A convenient ultraviolet irradiation technique for *in situ* synthesis of CdS nanocrystallites at room temperature

C. Y. Wang, X. Mo, Y. Zhou, Y. R. Zhu, H. T. Liu and Z. Y. Chen*

Structure Research Laboratory, Department of Chemistry, University of Science and Technology of China, Hefei 230026, P.R. China. E-mail: wcy@mail.ustc.edu.cn or czy@ustc.edu.cn

CdS nanocrystallites with cubic or hexagonal phase structures have been synthesised at room temperature *via* precipitation of Cd^{2+} ions with homogeneously released S^{2-} ions, generated from the decomposition of thioacetamide by ultraviolet irradiation reduction.

Semiconductor nanoparticles with dimensions comparable to the Bohr radius exhibit strongly size-dependent optical and electrical properties, leading to quantum dot lasers, single electron transistors and a host of other applications.[1] Many studies have focused on the preparation of metal chalcogenide nanoparticles. The synthesis methods for metal chalcogenides involve the direct reaction of metals with sulfur powders under high temperature,[2] the thermal decomposition of molecular precursors containing M–S bonds,[3,4] or the use of poisonous H_2S as the S^{2-} source at higher temperature.[5] Yu *et al.* have reported a new solvothermal approach for fabrication of metal chalcogenides by reaction of metal oxalates with chalcogens in organic media at lower temperatures (100–200 °C).[6,7] The conventional room-temperature synthesis method involves the precipitation of metal ions with Na_2S as the source of S^{2-} ions,[8,9] in which the inhomogeneity at an early stage results in a broadening of the product particle size distribution. Recently, Parkin *et al.* reported a convenient, low-temperature synthesis of metal chalcogenides, in which the metal (Pb, Ag, Zn, and Cd) was reacted with the chalcogen in liquid ammonia for 2–12 h or in *n*-butylamine for 12–72 h to produce highly crystalline PbE, Ag_2E and X-ray amorphous ZnE and CdE (E=S, Se).[10] γ-Irradiation has been used to prepare CdS nanoparticles by homogeneous release of S^{2-} from the decomposition of $Na_2S_2O_3$.[11] It is known that all of the CdS synthesized 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).[12]

Herein, we report the synthesis of CdS nanocrystallites with cubic or hexagonal phase structure at room temperature by utilizing homogenous release of S^{2-} from the decomposition of thioacetamide upon ultraviolet irradiation. It is found that the solvent has a great influence on the phase structure, the product composition and the mean size of the CdS nanocrystallites obtained using this ultraviolet irradiation technique. The technique may be extended to prepare other semiconductor nanoparticles, including ZnS, Ag_2S, PbS, NiS and CuS.

In a typical procedure, two 30 W low-pressure mercury pillar lamps ($\lambda=253.7$ nm) were used as the irradiation source. Analytically pure thioacetamide (TAA), $CdCl_2\cdot2.5H_2O$, sodium dodecyl sulfate (SDS) and isopropyl alcohol were mixed in appropriate proportions in distilled water (sample A) and 95% alcohol (sample B), respectively. The products were obtained by irradiation of the solution. The yellow product was collected and washed with distilled water and absolute alcohol. Finally, the products were dried under vacuum at 50 °C.

The X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of $0.02°$ s^{-1} in the 2θ range 10–70° using a Rigaku D_{max} γ_A X-ray diffractometer with Cu-Kα radiation ($\lambda=0.154178$ nm). Fig. 1 shows the XRD patterns of the CdS samples produced by UV irradiation for 20 h, using $CdCl_2\cdot2.5H_2O$ as the Cd^{2+} source and TAA as the S^{2-} source. The solvents were distilled water (Fig. 1a, sample A) and 95% alcohol (Fig. 1b, sample B), respectively. All three peaks in Fig. 1a, at about 26.8, 43.9 and 52.0°, can be indexed to cubic phase β-CdS by comparison with data from JCPDS file no. 10-454. The broadness of the peaks indicates that the dimensions of the CdS nanoparticles are very small. Employing Scherrer's equation, the mean size of the β-CdS nanocrystallites is estimated to be 6 nm. However, all the peaks in Fig. 1b are indexed to hexagonal phase CdS with cell parameters $a=0.4133$ and $c=0.6728$ nm, which are close to the reported values (JCPDS file no. 41-1049). Furthermore, it is noticeable that the degree of broadening of the peaks in Fig. 1b is greater than that in Fig. 1a, which indicates that the mean size of the CdS nanocrystallites corresponding to Fig. 1b is smaller than that of the product corresponding to Fig. 1a. Employing Scherrer's equation, the mean particle size of the hexagonal phase CdS was estimated to be 4 nm. The synthesis of CdS nanocrystallites may be expressed as follows:[13]

$$CH_3CSNH_2 \xrightarrow{\text{UV irradiation}} CH_3CN + H_2S(\leftrightarrow CH_3CN + 2H^+ + S^{2-}) \quad (1)$$

$$Cd^{2+} + S^{2-} \leftrightarrow CdS \quad (2)$$

The surface analyses of the samples by X-ray photoelectron spectroscopy (XPS) were carried out with a VG-ESCALAB-MK-II instrument. The results obtained by XPS illustrate the presence of elemental Cd and S in a 1.00:0.89 ratio in the surface of sample A, and in a 1.00:0.96 ratio in the surface of sample B. Elemental analyses of the samples were also carried out using a Perkin-Elmer 1100B atomic absorption spectrophotometer and combustion neutration titration. The results
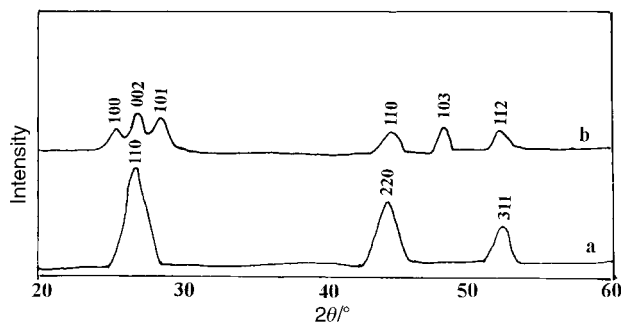
Fig. 1 XRD patterns of the CdS samples produced by UV irradiation for 20 h, using $CdCl_2\cdot2.5H_2O$ as the Cd^{2+} source and TAA as the S^{2-} source. (a) Sample A, using distilled water as solvent; (b) sample B, using 95% alcohol as solvent.
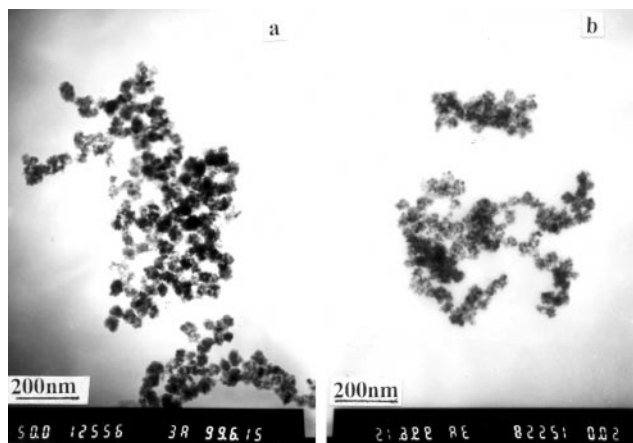
Fig. 2 TEM images of the CdS samples produced by UV irradiation for 20 h, using $CdCl_2 \cdot 2.5H_2O$ as the Cd^{2+} source and TAA as the S^{2-} source. (a) Sample A, using distilled water as solvent; (b) sample B, using 95% alcohol as solvent.

obtained show the presence of elemental Cd and S in a 1.00 : 0.95 ratio in sample A, and in a 1.00 : 0.98 ratio in sample B.

TEM images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Fig. 2a and b present the TEM images of the CdS samples, corresponding to Fig. 1a (sample A) and Fig. 1b (sample B), respectively. The images show that the CdS nanoparticles are well and homogeneously dispersed with a narrow size distribution in both sample A (Fig. 2a) and sample B (Fig. 2b). The observed sizes of the CdS particles are about 5–6 nm in sample A (Fig. 2a), and about 4–5 nm in sample B (Fig. 2b), respectively. The results correspond well with the values calculated by the XRD line-width technique.

The results above all show that the solvent has a great influence on the structural phase, product composition and mean size of the CdS produced. The stability of the initially produced CdS crystal nucleus is influenced by the size of the nucleus and the dielectric constant of the reaction medium. The smaller sized nucleus is more unstable and easier to dissolve because of the lower binding energy of the smaller crystal nucleus. The ions coming from the dissolution of the smaller crystals are crystallized on the bigger nucleus *via* an aging procedure. In principle, the aging effects could be inhibited in a solvent with a lower dielectric constant due to the higher dissolution energy. This directly results in a reduction in the mean size of the particles produced. The above mechanism is similar to particle growth by Ostwald ripening.[14,15]

It is well known that the only structural differences between hexagonal CdS and cubic CdS are in the close-packing model;

the former has an ABAB structure, whereas the latter is ABCABC packed.[16,17] It is considered that kinetic factors are important in defining the crystal structure.[18] The difference in properties between the solvents could influence the dissolution and transmission of ions in solution, which may lead to the different kinetic processes. Especially since the effect of the solvent is more obvious in a liquid–solid reaction system.[19]

In summary, we have succeeded in synthesizing cubic and hexagonal CdS nanocrystallites in aqueous and 95% alcohol solution, respectively, at room temperature, using an ultraviolet irradiation reduction technique. The mean size of the hexagonal particles is smaller than that of cubic particles. The present ultraviolet irradiation reduction technique may be extended to prepare other semiconductor nanoparticles including ZnS, Ag_2S, PbS, NiS and CuS.

Notes and references

1 R. F. Service, *Science*, 1996, **271**, 920.
2 C. Kaito, Y. Saito and K. Fujita, *J. Cryst. Growth*, 1989, **94**, 967.
3 D. M. Milhemy and E. Matijevic, *J. Chem. Soc., Faraday Trans.*, 1984, 563.
4 B. Ludoph and M. A. Malik, *Chem. Commun.*, 1998, 1849.
5 N. L. Pickett, D. F. Foster and D. J. Cole Hamilton, *J. Mater. Chem.*, 1996, **6**, 507.
6 S. H. Yu, Y. S. Wu and J. Yang, *Chem. Mater.*, 1998, **10**, 2309.
7 S. H. Yu, J. Yang and Y. S. Wu, *J. Mater. Chem.*, 1998, **8**, 1949.
8 N. Herron and Y. Wang, *J. Am. Chem. Soc.*, 1990, **112**, 1322.
9 W. Chen, Z. Liu and Z. Wang, *Solid State Commun.*, 1996, **100**, 101.
10 G. Henshaw, I. P. Parkin and G. J. Shaw, *Chem. Commun.*, 1996, 1095.
11 Y. D. Yin and X. L. Xu, *Chem. Commun.*, 1998, 1641.
12 R. J. Bandaranayak and G. W. Wen, *Appl. Phys. Lett.*, 1995, **67**, 831.
13 T. D. Sugimoto and G. E. Dirige, *J. Colloid Interface Sci.*, 1995, **716**, 442.
14 R. Rossetti, R. Hull and J. M. Gibson, *J. Chem. Phys.*, 1985, **82**, 552.
15 R. Rossetti, R. Hull and J. M. Gibson, *J. Chem. Phys.*, 1984, **80**, 4464.
16 R. Sato, *Nature*, 1959, **184**, 2005.
17 W. O. Milligan, *J. Phys. Chem.*, 1943, **47**, 537.
18 H. Miniti and M. Eyal, *Chem. Phys. Lett.*, 1991, **183**, 277.
19 W. S. Sheldrick and M. Wachhold, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 206.

Communication a908983g