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# Coordination Polymer Route to Wurtzite ZnS and CdS Nanorods

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**Wurtzite MS nanorods were synthesized from coordination polymer [$M$(tp)(4,4′-bipy)]$_\infty$ at 140°C under solvothermal condition ($M$ = Zn, Cd). The morphology determined by TEM gives the average diameters of width/length as 50/200 nm and 20/75 nm for ZnS and CdS, respectively. X-ray powder diffraction and XPS spectra proved that the as-prepared products were pure ZnS and CdS, respectively.** © 2002 Elsevier Science (USA)

***Key Words:*** **semiconductor; nanorods; coordination polymer; zinc sulfide; cadmium sulfide; solvothermal.**

## 1. INTRODUCTION

One-dimensional (1-D) nanostructures are currently being investigated in great detail for their unique electronic and mechanical properties and their potential implementation as devices (1). In contrast to the synthesis of zero-dimensional systems, the preparation of one-dimensional systems is more difficult. The focus of researchers has been on how to control the growth of nanocrystals. The current process of constructing the one-dimensional nanostructures has been mainly through the template route. All kinds of templates, such as liquid crystals, self-assembled monolayers (SAMs), polymers, micelles, carbon nanotubes, porous aluminum oxide, mesoporous silica, usually were used (2). Most recently, Peng *et al.* successfully obtained rod-like II–VI semiconductor CdSe by injection of multiple surfactant to the stock solution (3a). Yang and Li reported the synthesis of 1-D bismuth metal by low-temperature hydrothermal reduction method (3b). These works indicate that 1-D nanostructure materials synthesized without a template show great ability to control the growth of nanocrystals. Thus, it began to attract the attention of chemists as a new route to 1-D nanostructure.

Research on metal-directed supramolecular complexes has rapidly been expanding due to their interesting topologies and potential applications as functional materials (5). On the other hand, no report has focused on the control of the growth of nanocrystals by coordination polymers. However, the phenomenon in which coordination environment of metal ions affect the shape of nanostructures has been observed by many groups. For example, Qian *et al.* found that the chelate ability of ethylenediamine with $Cd^{2+}$ is in favor of the growth of CdS nanorods (6). Trindade *et al.* used bismuth(III) dialkyldithiocarbamates to prepare $Bi_2S_3$ nanofibers (7). Here, we report the synthesis of ZnS and CdS nanorods using coordination polymers with three-dimensional frameworks: [Zn(tp)(4,4′-bipy)]$_\infty$ and [Cd(tp)(4,4′-bipy)]$_\infty$ (tp: terephthalate, 4,4′-bipy: 4,4′-bipyridine), respectively. This method is simple and needs only one step at 140°C for 10 h.

## 2. EXPERIMENTAL SECTION

[Zn(tp)(4,4′-bipy)]$_\infty$ and [Cd(tp)(4,4′-bipy)]$_\infty$ were prepared previously (8). Analytically pure thiourea (0.05 mol) and [Zn(tp)(4,4′-bipy)]$_\infty$ or [Cd(tp)(4,4′-bipy)]$_\infty$ (0.001 mol) were added into a Teflon-lined stainless-steel autoclave that had been filled with ethanol up to 90% of its capacity (25 $cm^3$). The autoclave was maintained at 140°C for 10 h, and then cooled to room temperature naturally. Excess thiourea dissolved in ethanol and could be easily removed. The white ZnS or yellow CdS powders were separated by centrifugation and washed with distilled water and ethanol three times, then dried *in vivo* for consequent characterization.

Powder X-ray diffraction (PXRD) patterns were measured by D/max-$\gamma$ rotating anode X-ray diffractometer equipped with a Ni-filtered Cu$K\alpha$ radiation ($\lambda$ = 0.154178 nm) employing a scanning rate of 0.05°/s in $2\theta$ range from 20 to 70°. Transmission electron microscopy (TEM) was performed with a Hitachi H-800 transmission electron microscope at an acceleration voltage of 200 kV. The purity and composition of the products were examined by X-ray photoelectron spectra (XPS) on an ESCALab

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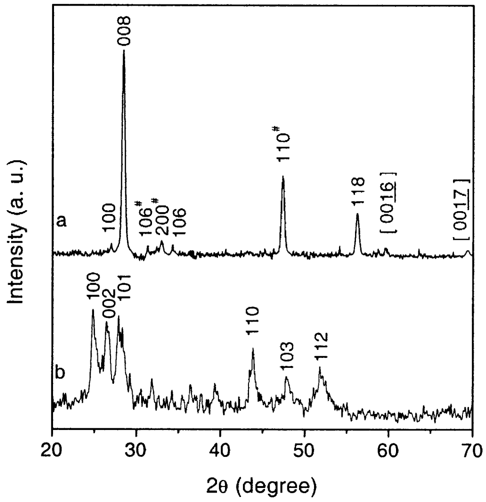

**FIG. 1.** PXRD pattern of the product: (a) Sample **1**, (b) Sample **2**.

MKII instrument with MgKα radiation as the exciting source.

## 3. RESULTS AND DISCUSSION

The powder X-ray diffraction (PXRD) patterns of samples are shown in Fig. 1. All of the distinct diffraction peaks in Figs. 1a and 1b can be indexed as hexagonal wurtzite phase ZnS (**1**) (JCPDS Card File No. 39-1363) and CdS (**2**) (JCPDS Card File No. 41-1049), respectively. Estimated from the half-width of diffraction peaks (110) using Scherrer formula, the dimensions of the ZnS and CdS are about 46 and 15 nm, respectively.

Figure 2 shows the typical TEM images of the products. Figure 2a shows an elecronic diffraction (ED) pattern of **1**. Three typical diffraction spots are indexed as the 008, 106 and 110 planes by the ratio of $1/d_{hkl}$. From the typical TEM

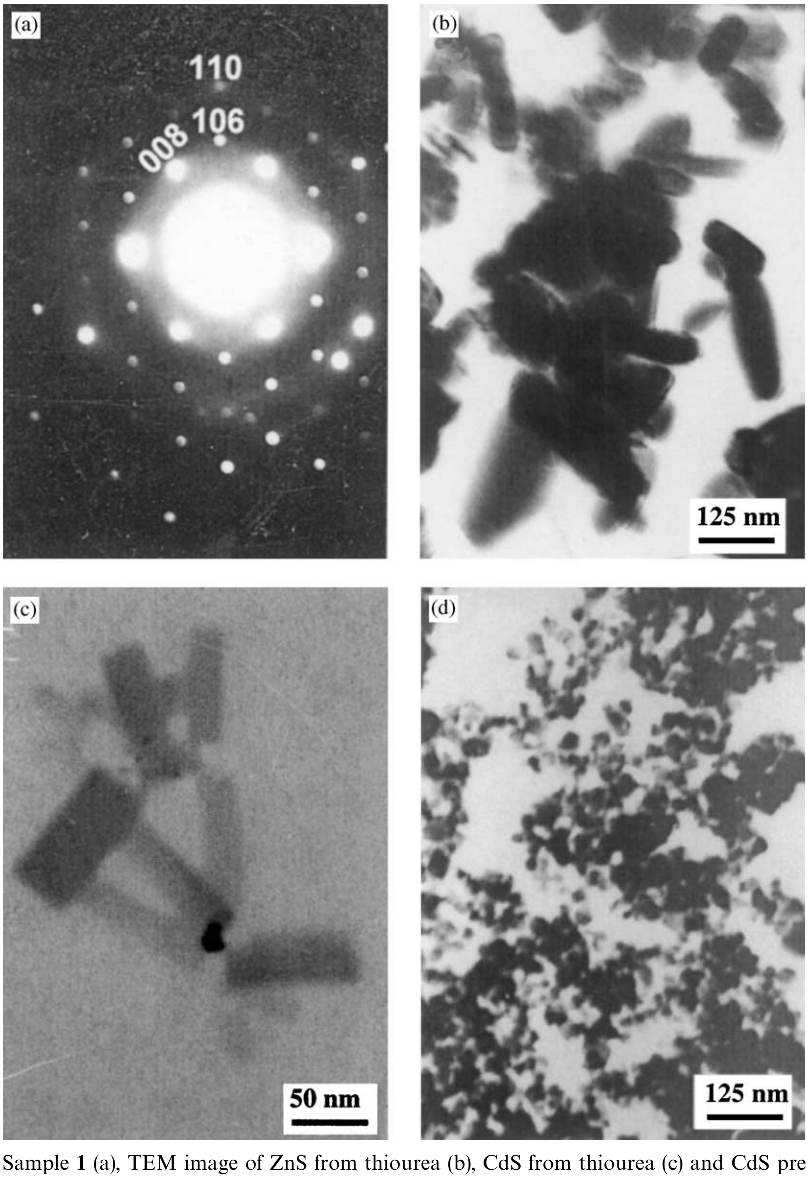

**FIG. 2.** ED pattern of Sample **1** (a), TEM image of ZnS from thiourea (b), CdS from thiourea (c) and CdS prepared from $NaS_2O_3$ (d).

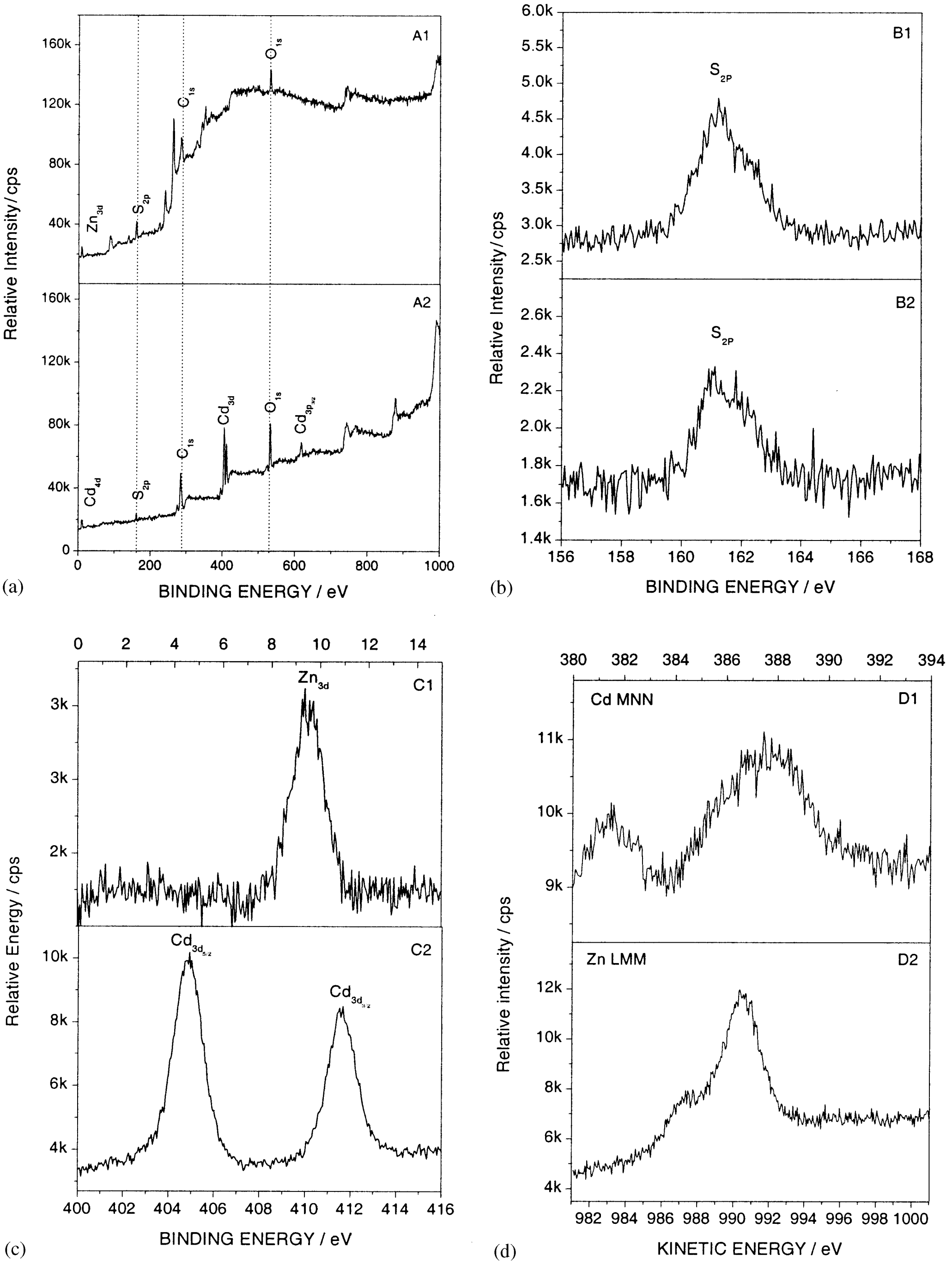

**FIG. 3.** XPS spectra of Samples **1** and **2**: (a) survey spectrum of ZnS and CdS, (b) $S_{2p}$ of ZnS and CdS, (C) $Zn_{3d}$ and $Cd_{3d}$ of ZnS and CdS, (d) Zn LMM and Cd MNN of ZnS and CdS.

images of **1** (Fig. 2b) and **2** (Fig. 2c) we can see that both **1** and **2** have rod morphology. The diameters of width/length are 50 ± 12/200 ± 50 and 20 ± 10/75 ± 25 nm for **1** and **2**, respectively.

The purity and composition of **1** and **2** were examined by XPS, which are shown in Fig. 3, including (a) the survey spectra of **1** and **2**, (b) $S_{2p}$ of of **1** and **2**, (c) $Zn_{3d}$ and $Cd_{3d}$ of **1** and **2**, respectively, (d) Zn LMM and Cd MNN of **1** and **2**, respectively. In ZnS, the binding energy values are 161.3 eV for $S_{2p}$ and 9.45 eV for $Zn_{3d}$, and the kinetic energy for Zn LMM is 990.2 eV. In CdS, the binding energy values are 161.0 eV for $S_{2p}$, 404.9 eV for $Cd_{3d5/2}$ and 411.5 eV for $Cd_{3d3/2}$, and the kinetic energy of Cd MNN is 381.5 eV. These results are consistent with the values reported by

Wagne (9). From the survey spectra of **1** and **2** we can see that the product was pretty pure. Quantification of peaks gave a ratio of Zn to S and Cd to S as 1.02:1 and 1:1.03, respectively.

In order to study the effect of sulfur source on the morphology of products, we also used $CS_2$ and $Na_2S_2O_3$, which are easy to handle and usually effective, as sulfur source. In our experiments, the metal sulfide could not be synthesized as we used $CS_2$ as the sulfur source. On the other hand, spherical particles of CdS 12 nm in diameter were synthesized from $[\mathrm{Cd(tp)(4,4'\text{-}bipy)}]_\infty$ and $Na_2S_2O_3$ under the same condition for the preparation of samples **1** and **2**. Its typical TEM image is shown in Fig. 2d. Thus, thiourea is a good sulfur source for the preparation of *MS* (Zn,Cd) nanorods through this route. Furthermore, the coordination polymers $[\mathrm{Zn(tp)(4,4'\text{-}bipy)}]_\infty$ and $[\mathrm{Cd(tp)(4,4'\text{-}bipy)}]_\infty$ used as metal ions source both show three-dimensional coordination frameworks constructed with mixed tp and 4,4′-bipy (8). It should also be mentioned that tp, as a negatively charged polycarboxylate, exhibits a variety of bridging abilities and a strong tendency to form large, tightly bound metal cluster aggregates whereas the neutral ligand 4,4′-bipy may be much labile in the reaction. Therefore, the possible mechanism is that thiourea molecules, with the ability to coordinate with metal ion, attack the $M^{2+}$ sites available by leaving of neutral 4,4′-bipy molecules. In addition, the high pressure in the autoclave and the sequent precipitate of *M*S led to the reaction shift to right although the coordination polymer itself is very stable without the sulfur source. It is worth noting that we obtained ZnSe nanowires 5 nm in width and 3 μm in length by using a chain-like complex (10). These facts indicate that the sizes and shapes of the nanostructures are related to the structure of the coordination polymer and the source of sulfur, although the mechanism requires further investigation.

In summary, wurtzite ZnS and CdS nanorods were synthesized under solvothermal condition at 140°C by using coordination polymers $[\mathrm{Zn(tp)(4,4'\text{-}bipy)}]_\infty$ and $[\mathrm{Cd(tp)(4,4'\text{-}bipy)}]_\infty$, respectively. Both the structure of the coordination polymer and source of sulfur may affect the growth of nanocrystals.

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