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γ-Irradiation preparation and phase control of nanocrystalline CdS†

Zhengping Qiao,[a,b] Yi Xie,[b] Xiaojun Li,[b] Cheng Wang,[b] Yingjie Zhu[b] and Yitai Qian[a,b]

[a]Structure Research Lab., [b]Department of Chemistry, University of Science & Technology of China, Hefei, Anhui, 230026, P. R. China. E-mail: yxie@ustc.edu.cn

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γ-Irradiation has been successfully used to prepare nanocrystalline CdS of sphalerite and wurtzite structure at room temperature. Sodium thiosulfate, mercaptoethanol and carbon disulfide were used as sulfur sources in aqueous solution or anhydrous ethanol. The formation of sphalerite and wurtzite can be controlled by using different sulfur sources in different solvents. Generally, the sulfur sources and solvents with lower polarity tend to produce the cubic wurtzite phase, while those with strong polarity give the hexagonal sphalerite phase. TEM images show that the products in anhydrous ethanol show superior dispersion, and those in aqueous solution aggregate more extensively. Possible mechanisms of the formation of cadmium sulfide in the different systems are proposed.

Introduction

In recent years, the synthesis and characterization of chalcogenides of different groups have attracted significant interest and still are the subject of intense investigation owing to their important nonlinear properties, luminescent properties, quantum size effects and other important physical and chemical properties.[1–4] Among these materials, cadmium sulfide is amongst the most interesting owing to its high photosensitivity and attractive application in photoconducting cells. CdS is also well known for application in a variety of optoelectronic devices including thin film solar cells and photodetectors.[5] The structures adopted by CdS have also been attracting attention. Two typical structures are observed: cubic sphalerite phase and hexagonal wurtzite phase, both of which are stable phases.

Considerable progress has been made in the synthesis of group II–VI semiconductor nanocrystallines. Conventionally, solid state reactions, aqueous solution reactions, gas phase reactions, and use of precursors have been used to prepare chalcogenides including CdS.[6–8] However, the above methods generally require high temperature ($>500\,^{\circ}$C) or use of toxic H_2S. Using organometallic precursors provides another route to CdS,[9] but most of these are toxic, readily hydrolyzed and oxidized and difficult to handle. Recently, Parkin and coworkers reported that many chalcogenides can be obtained at room temperature in liquid ammonia. However, the reactants must initially be dissolved and the liquid ammonia is evaporated at $-77\,^{\circ}$C. Furthermore, such reactions in liquid ammonia may lead to explosions and all the operations must be conducted with blast proofing and behind a safety screen.[10,11]

γ-Irradiation has been developed as a new method to prepare nanocrystalline metals, alloys, metal oxides and glass-metal, silver/polyacrylamide nanocomposites.[12–15] Hayes *et al.* obtained CdS colloids from solutions containing cadmium ions and a thiol (3-mercaptopropane-1,2-diol, RSH) by use of γ-radiation.[16] Here, we report the extension of this method to the preparation of nanocrystalline cadmium sulfide. Different sulfur sources, *i.e.* sodium thiosulfate, mercaptoethanol and carbon disulfide were successfully used to obtain nanocrystalline CdS. The whole process is carried out at room temperature and ambient pressure. The amounts of the two phases of CdS (wurtzite and sphalerite) can be controlled by choosing different sulfur sources and solvents.

Experimental

Solutions were prepared by dissolving an appropriate amount of analytically pure cadmium salts and various sulfur sources in distilled water or anhydrous ethanol. The cadmium salt was cadmium chloride. The sulfur sources were sodium thiosulfate, mercaptoethanol and carbon disulfide. Isopropyl alcohol was added as a scavenger for hydroxyl radicals. Solutions were irradiated in the field of a 2.59×10^{15} Bq ^{60}Co γ-ray source with a radiation dose of 3.0×10^{4} Gy. The irradiated solutions were kept for several hours to precipitate powders. Yellow precipitates were collected and washed successively with absolute ethanol and distilled water to remove any by-products. The final product was washed with acetone and then dried *in vacuo* at room temperature for 4 h.

The samples were characterized by X-ray powder diffraction (XRD) patterns employing a scanning rate of $0.05^{\circ}\,s^{-1}$ in 2θ range from 20–60°, using a Japan Rigaku Dmax γ_A X-ray diffractometer equipped with graphite monochromatized Cu-Kα radiation ($\lambda=1.54178$ Å). The morphology and particle sizes were determined by transmission electron microscopy (TEM). The TEM images were taken with a Hitachi Model H-800 transmission electron microscope with an accelerating voltage of 200 kV. The product purity and composition were examined by X-ray photoelectron spectra (XPS) on an ESCALab MKII instrument with Mg Kα radiation as the exciting source. Absorption spectra were recorded on a UV-2100 Schimadzu UV–VIS spectrophotometer using quartz cells.

Results and discussion

Some typical compositions of solutions are given in Table 1. The XRD patterns of samples A1–A3, which were synthesized in aqueous solution, are shown in Fig. 1 from which it can be seen that the patterns of A1 and A2 are similar. All the peaks

Table 1 Composition of solutions[a]

Sample	Metal ion source	Sulfur ion source	Solvent
A1	$CdCl_2$ (0.05 M)	$Na_2S_2O_3$ (0.1 M)	H_2O
A2	$CdCl_2$ (0.05 M)	HOC_2H_4SH (0.5 M)	H_2O
A3	$CdCl_2$ (0.02 M)	CS_2 (0.2 M)	H_2O
N1	$CdCl_2$ (0.02 M)	$Na_2S_2O_3$ (0.04 M)	EtOH
N2	$CdCl_2$ (0.02 M)	HOC_2H_4SH (0.2 M)	EtOH
N3	$CdCl_2$ (0.02 M)	CS_2 (0.2 M)	EtOH

[a]Scavenger: 3 M Pr^{i}OH.

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†*Supplementary data available*: XPS and UV spectra available from BLDSC (No. SUP 57472, 2pp.). See Information for Authors, 1999, Issue 1 (http://www.rsc.org/materials).

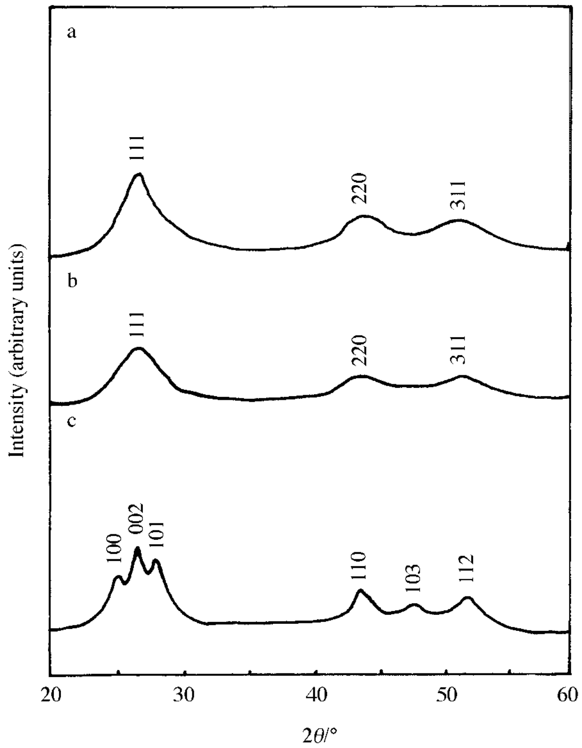

Fig. 1 XRD patterns of the products using different sulfur sources in aqueous solution: (a) sodium thiosulfate, (b) mercaptoethanol, (c) carbon disulfide.

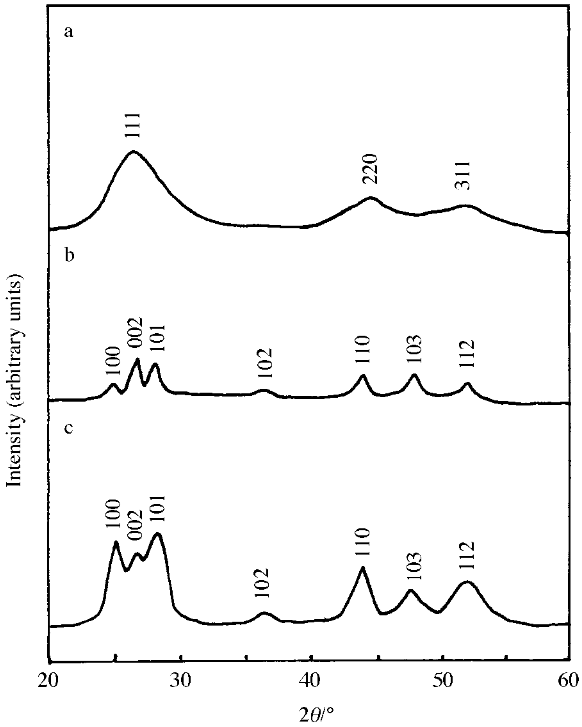

Fig. 2 XRD patterns of the products using different sulfur sources in alcohol solution: (a) sodium thiosulfate, (b) mercaptoethanol, (c) carbon disulfide.

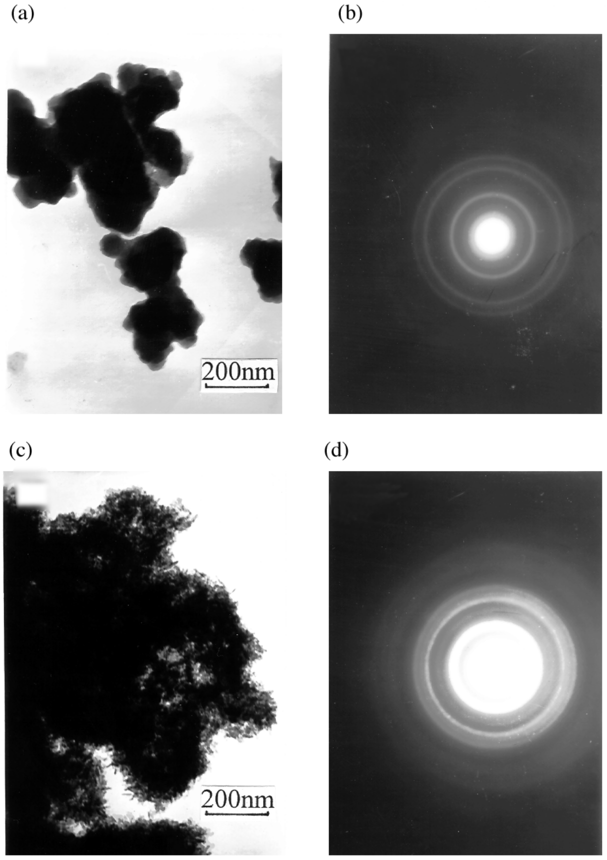

Fig. 3 TEM and ED of two typical samples: TEM (a) and ED (b) of sample A1; TEM (c) and ED (d) of sample N3.

in Fig. 1(a) and (b) could be indexed to the cubic CdS phase with a cell constant of *ca.* 5.406 Å, close to the reported value for CdS in sphalerite (JCPDS No.10–454). The pattern of A3 was different and all the peaks in Fig. 1(c) were indexed to the hexagonal CdS phase with $a = 4.141$ Å and $c = 6.72$ Å, close to the reported data for CdS with wurtzite structure (JCPDS No. 41–1049). Detailed scrutiny reveals that the (002) reflection is the most intense in Fig. 1(c), whereas the (101) reflection should be the strongest peak in the pure wurtzite phase. It is also observed that the strongest peak in Fig. 1(c) is also at the same position as that of the cubic sphalerite phase. Thus we consider the product using carbon disulfide as sulfur source in aqueous solution as being a mixture of wurtzite with sphalerite as a minor component.

The corresponding XRD patterns of the samples N1–N3, which were synthesized in absolute ethanol, are shown in Fig. 2. From the alcohol system, CdS in the sphalerite phase was obtained using sodium thiosulfate as the sulfur source. By contrast, CdS in the wurtzite phase was obtained using carbon disulfide or mercaptoethanol as sulfur sources.

In all of the patterns, broadening of the peaks indicates the nanocrystalline nature of the samples. The crystalline sizes of the samples, which were calculated from the half-width of diffraction peaks using the Scherrer formula, are 3.1, 3.0 and 7.0 nm for samples A1–A3 and 2.5, 10.2 and 9.1 nm for samples N1–N3. The nanocrystalline nature of the products is also reflected by their UV spectra. By comparing the absorption edge of as-prepared CdS nanoparticles with that of bulk CdS in the UV spectrum, an obvious blue shift was detected, indicating the small dimensions of the as-prepared CdS nanocrystallines (SUP 57472).

TEM images and ED patterns of two typical samples are shown in Fig. 3. Fig. 3(a) and (b) refer to sample A1 and Fig. 3(c) and (d) refer to sample N3. It can be seen that the small particles aggregate into secondary particles owing to their extremely small dimensions and high surface energy. Therefore the size and size distribution of the nanoparticles is difficult to determine precisely by simply viewing the TEM image. Careful observation reveals that the products from absolute ethanol are better dispersed and show a narrower size distribution than those from water. Aggregation of the products from aqueous solution is obviously more significant than that in alcohol although the size of crystallites is much smaller from the XRD patterns. This is a common phenomenon in the formation of nanocrystalline CdS by γ-irradiation. From the above, we can conclude generally that solvents with lower polarity may ameliorate aggregation of the nanocrystalline products. The electron diffraction pattern of sample A1 [Fig. 3(b)] is typical for the cubic sphalerite phase and that of sample N3 [Fig. 3(d)] is typical for the hexagonal wurtzite phase. In Fig. 3(b), the three diffraction rings correspond to the (111), (220) and (311) reflections, which is fully consistent with the XRD results. In Fig. 3(d), the diffraction rings also accord well with each reflection of hexagonal wurtzite CdS.

The purity and composition of the products were examined by XPS and the results showed that the products are fairly pure and their compositions were close to the formula of CdS (SUP 57472).

In these γ-irradiation processes, the mechanism of the formation of nanocrystalline sulfide materials is not very clear with few reports speculating upon the transformation of sulfur sources upon γ-irradiation. However, some probable reactions may be proposed. It is clear that as a result of reduction of cadmium ions with hydrated electrons produced in solution by γ-radiation, cadmium ions in lower valence are formed:[17]

$$H_2O \xrightarrow{\gamma\text{-radiation}} e_{aq}{}^-, H_3O^+, H, H_2, OH, H_2O_2 \tag{1}$$

$$e_{aq}{}^- + Cd^{2+} \rightarrow Cd^+ \tag{2}$$

Research on γ-irradiation of carbon disulfide indicates the formation of non-ionic intermediates, possibly as $S^\bullet$ radicals[18] and free sulfur might be liberated when such $S^\bullet$ radicals collide in solution:

$$CS_2 \xrightarrow{\gamma\text{-radiation}} S^\bullet + CS^\bullet \tag{3}$$

However, we do not observe any sulfur impurity in our experiments. Precipitation of CdS probably prevents the formation of sulfur from $S^\bullet$ radicals.

$$S^\bullet + Cd^+ \rightarrow CdS \tag{4}$$

For sodium thiosulfate as the sulfur source, S^{2-} was homogeneously released from its decomposition.[19,20] Research of γ-irradiation on sodium thiosulfate indicates the following radiolytic reaction:[21]

$$2S_2O_3{}^- + 4OH^- + 2H^+ \xrightarrow{\gamma\text{-radiation}} HS^- + 3SO_3{}^{2-} + 3H^+ + H_2O \tag{5}$$

Hayes *et al.* report that aqueous thiols upon γ-irradiation release sulfide ions into the solution.[16]

$$RSH + e_{aq}{}^- \rightarrow R^\bullet + HS^- \tag{6}$$

Mercaptoethanol which contains an SH group may also release HS^- ions under γ-irradiation. For both sodium thiosulfate and mercaptoethanol, HS^- is released upon γ-irradiation of the solution and CdS can be formed as follows:

$$HS^- \rightarrow S^{2-} + H^+ \tag{7}$$

$$Cd^{2+} + S^{2-} \rightarrow CdS \tag{8}$$

In the γ-irradiation process, both the sulfur sources and the solvents influence the formation of CdS with different structures. Generally, lower polarity of sulfur sources and solvents favors formation of the wurtzite structure. Conversely, higher polarity of sulfur sources and solvents favors the formation of the sphalerite structure.

Although both sphalerite and wurtzite are stable phases for cadmium sulfide, the lattice energy of the hexagonal wurtzite arrangement is slightly greater than that of the cubic sphalerite arrangement. In reality, the sphalerite and wurtzite are best regarded as two extremes of a structural spectrum, which ranges from the pure cubic sphalerite to pure hexagonal wurtzite structure.[22] In our experiments, it is reasonable that more energy will be released in reaction (4) where $S^\bullet$ radicals are involved in the formation of CdS. Thus for carbon disulfide in ethanol, which releases $S^\bullet$ radicals upon γ-irradiation, the product is the wurtzite phase. However, an amount of the sphalerite phase appears in aqueous solution, possibly because the radical is easily quenched in water.

For sulfur sources with strong polarity such as sodium thiosulfate, the released energy of reactions (7) and (8) between ions is probably only sufficient to allow the formation of the sphalerite phase.

When the sulfur source is mercaptoethanol, the polarity of which is inbetween that of sodium thiosulfate and carbon disulfide, the solvent plays an important role in the structure of the product; sphalerite in water and wurtzite in anhydrous ethanol.

Conclusions

γ-Irradiation has been successfully used to prepare nanocrystalline CdS in sphalerite and wurtzite forms at room temperature. Sodium thiosulfate, mercaptoethanol and carbon disulfide were used as sulfur sources in both aqueous solution and anhydrous ethanol. The formation of sphalerite and wurtzite can be controlled by using different sulfur sources in different solvents. In general, the sulfur sources and solvents with lower polarity tend to produce the hexagonal wurtzite phase, while those with strong polarity produce the cubic sphalerite phase. TEM images show that the products in anhydrous ethanol are better dispersed, whereas those in aqueous solution aggregate more extensively. Possible mechanisms for the formation of cadmium sulfide in the different systems have been proposed.

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