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# General Synthesis of Semiconductor Chalcogenide Nanorods by Using the Monodentate Ligand *n*-Butylamine as a Shape Controller[**]

Jian Yang,* Can Xue, Shu-Hong Yu,* Jing-Hui Zeng, and Yi-Tai Qian

Currently, research on fundamental properties and practical applications of nanomaterials are attracting much attention.[1] However, most studies have focused on the size effect of nanocrystals. In fact, the shape of semiconductor nanomaterials has considerable influence on physical properties and is also important in many potential applications, such as solar cells, light-emitting diodes, and scanning-microscopy probes.[2] In spite of this, since little is known about the mechanism of crystal growth of anisotropic nanocrystals, shape control of nanocrystals remains a challenge to synthetic chemists.[1c,3]

Over the past few years, remarkable progress has been made in the shape control of nanomaterials. Alivisatos et al. controlled the size and shape of CdSe nanocrystals in the presence of strong ligands.[4] This approach was extended to control the size and shape of magnetic cobalt nanocrystals.[5] Lieber et al. developed a laser-assisted catalytic growth (LCG) technique to synthesize a broad range of binary and ternary semiconductor nanowires by a vapor–liquid–solid (VLS) mechanism.[6] Highly crystalline III–V semiconductor nanowires were synthesized by a solution–liquid–solid (SLS) method introduced by Buhro et al.[7] Recently, Weller et al. grew ZnO nanorods by oriented attachment of small quasi-spherical particles by concentrating and refluxing a solution.[8] Very thin one- (1D) and two-dimensional (2D) $CdWO_4$ nanocrystals with controlled aspect ratios were conveniently fabricated at ambient temperature or by hydrothermal ripening.[9] However, to the best of our knowledge, a general route for the synthesis of various semiconductor chalcogenide nanorods under mild solution conditions has still not been realized.

We have successfully controlled the size and shape of semiconductor nanocrystals by means of solvothermal reactions.[10–12] In-depth studies on the formation processes of these nanorods provided useful guidelines for the preparation of 1D nanocrystals.[10,11] We found that the anisotropic nature of the building blocks in the crystal structure, which are infinite linear chains in the case of $M_2S_3$ (M = Sb, Bi), plays a crucial role in the formation of nanorods.[11,12] In other words, this 1D growth of nanocrystals is actually the outward embodiment of the internal crystal structure.

The temporal evolution of CdS nanocrystals in solvothermal reactions demonstrated that ethylenediamine (en) molecules adsorbed on the surface of CdS play a critical role in the formation of nanorods.[10] FTIR spectra of these en molecules show that they are not in chelating (*cis*) configuration but in *trans* configuration. Reetz et al. reported that a nonchelating coordination mode of $\alpha$-hydroxycarboxylates on a metal surface is likely to be the morphology-determining factor in shape-selective preparation.[13] However, on the basis of IR data alone, it is difficult to judge whether the mode of coordination between $Cd^{2+}$ on the surface and en molecules is monodentate (Scheme 1 a) or bridging (Scheme 1 b), although it is possible that the en molecules in both cases are in the *trans* configuration.

Because *n*-butylamine has only one anchor atom, its coordination mode with metal ions must be monodentate (Scheme 1 c), and hence we employed it as solvent to clarify this point. First, CdS nanocrystals were chosen as the target to examine whether the same reaction in a monodentate ligand can produce nanorods. In the IR spectrum of the as-prepared CdS nanocrystals, the characteristic absorption peak at 1573.0 $cm^{-1}$ can be unambiguously assigned to the $NH_2$ bending vibration, which is shifted to lower frequency relative to that of pure *n*-butylamine[14] (see Supporting Information). A red shift of the C–N bending vibration resulting from

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[*] Dr. J. Yang,[+] [++] Dr. S.-H. Yu,[++] Mr. C. Xue, Dr. J.-H. Zeng,
Prof. Y.-T. Qian
Department of Chemistry and Structure Research Laboratory
University of Science and Technology of China
Hefei, Anhui 230026 (P. R. China)
Fax: (+86) 551-360-7402
E-mail: jyang2000@ustc.edu.cn
shyu@ustc.edu.cn

[+] Present address: Department of Chemistry
National Taiwan Normal University
Tingchow Road, Sec. 4, 88, Taipei 116 (R. O. C.)

[++] Present address: Max Planck Institute of Colloids and Interfaces
Department of Colloid Chemistry
MPI Research Campus Golm
14424, Potsdam (Germany)

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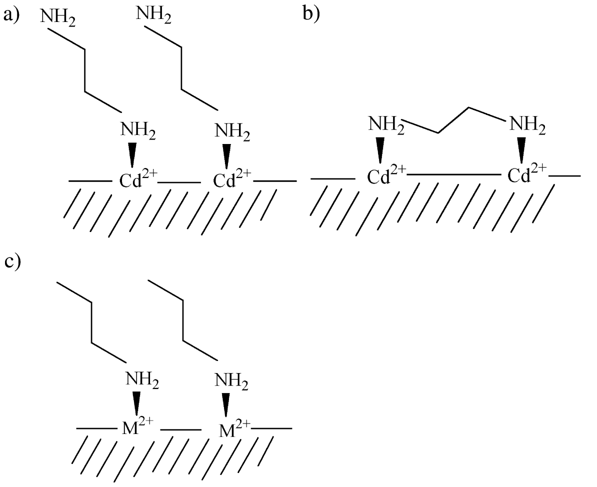

Scheme 1. Possible surface coordination modes: a) monodentate mode of en molecules; b) polydentate mode of en molecules; c) monodentate mode of *n*-butylamine.

coordination was also observed.[14] These results indicate that the N atom of *n*-butylamine is coordinated to metal ions on the surface of CdS nanocrystals.

The XRD pattern (Figure 1 a) of CdS obtained at 220 °C for 12 h can be identified as that of a hexagonal phase (JCPDS Card, No. 41-1049). The lattice constants calculated from this pattern ($a = 4.12$ Å, $c = 6.68$ Å) are in good agreement with the reported values. The crystal dimensions, which can be roughly estimated by using the Scherrer equation, are 50 and 9 nm based on (002) and (110) reflections, respectively. The large difference between the coherence lengths in the [002] and [110] directions implies an unusual shape of the products.[14] This result agrees well with that observed by TEM (Figure 1 b). Short nanorods, 7–10 nm in width and 30–55 nm in length can be readily observed. We believe that the abundance of (002) planes in and the anisotropic shape of the nanorods result in the remarkable increase in intensity and sharpening of the (002) reflection.[15]

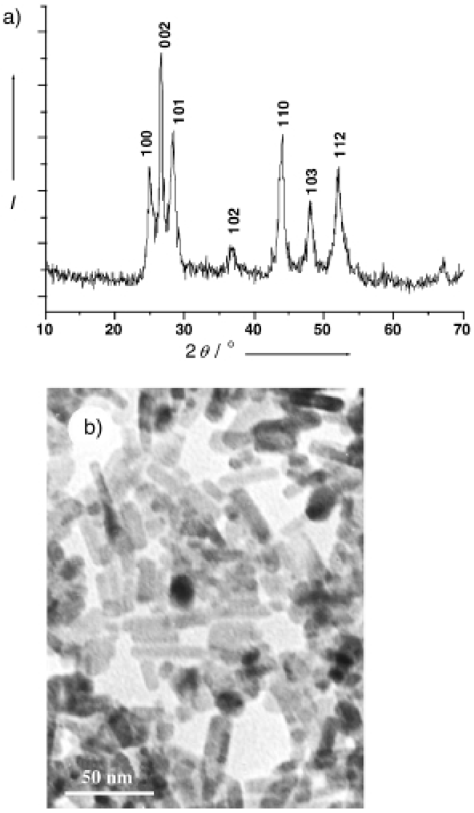

Figure 1. a) XRD pattern and b) TEM image of CdS nanocrystals obtained at 220 °C for 12 h.

Because the mode of coordination between *n*-butylamine and $Cd^{2+}$ on the surface of CdS is monodentate (Scheme 1 c), the existence of rodlike nanoparticles in the products indicates that one anchor atom in a ligand is necessary and sufficient for the formation of nanorods, even though more anchor atoms may be present in a ligand. The close interaction between anchor atoms in ligands (Lewis base) and metal ions on the surface (Lewis acid) is another prerequisite for the formation of nanorods, because this weak interaction means that ligand molecules will not impose effective influence on the nucleation and growth of nanoparticles.[16] Altering the strength of interaction between ligands and metal ions could control the shape and size of various chalcogenides nanocrystals, as demonstrated previously in the synthesis of CdS nanocrystals.[16]

According to the above two conclusions, nanorods can be synthesized by choosing an appropriate monodentate ligand as solvent. If this is correct, it should be extendible to many other chalcogenides. *n*-Butylamine should be a suitable solvent because its $NH_2$ group can interact with many metal ions. PbSe and ZnSe are important semiconductors with extensive practical applications, but few strategies for the preparation and characterization of 1D nanocrystals thereof have been reported up to now.[6,17] Hence, we chose PbSe, ZnSe, and CdSe as targets for examining this deduction.

Figure 2 a presents the XRD pattern of CdSe nanocrystals obtained at 160 °C for 12 h. According to this pattern, the product consists of a mixture of hexagonal-phase CdSe (JCPDS Card, No. 8-459) and cubic-phase CdSe (JCPDS Card, No. 19-191). As shown in Figure 3 a, the as-prepared CdSe consists of nanorods 12–16 nm in width and 200–300 nm in length. A bundle of typical nanorods is shown in Figure 3 b. A selected-area electron diffraction (SAED) pattern (inset in Figure 3 b) on this sample revealed that the nanorods grew along the close-packing direction.

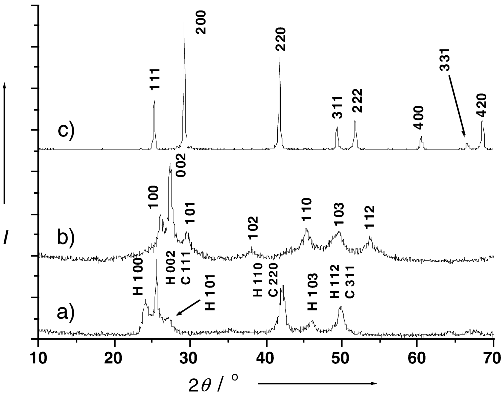

Figure 2. XRD pattern of a) CdSe nanocrystals (160 °C, 12 h, H: hexagonal, C: cubic), b) ZnSe nanocrystals (220 °C, 12 h), c) PbSe nanocrystals (80 °C, 12 h).

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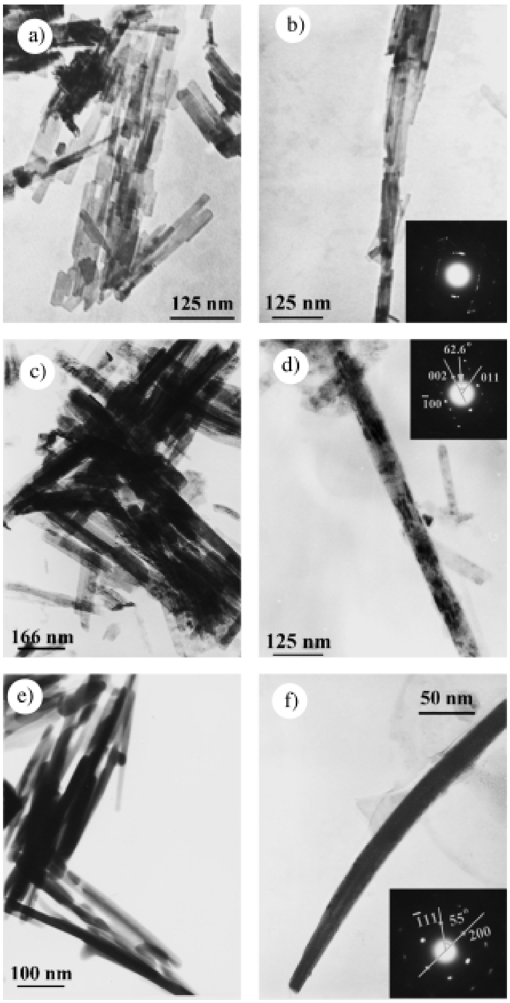

Figure 3. TEM images of a), b) CdSe nanocrystals (160 °C, 12 h); c), d) ZnSe nanocrystals, (220 °C, 12 h); e), f) PbSe nanocrystals (80 °C, 12 h).

The XRD pattern of ZnSe obtained at 220 °C for 12 h (Figure 2 b) can be indexed as a hexagonal-phase ZnSe (JCPDS Card, No. 15-105). The lattice constants calculated from this pattern ($a = 3.98$ Å, $c = 6.53$ Å) are in accordance with the reported values. However, the unusually high intensity of the (002) reflection indicates preferential growth of nanocrystals.[10]

The TEM image in Figure 3 c shows that the as-prepared ZnSe nanocrystals are nanorods with diameters in the range of 25–50 nm and lengths of up to 1 μm. A well-crystallized single ZnSe nanorod with the growth direction along the $c$ axis is presented in Figure 3 d. To the best of our knowledge, it is the first reported synthesis of wurtzite ZnSe nanorods. Elemental analysis by energy-dispersive spectroscopy (EDS) gave a molar Zn:Se ratio of 51.5:48.5, which coincides with the formula ZnSe. The Zn 2p and Se 3d lines in the XPS spectrum are at 1022.45 and 54.80 eV, respectively, consistent with the reported values of ZnSe[18] (see Supporting Information). Quantitative analysis of the peak areas gave a molar Zn:Se ratio of 1.04:1, which agrees well with the result from EDS.

The XRD pattern of PbSe obtained at 80 °C for 12 h (Figure 2 c) can be indexed as a cubic-phase PbSe (JCPDS Card, No. 6-354). The lattice constant calculated from this pattern ($a = 6.12$ Å) is in good agreement with the reported value. The TEM image of the PbSe nanocrystals (Figure 3 e) shows many nanorods 12–20 nm in width and 200–450 nm in length. Figure 3 f shows a typical nanorod with the growth direction along ⟨200⟩, as revealed by the SAED pattern (inset in Figure 3 f). Elemental analysis by EDS on this sample gave a molar ratio of Pb and Se close to the formula PbSe. The Pb 4f and Se 3d lines at 137.95 and 53.15 eV, respectively, in the XPS spectrum of this sample are consistent with the reported values of PbSe[18] (see Supporting Information).

The above-mentioned chalcogenide nanorods were synthesized under optimized experimental conditions. Any change in these conditions leads to a change in the size and shape of the product. The influence of reaction temperature on the product is larger than that of reaction time, which is illustrated here for CdS. As shown in Figure 4 a, CdS powders prepared at 160 °C consist of irregular nanoparticles. At 220 °C, short nanorods with an aspect ratio of about 4–5 are obtained (Figure 4 b). These results indicate that selecting the proper experimental conditions is also important for the formation of nanorods.

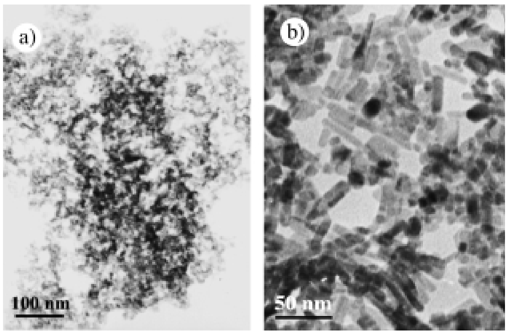

Figure 4. CdS nanocrystals prepared at different temperatures for 12 h: a) 160 °C; b) 220 °C.

In summary, the successful preparation of CdS nanorods in $n$-butylamine demonstrates that chalcogenide nanorods can be prepared by using a monodentate ligand as solvent. This result implies that one anchor atom in a ligand is necessary and sufficient for the formation of 1D nanocrystals, even though more anchor atoms may be present in a ligand. Close interaction between anchor atoms in ligands and metal ions on the surface is another prerequisite for nanorod formation, and $n$-butylamine is suitable for the syntheses of other chalcogenide nanorods, because its $NH_2$ group can interact with many different metal ions. The notion that solvothermal synthesis of nanorods can only be carried out in the presence of polydentate ligands must now be revised. Furthermore, this route not only provides a possible general route to other chalcogenide nanorods on a large scale, but also a guide for further rational design of 1D chalcogenides.

## *Experimental Section*

All chemicals were of analytical grade and were used without further purification. 1.5 mmol of a metal salt ($Cd(NO_3)_2 \cdot 4H_2O$ for CdS, CdSe; $Zn(NO_3)_2 \cdot 6H_2O$ for ZnSe; $Pb(CH_3COO)_2 \cdot 3H_2O$ for PbSe) and 1.5 mmol

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of thiourea (or Se) were added to 20 mL of *n*-butylamine. The resulting solution was stirred for several minutes and then sealed in a stainless steel autoclave with a Teflon liner. This autoclave was maintained at the appropriate temperature (80–220 °C) for 12 h. Subsequently, the autoclave was allowed to cool to room temperature. The solution from the autoclave (except for CdS) was filtered and the obtained powders were washed with distilled water and absolute ethanol and dried in vacuum at 70 °C for 1 h. CdS powders were separated from the solution by centrifugation and washed with absolute ethanol.

X-ray powder diffraction patterns were obtained on a Japan Rigaku DMax-γA rotating-anode X-ray diffractometer with graphite-monochromatized $\mathrm{Cu}_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). TEM photographs and SAED patterns were recorded on a Hitachi Model H-800 transmission electron microscope at an accelerating voltage of 200 kV. The samples were dispersed in absolute ethanol in an ultrasonic bath. Then the suspensions were dropped onto Cu grids coated with amorphous carbon films. XPS spectra were recorded on a VEGSCALAB MKII X-ray photoelectron spectrometer with nonmonochromatized $\mathrm{Mg}_{K\alpha}$ radiation as the excitation source. IR spectra were recorded on a Bruker Vector-22 FT-IR spectrometer from 4000 to 400 cm$^{-1}$ at room temperature on KBr mulls.

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# Electron-Transfer Dynamics of Cytochrome C: A Change in the Reaction Mechanism with Distance[**]

Jianjun Wei, Haiying Liu, Dimitri E. Khoshtariya,
Hiromichi Yamamoto, Allison Dick, and
David H. Waldeck[*]

Redox processes are ubiquitous in nature, and the understanding of electron transfer in complex systems, for example, biological structures such as proteins, membranes, and the photosynthetic reaction center, is an outstanding challenge. Here we provide new results on the electron-transfer dynamics of the protein cytochrome c as a function of distance from a metal electrode. Comparison of this distance-dependence with previous studies indicates that a conformationally gated mechanism involving a large amplitude protein motion is not operative, but a change in the electron-transfer mechanism occurs and is linked to the protein environment.

The redox protein cytochrome c is very well characterized and numerous studies of its electron transfer have been performed, both under homogeneous and heterogeneous conditions.[1] A number of research groups have immobilized cytochrome c on gold electrodes that are coated with a self-assembled monolayer (SAM) of -S-$(\mathrm{CH}_2)_{n\text{-}1}$-COOH, presumably by binding to the protein's lysine groups.[2] The electronic coupling strength between the electrode and the protein can be varied by changing the length of the alkane chain. At large SAM thicknesses the electron-transfer rate constant declines exponentially with distance (electron tunneling mechanism), but it is distance-independent at lower thicknesses, hence there is a change in the rate-limiting step and the mechanism of reaction. More recently, mixed monolayer films of pyridine-terminated alkanethiols embedded in an alkanethiol diluent have been used to directly tether the heme to the surface.[3] This strategy for immobilization (Figure 1) should eliminate large-amplitude conformational motion of the protein on the surface of the SAM as a gating mechanism for the electron transfer, because the heme is directly linked to the alkanethiol tunneling barrier.

The immobilization of the cytochrome on the film has been demonstrated through electrochemical control experiments and by direct imaging by STM.[3b] The primary evidence for binding near the heme is the negative shift of the redox potential, relative to that in solution, and the differential adsorption strength of different functional end groups

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[*] Prof. Dr. D. H. Waldeck, J. Wei, H. Liu, H. Yamamoto, A. Dick
Department of Chemistry
University of Pittsburgh
Pittsburgh, PA 15260 (USA)
Fax: (+1) 412–624–8611
E-mail: dave@pitt.edu

D. E. Khoshtariya
Institute of Molecular Biology and Biophysics
Georgian Academy of Sciences
Gotua 14, Tbilisi 380060 (Georgian Republic)

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