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Communications

Nonaqueous Synthesis of CdS Nanorod Semiconductor

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Material scientists are attempting to produce novel materials. Development of a controlled-synthesis method is always the most important goal. One-dimensional nanostructures as building blocks for many novel functional materials are currently the focus of considerable interests.¹⁻⁷ The control of nucleation and growth of 1D nanostructural materials is becoming critical. This study will help us to understand the chemical control synthesis of crystal growth processes at the atomic level.

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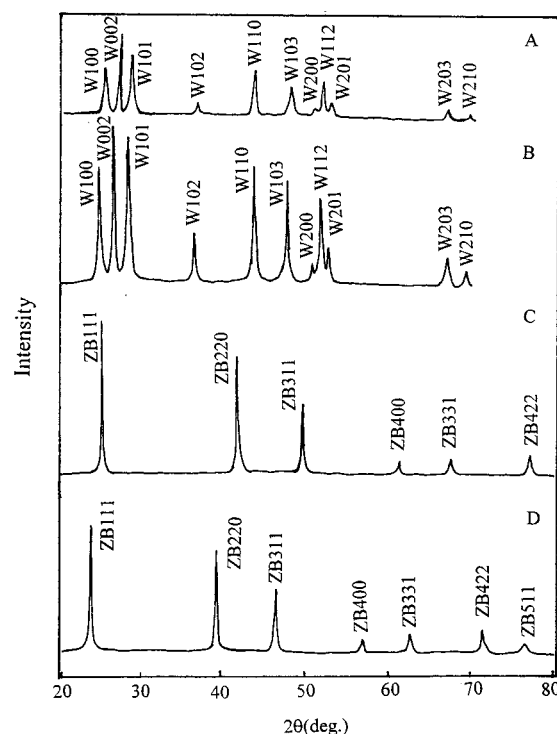


Figure 1. X-ray diffraction (XRD) patterns of obtained samples: (A) CdS (prepared with Cd and S); (B) CdS (prepared with CdCl₂ and S); (C) CdSe; (D) CdTe (W, wurtzite structure; ZB, zinc-blend structure.)

The vapor-liquid-solid (VLS) mechanism^{3,4} and the vapor-solid (VS) mechanism⁸ for crystalline whisker or fiber growth at high temperature are widely known. A hydrothermal liquid-solid (LS) whisker or fiber growth

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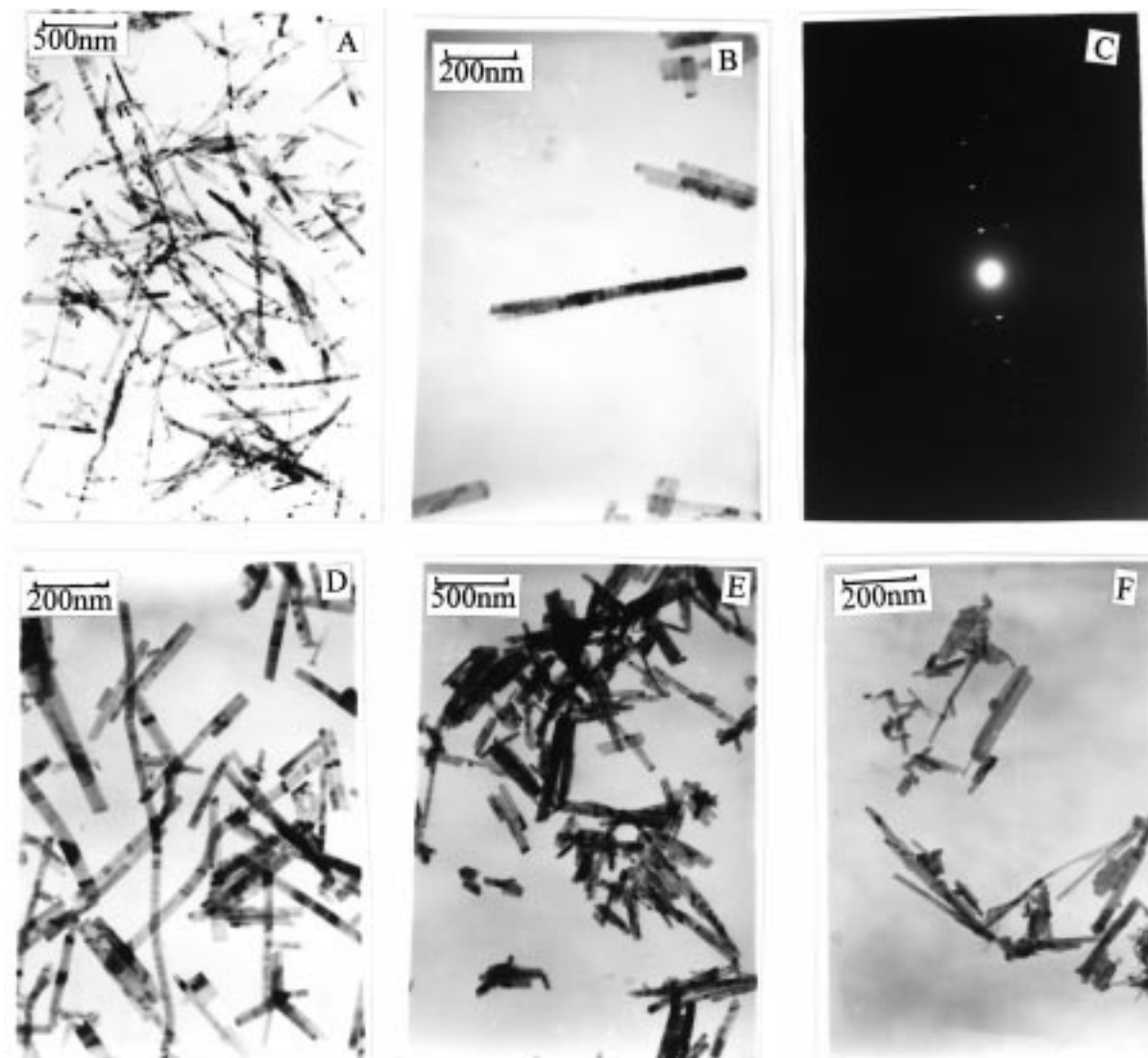


Figure 2. Transmission electron microscopy (TEM) images of the obtained samples and electron diffraction pattern of CdS. (A) TEM image of CdS prepared with Cd and S; (B) TEM image of a single CdS nanorod prepared using the same conditions as A; (C) selected area electron diffraction pattern of the sample shown in B; (D) CdS prepared with CdCl₂; (E) CdSe prepared with Cd and Te; (F) CdTe prepared with Cd and Te.

mechanism was proposed by Shi Erwei⁹ and Masahiro.¹⁰ Recently, Buhro proposed a solution-liquid-solid (SLS) mechanism for the growth of III-V semiconductor fibers⁷ in organic solution. Stupp reported CdS, CdSe semiconductor superlattices by molecular assemblies⁵ in an amphiphile-solvent mesophase. Here, we report a nonaqueous synthetic route based on specific molecular interaction with organic solvent intermolecular and inorganic-organic interfaces that can result in the controlled nucleation and growth of CdS, CdSe, and CdTe semiconductor nanorods in ethylenediamine. This nonaqueous organic media may provide a template for inorganic atom or ion self-assembling at the atomic level.

We chose CdS, CdSe, and CdTe as the materials to be synthesized in our nonaqueous system because of their potential importance as nonlinear optical materials,¹¹ quantum size effect semiconductors,¹² materials

for electroluminescent devices,¹³ and other interesting physical properties and chemical properties. They are also functional materials with technological applications.^{5,14,15} Many methodologies¹¹⁻²⁰ have been developed to synthesize solid nanoscale CdS, but they all produce solid semiconductor particles or small clusters

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with morphologies never very far from spherical particles. CdS with a dendritic structure has been synthetic under Langmuir monolayers.^{6,21,22}

CdS nanorods were synthesized in ethylenediamine nonaqueous solvent systems with the reaction of cadmium metal powder and sulfur at 120–190 °C under pressure in an autoclave:



0.005 mol of elemental S (99.999%) and Cd powder (99.999%) were stoichiometrically put into a Teflon-lined stainless steel autoclave of 100 mL capacity, then the autoclave was filled with ethylenediamine up to 70% of the total volume. The autoclave was maintained at 120–190 °C for 3–6 h without shaking or stirring during the heating period and then allowed to cool to room temperature. A bright-yellow precipitate was collected that was washed with distilled water to remove residue of ethylenediamine. The final product was dried in a vacuum at 100 °C for 2 h.

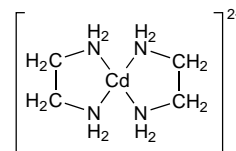
The X-ray powder diffraction (XRD) pattern was recorded on a Japan Rigaku Dmax rA X-ray diffractometer with Cu K radiation ($\lambda = 1.54178 \text{ \AA}$). In the XRD pattern (Figure 1A), all the reflections can be indexed to the hexagonal cell of CdS (wurtzite structure) with lattice constants $a = 0.4141 \text{ nm}$ and $c = 0.6720 \text{ nm}$ (equal to the values of JCPDS 41-1049), which are near the reported value.⁶ The unusually strong (002) peak in the pattern indicates a preferential orientation of [001] in CdS nanorod.

Elemental analysis of the sample was carried out through common EDTA coordinating titration²³ and a barium sulfate gravimetric method. The elemental composition of Cd:S was about a 50:50 atomic ratio. It was also confirmed by energy-dispersive X-ray fluorescence analysis (EDAX) with an EDAX 9100.

Transmission electron microscopy (TEM) images were taken with an Hitachi H-800 transmission electron microscope. The CdS crystallites synthesized in the

ethylenediamine nonaqueous system appear to display rodlike monomorphology with lengths of 300–2500 nm and widths of 25–75 nm (Figure 2A). Figure 2C shows the electron diffraction patterns of selected areas (Figure 2B) of a single CdS nanorod with a diameter of 36 nm and a length of 720 nm. It shows that the CdS nanorod is a single crystal. The nanorod axis (growth direction) was [002]. It was consistent with the XRD pattern (Figure 1A and B).

In our synthetic system, the result of CdS nanorod formation indicated that the nucleation and growth were well-controlled. The ethylenediamine nonaqueous solvent plays an important role in controlling nucleation and growth of CdS nanorod. The solvent molecule may act as a bidentate ligand in sulfur–solvent solution to form relatively stable Cd^{2+} complexes (the stability constants $\log \beta_2 = 10.09$).



The stability of the complexes is expected to decrease with the increase of the temperature. At some relatively high temperature, for example, above 120 °C, sulfur may coordinated to the above complex to form a one-dimensional CdS nanorod structure and the volatile coordinated ligands are lost gradually. 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 speculate this nanorod growth mechanism as a templating mechanism. To improve the understanding of the templating effects, in the same ethylenediamine nonaqueous system, we synthesized the CdS, CdSe, and CdTe by only varying the reactants: Cd was changed to CdCl_2 and S to Se and Te, with all other conditions kept constant. The results showed that all of the CdS, CdSe, and CdTe samples obtained had a nanorod morphology (Figure 2D–F). The CdS nanorods were of the wurtzite structure, but the CdSe and CdTe had the cubic zinc-blend structure (Figure 1B–D). We also substituted ethylenediamine with 1,6-diaminohexane, pyridine, and diethylamine as solvent and found that in 1,6-diaminohexane the obtained CdS was also rodlike and in pyridine and diethylamine the obtained samples both showed spherical morphology.²⁴ In ethylenediamine, InAs whiskers were also successfully synthesized.²⁵ The above results indicated that only in bidentate solvent, such as ethylenediamine and 1,6-diaminohexane, the obtained samples had rodlike morphology. The results further supported the proposed templating mechanism.

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