

Room Temperature Synthesis of Cubic Nanocrystalline CdSe in Aqueous Solution

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Received November 12, 1999; in revised form February 1, 2000; accepted February 3, 2000

Reaction of an alkaline selenium solution with an aqueous solution of cadmium complex produces cubic nanocrystalline CdSe with an average particle size of 5 nm at room temperature under atmospheric pressure. The product was characterized through XRD, TEM, and XPS. The alkaline selenium solution makes CdSe crystallize well in aqueous solution. The use of cadmium complex instead of cadmium ion as a reagent can greatly reduce the byproduct. Furthermore the synthesis is performed conveniently and safely. © 2000 Academic Press

Key Words: selenium source; cadmium complex; precipitation; nanocrystalline materials; cadmium selenide.

INTRODUCTION

Increasing attention is being paid to II–VI materials because of their potential importance as nonlinear optical materials (1, 2) and quantum size effect semiconductors (3, 4). These materials are chemically and structurally simple and are therefore attractive as synthesis targets in model studies.

Traditionally, cadmium selenide is prepared through solid state reaction between elemental cadmium and selenium at high temperature (5, 6). So far considerable progress has been made in the synthesis of II–VI semiconductor compounds (7–11). However, these methods involved using either toxic organometallic precursors, toxic gas H₂Se, or a complex process. Since these II–VI materials form defects and interdiffuse at temperatures above ca. 500°C, low temperature growth is a major consideration. Usually, a solution-phase synthesis can reduce the reaction temperature. The common reaction of Na₂E (E = S, Se, Te) and CdCl₂ in aqueous solution produced amorphous CdE, which needed to be crystallized at 200–500°C (12). Therefore nonaqueous solvent has been chosen to synthesize CdE crystallites in recent studies. A room temperature liquid ammonia route has been reported to prepare metal chalcogenides, but the

obtained products CdE were still X-ray amorphous (13). In ethylenediamine CdE nanorods were reported to have been synthesized through a solvothermal method in the temperature range 120–180°C (14, 15).

In this paper, we choose an alkaline selenium solution as a selenium source and have successfully synthesized cubic nanocrystalline CdSe in aqueous solution at room temperature under atmospheric pressure. The synthesis reaction proceeds rapidly and safely.

EXPERIMENTAL SECTION

All reagents were of 99.9% purity from Shanghai Chemistry Co. and were used without further purification. Manipulations and reactions were carried out in air. The alkaline selenium aqueous solution was prepared as follows: 0.56 mol of NaOH and 0.0025 mol of elemental Se were added to 50 ml of distilled water. The mixture reached about 80°C in a few minutes because the dissolution of NaOH in water was an exothermic process and the produced heat can guarantee the dissolution of elemental Se.

CdCl₂·2.5H₂O (0.0026 mol) was added to 10 ml of EDTA aqueous solution (0.3 M) and then the mixture was combined with the alkaline selenium aqueous solution through rapid stirring. A great amount of red-brown precipitate occurred. After being filtered and washed with dilute HCl solution (0.1 M) and distilled water, the precipitate was dried under vacuum at 50°C for 4 h. The final product was collected for characterization.

The X-ray powder diffraction (XRD) pattern was recorded on a Rigaku D/max-rA rotation anode X-ray diffractometer with Ni-filtered CuK α radiation. The morphology and particle size of crystallites were determined by transmission electron microscopy (TEM) and the degree of crystallinity was confirmed by the selected area electron diffraction pattern. The images were taken with Hitachi H-800 transmission electron microscope. Further evidence for the formation of CdSe was detected by X-ray

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photoelectron spectra (XPS) recorded on an ESCALab MKII instrument with $AlK\alpha$ X-ray as the excitation source. Optical absorption spectra were collected at room temperature on a Shimadzu ultraviolet-visible (UV-vis) absorption diode array spectrometer using 1-cm quartz cuvettes. Samples were prepared by dispersing CdSe nanocrystallites in alcohol.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of the product CdSe. All peaks in the pattern can be indexed to cubic CdSe. After refinement, the cell constant is calculated to be $a = 0.61$ nm, close to the reported value (16). No impurity phase is detected by XRD. The broadening of these diffraction peaks indicates that the sample may be nanosized. Estimated from the Scherrer formula, the average particle size of the sample is 5 nm.

A TEM image (Fig. 2) of a typical sample of nanocrystalline CdSe shows that the particles are spherical and slightly agglomerated. The particle size ranges from 4 to 7 nm, which is consistent with the XRD analysis. The selected area electron diffraction pattern furthermore identifies that the nanocrystalline CdSe is a cubic blende structure. From the pattern, the reflections of planes 111, 220, and 311 are clearly seen.

Figure 3 shows the results of XPS analysis. The C 1s line of carbon contamination appears at 284.8 eV and all binding energies are corrected accordingly. No obvious peaks for cadmium oxide, hydroxide, or selenium oxide are observed indicating high purity of the product. The two strong peaks at 405.45 and 54.20 eV correspond to Cd $3d_{5/2}$ and Se

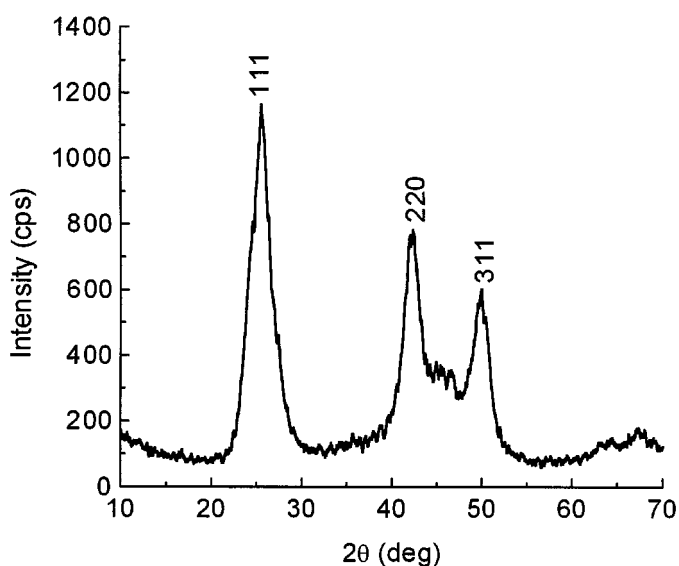


FIG. 1. X-ray powder diffraction (XRD) pattern of the product CdSe.

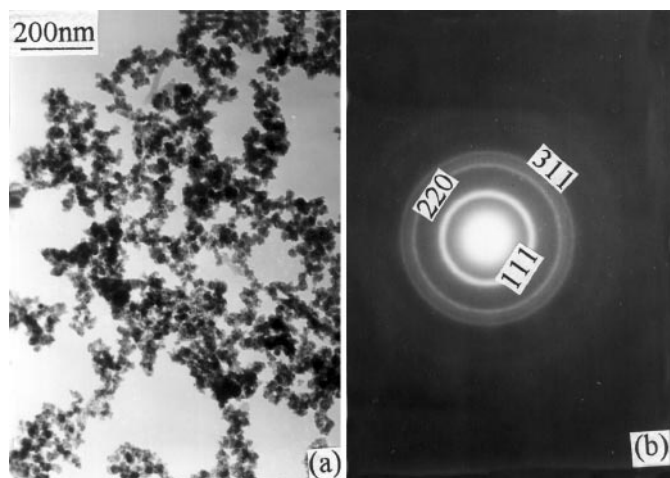
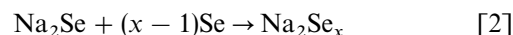
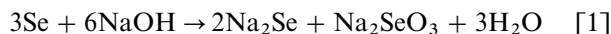


FIG. 2. Transmission electron microscopy (TEM) image (a) and selected area electron diffraction pattern (b) of the product CdSe.

$3d$ binding energy for CdSe, respectively. This result is close to that of bulk CdSe (17).

Figure 4 shows the UV-vis absorption spectrum of the obtained CdSe nanocrystallites. The absorption band yielded an onset near 660 nm and absorption peak at 620 nm, which was shifted from 716 nm bulk band gaps. The result shows the effect of quantum confinement, which is consistent with that reported by Murray *et al.* (8).

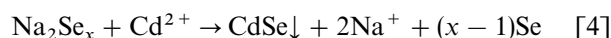
In our route, the reactions may take place as follows: Dissolution reaction of selenium



Complex reaction



Precipitation reaction



The selenium source is a deep red aqueous solution containing Se^{2-} , $[\text{SeO}_3]^{2-}$ and Se_x^{2-} ions. The solution is only stable with excessive OH^- ($[\text{OH}^-] > 10$ M) at room temperature. If it is diluted with water, Se will precipitate. Therefore the volume of cadmium complex solution is much smaller than that of the alkaline selenium solution in order to avoid much dilution of the selenium source.

When the alkaline selenium solution reacts with the complex solution, a red-brown precipitate of CdSe occurs at

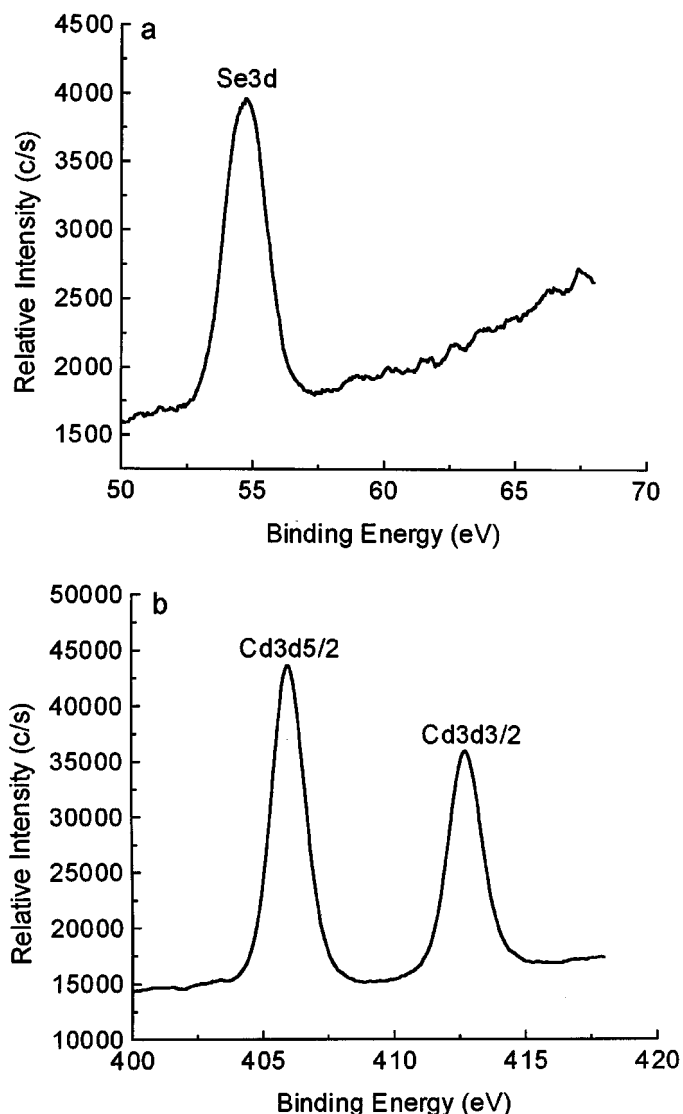


FIG. 3. X-ray photoelectron spectra (XPS) analysis of the product CdSe: (a) Se 3d; (b) Cd 3d.

once. CdSeO_3 has not been found in the product through XRD and XPS analysis. In Eq. [4], the freshly produced selenium is active and can dissolve in the excessive alkaline solution at once. Equations [4] and [5] indicate that cadmium ion Cd^{2+} is the direct reagent for preparing CdSe. In fact at the beginning of the reaction, only a very small amount of Cd^{2+} exists in the cadmium complex solution. With the precipitation of CdSe, the equilibrium state of the complex is destroyed and free Cd^{2+} ion continuously dissociating from the complex reacts with $[\text{Se}_x]^{2-}$ or Se^{2-} . The reason for using cadmium complex instead of Cd^{2+} as a reagent is that cadmium complex is much more stable than Cd^{2+} in alkaline solution and can reduce the byproduct of cadmium hydroxide greatly. With appropriate excess

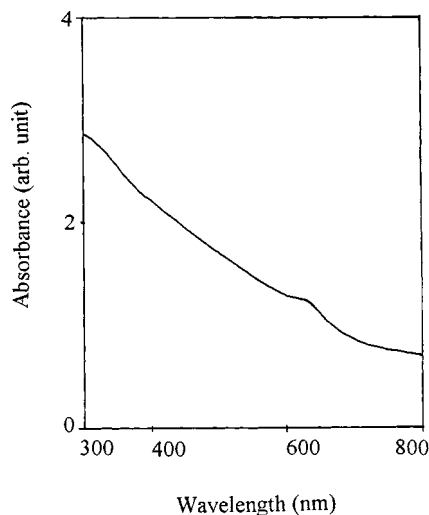


FIG. 4. UV-vis absorption spectrum of the obtained CdSe nanocrystallites.

of cadmium complex, the byproduct will not be formed. Even if a small amount of $\text{Cd}(\text{OH})_2$ occurs in the final product, it can be removed by washing with dilute HCl (0.1 M) solution, which cannot decompose CdSe. At the end of reactions, excessive cadmium complex can be easily removed by washing with water. If reagent elemental Se is excessive, it will precipitate in the product in post-treatment of washing and be difficult to remove.

CONCLUSION

In summary, cubic nanocrystalline CdSe with an average particle size of 5 nm has been successfully obtained at room temperature under atmospheric pressure. The alkaline selenium solution makes the final product crystallize well in aqueous solution. The cadmium complex as a reagent reduces the byproduct greatly. The technique established in aqueous solution makes the synthesis of nanocrystalline CdSe convenient, economic, and safe.

ACKNOWLEDGMENT

This work is supported by the Chinese National Foundation of Natural Science Research and Climbing Program Research-National Foundation Project.

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