Sonochemical Synthesis and Phase Control of Nanocrystalline CdS

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Sonochemical reaction has been successfully used to prepare CdS nanocrystalline with either hexagonal or cubic phase structure at room temperature. It was found that the solvent has a great influence on the phase structure. The product was characterized by X-ray diffraction and transmission electron microscope. The possible mechanisms for the formation of CdS nanocrystalline in different solvents are proposed.

In recent years, a larger number of techniques have been developed to permit the controlled synthesis of nanostructured materials, not only the size but also the morphology. The wide band gap II–VI nanoscale semiconductors are of current interest for optoelectronic applications such as light emitting diodes and optical devices.[1,2] Among these materials, CdS is the most interested one owing to its high photosensitivity and potential applications in photoconducting cells.[3] The structures adopted by CdS have also been attracting much attention, and two typical structures are observed: cubic and hexagonal phases, both of them are synthesized at room temperature.

Generally, the synthesis methods for metal chalcogenides involve non-aqueous solvents,[2,4,5] reversed micelles,[6,7] vesicles,[8] zeolites,[9,10] polymer[11] and other methods.[12,13] Recently, Parkin and co-workers reported the synthesis of metal chalcogenides in liquid ammonia or in *n*-butylamine for a prolonged time.[14] It is known that all of the CdS synthesized at above room temperature was either amorphous or cubic and needed to be crystallized or to undergo a phase transition from cubic to hexagonal at higher temperatures (>300 °C).[15] Complete control over the structural properties, such as CdS nanoparticles is needed, because they may hold the key to many future applications.

Recently, sonochemical processing has proved to be a useful technique for generating novel materials with unusual properties.[16] The chemical effects of ultrasound arise from acoustic cavitation, that is, the formation, growth and implosive collapse of a sonochemical bubble in a liquid that produces unusual chemical and physical environments.[16] The extreme conditions thus attained have been exploited to prepare nanoscale metals, metal oxides and nanocomposites.[17–19] Here, we report a convenient one-step route to synthesize CdS nanocrystals via a sonochemical reaction. The whole process is carried out at ambient temperature and pressure. CdS nanocrystalline with either cubic or hexagonal phase can be easily obtained by changing solvent.

In a typical procedure, solutions were prepared by dissolving 1.142 g $CdCl_2 \cdot 2.5H_2O$ (AR grade) and 2.482 g $Na_2S_2O_3 \cdot 5H_2O$ (AR grade) in either 100 mL of doubly distilled water (solution A) or a mixed solution of 23 mL $(CH_3)_2CHOH$ (99%) and 77 mL of doubly distilled water (solution B). Then the two solutions were separately put into two conical flasks with covers. And the flasks were put in a sonication bath. Before irradiation with 40-kHz ultrasonic wave at 100-W output power at room temperature, the flasks were purged with Ar gas to eliminated oxygen. During irradiation, the flowing water was utilized to cool the glass vessel in the bath. After 7 h of sonication, the precipitates were collected and washed in sequence with distilled water and ethanol. Finally, the yellow product was dried in vacuum at 50 °C for 2 h.

The obtained samples were characterized by X-ray diffraction (XRD)(MXP 18 AHF) and transmission electron microscopy (TEM)(Hitachi Model H-800). X-ray photoelectron spectrum (XPS)(VG-ESCALAB-MK-II) was used to examined the chemical composition and purity of the samples.

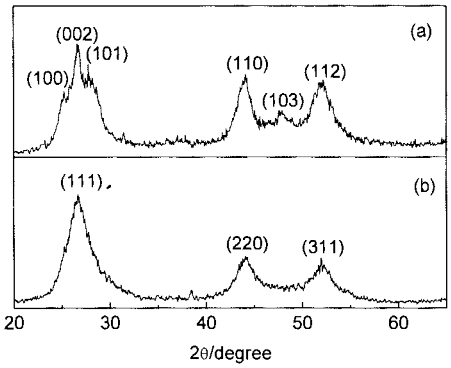

Figure 1. X-ray diffraction patterns of CdS particles synthesized by ultrasonic irradiation in aqueous solution: (a) without and (b) with isopropyl alcohol addition.

Figure 1 shows the XRD patterns of the CdS samples produced by ultrasonic irradiation for 7 h. The solvent was either solution A (Figure 1a, sample A) or solution B (Figure 1b, sample B). All the peaks in Figure 1a can be indexed as hexagonal CdS with lattice parameters a = 4.140 Å and c = 6.726 Å, which are close to the reported values (JCPDS Card File, No. 41-1049). No impurity XRD peaks were detected. While, comparing three peaks in Figure 1b, at about 26.72°, 44.06° and 51.98°, with the data of the JCPDS file (JCPDS Card File, No. 10-454), it was found that the CdS nanoparticles are identified as β-CdS, which belongs to the cubic crystal system. No peaks attributable to other phases were observed. Note the three characteristic peaks at 24.828°, 28.216° and 47.885° for hexagonal CdS disappear from Figure 1b for cubic CdS. The broadening of the peaks indicated that the particles were of nanometer scale. The mean crystallite diameter, d, can be determined from the linewidth of the XRD spectra by the Scherrer formula[20]: $d = 0.94\lambda/(B\cos\theta_B)$, where λ is the X-ray wavelength, B is the full width at half maximum of the diffraction peak, and θ_B is the half angle of the diffraction peak on the 2θ scale. From the formula we found that the average particle size is 5.3 nm for sample A and 3.5 nm for sample B, which are in agreement with that observed from TEM images shown below.

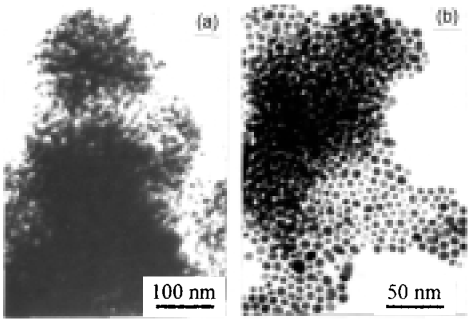

Figure 2. TEM images of CdS particles synthesized by ultrasonic irradiation in aqueous solution: (a) without and (b) with isopropyl alcohol addition.

Figure 2 shows the TEM micrographs of the as-prepared CdS nanoparticles. The particle size for sample A (Figure 2a) is about 8 nm and for sample B (Figure 2b) around 5 nm, which are all slightly larger than that from XRD. Careful observation reveals that the CdS nanoparticles from solution B, i.e., a mixed solution of isopropyl alcohol and distilled water are well dispersed and have a narrow size distribution than those from solution A, i.e., the distilled water. Aggregation of the particles from aqueous solution is obviously more significant than that in the mixed solution. From this result, we can conclude that isopropyl alcohol may ameliorate aggregation of the nanocrystalline particles and the formation mechanisms are different using different solvents.

The XPS analysis (for the spaces limited, the results are not shown here) indicated that the nanoparticles obtained using both the mixed solution and distilled water are all fairly pure and their compositions are close to the formula of CdS.

The above results show that the formation of CdS nanoparticles occurs in solution through sonochemical reaction. A little has been reported about the formation mechanism of CdS nanoparticles in the ultrasonic irradiation processes.[21] We suggest that Cd^{2+} ions would react with S^{2-} ions to give rise to either cubic or hexagonal CdS nanoparticles through the following reactions, which depends on the kind of the solvent.

The primary products of water sonication are the H and OH radicals formed within the collapsing gas bubble[17]:

$$H_2O)))))H\cdot + OH\cdot \qquad (1)$$

In pure aqueous solution, H· and OH· radicals are strong reducing radicals, which are able to reduce the ions or the atoms[22] and take place the reaction (2):

$$S_2O_3^{2-}+2OH\cdot +2H\cdot \rightarrow S^{2-}+2H^+ +SO_4^{2-}+2H_2O \qquad (2)$$

However, when the isopropyl alcohol, which is a scavenger of radicals such as OH·, was added in aqueous solution, the secondary reducing radicals $(CH_3)_2(OH)C\cdot$ was formed via hydrogen abstraction from the $(CH_3)_2CHOH$ by OH· radicals through the reaction (3)[17]:

$$OH\cdot +(CH_3)_2CHOH \rightarrow (CH_3)_2(OH)C\cdot +H_2O \qquad (3)$$

Being a reducing radical, $(CH_3)_2(OH)C\cdot$ reacts with $S_2O_3^{2-}$ ions rapidly to form S^{2-} ions. So S^{2-} was homogeneously released due to the reaction (4):

$$2(CH_3)_2(OH)C\cdot +S_2O_3^{2-} \rightarrow S^{2-}+2H^+ +SO_3^{2-} +2(CH_3)_2CO \qquad (4)$$

$$Cd^{2+}+S^{2-} \rightarrow CdS \qquad (5)$$

Reaction (5) represents the reaction leading to the formation of CdS nanoparticles. In the ultrasonic irradiation process, the sulfur sources from the different solvents would influence the formation of CdS nanoparticles and give the different structures. S^{2-} was homogeneously released from reaction (2) and reaction (4), which forms a hexagonal and cubic CdS by reaction (5), respectively. We also observed that the reaction forming the hexagonal CdS is more rapid than that forming the cubic CdS. It may be due to the fact that sulfur is easier formed by reaction (2) than by reaction (4). The above results show that the solvent has a great influence on the structure and particle size of CdS nanocrystalline. It is known that kinetic factors are important in defining the crystal structure.[23,24] The solvent will influence the dissolution and transmission of ions in solution, and might lead to the different kinetic factors.

In summary, ultrasonic irradiation has been successfully used to prepare hexagonal and cubic CdS nanocrystallites in an aqueous solution with and without isopropyl alcohol addition at room temperature, respectively. The advantage of this method is that it is a simple and efficient way to produce nanocrystallites. By appropriate control of the experimental conditions, we predict that the ultrasonic reduction method may be extended to the preparation of a variety of metal sulfide semiconductor nanoparticles.

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