG 400 may interact with $Cd(Ac)_2 \cdot 2.5H_2O$ or $Na_2S \cdot 9H_2O$ during first grinding; After absorbing free water and heat generating by the this exothermal reaction, the structure of PEG 400 turned to loose; Finally, PEG 400 could extend to form a chain structure, no twist at all. In fact, in the course of CdS formation, PEG 400 might act as soft template to control the growth of CdS.

We did some experiments to explore the growth mechanism just reported. It was found that the resultant sample showed spherical shape if no PEG 400 was added. This observation indicated that there was an interaction between PEG 400 and $Cd(Ac)_2 \cdot 2.5H_2O$ (or $Na_2S \cdot 9H_2O$). This could also be confirmed by little difference in IR absorbance between the first grinded mixture and two pure compounds. But little is known about the exact interaction between $Cd(Ac)_2 \cdot 2.5H_2O$ (or $Na_2S \cdot 9H_2O$) and PEG 400. When PEG 400 was substituted by PEG 2000, the sample also showed spherical shape. Because the chain of PEG

2000 is much longer than that of PEG 400, it is easier for PEG 2000 to twist together and more difficult to form straight chain structure in the same condition.[8]

In conclusion, CdS nanowires can be synthesized by solid-state reaction. This method can also be used to prepare other chalcogenide nanowires.

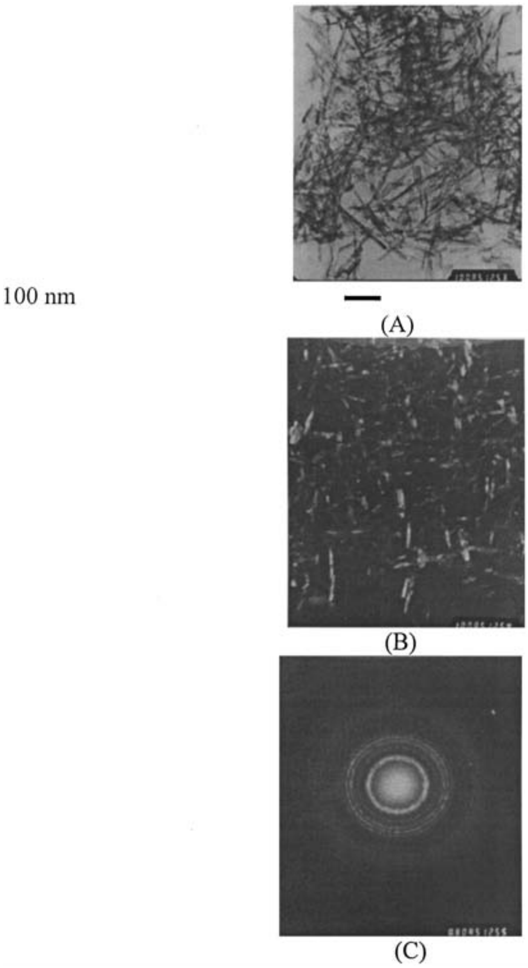

Figure 2. TEM images for as-obtained sample. (A) light field (B) SAED; (C) dark field.

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References

1 L. Smart and E. Moore, in "Solid state Chemistry," 2nd ed., Chapman and Hall, London (1996).
2 L. P. Wang and G. Y. Hong, *Mater. Res. Bull.*, **35**, 695 (2000).
3 X. R. Ye, D. Z. Jia, J. Q. Yu, X. Q. Xin, and Z. L. Xue, *Adv. Mater.*, **11**, 941 (1999).
4 E. G. Gillan and R. B. Kaner, *Chem. Mater.*, **8**, 333 (1996).
5 H. Weller, *Adv. Mater.*, **5**, 88 (1993).
6 A. Henglein, *Chem. Rev.*, **89**, 1861 (1989).
7 Y. D. Li, H. W. Liao, Y. Ding, Y. Fan, Y. Zhang, and Y. T. Qian, *Inorg. Chem.*, **38**, 1382 (1999).
8 J. H. Sun, Y. J. Gong, W. H. Fan, D. Wu, and Y. H. Sun, *Chem. J. Chin. Univ.*, **21**, 95 (2001).