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Solvothermal Route to Nanocrystalline CdSe

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THIS WORK IS DEDICATED IN THE MEMORY OF DR. JEAN ROUXEL

Nanocrystalline CdSe semiconductor was synthesized through a novel solvothermal process, in which $CdCl_2$, Se, and Na reacted at 120°C for 6 h in an autoclave, and ethylenediamine was used as a solvent. An XRD pattern indicated a hexagonal CdSe phase. TEM imaging showed that the product consisted of homogeneous granular particles with an average size of about 7 nm. Photoluminescence spectra of the 7-nm CdSe showed a 0.3-eV blue shift compared with that of the bulk materials, indicating its quantum confinement. © 1999 Academic Press

INTRODUCTION

In recent years, the synthesis and characterization of chalcogenides of different groups have attracted considerable attention due to their important nonlinear optical properties (1), photoluminescent properties (2), quantum size effects (3), and other important physical and chemical properties (4).

Considerable progress has been made in the synthesis of group II–IV semiconductor crystallites or nanocrystallites. Conventionally, Bridgman method, solid-state reaction, vapor–liquid methods were used to prepare chalcogenides including CdSe. However, the above methods require a high temperature (> 500°C). Using organometallic precursors was another route to CdSe (5, 6), but most of them were toxic, easy to hydrolyze and oxidize, and hard to deal with. Recently, I. P. Parkin reported that many kinds of chalcogenides have been obtained at room temperature in liquid ammonia. However, the reactants must be dissolved and the liquid ammonia evaporates at -77°C. Furthermore, reactions in liquid ammonia explode easily and all operations should be conducted with blast proofing and behind a safety screen (7, 8). Here we report a novel solvothermal route to nanocrystalline CdSe in ethylenediamine at 120°C for 6 h:

$$CdCl_2 + Se + 2Na \rightarrow CdSe + 2NaCl.$$

This one-step method was simple and convenient and was carried out at relatively lower temperature. It does not require the preparation of hydrolysis $Na(K)_2Se$, toxic H_2Se, or organometallic precursors, which were usually used in preparing selenides.

EXPERIMENTAL

In our experiments, an appropriate amount of analytically pure $CdCl_2 \cdot 2.5H_2O$ and Se powder were put into a 100 ml stainless autoclave with a Teflon liner, then the autoclave was filled with ethylenediamine up to its 80% volume. The autoclave was maintained at 120°C for 6 h just after excessive sodium had been put into it, then it was cooled to room temperature naturally. A dark red precipitate was collected and washed with absolute ethanol and distilled water in sequence to remove the possible excessive Na and other impurities. The final product was dried in vacuum at 80°C for 2 h.

The sample was characterized by X-ray powder diffraction (XRD) patterns employing a scanning rate of $0.02° \, s^{-1}$ in the 2θ range from 20° to 80°, using a Japan Rigaku D/max γA X-ray diffractometer equipped with graphite-monochromatized Cu$K\alpha$ radiation ($\lambda = 1.54178$ Å). The X-ray photoelectron spectra (XPS) were recorded on a VGESCALAB MKII X-ray photoelectron spectrometer, using nonmonochromatized Mg$K\alpha$ X-ray as the excitation source. The morphology and particle size was determined by transmission electron microscopy (TEM). The TEM images were taken with a Hitachi H-800 transmission electron microscope. The photoluminescence (PL) spectra of the as-prepared CdSe were measured in a Hitachi 850-fluorescence spectrophotometer with a Xe lamp with 488-nm excitation. The excitation spectra was recorded with the emission wavelength at 600 nm. The spectra were collected at room temperature using 1-cm quartz cuvettes. The samples were prepared by dispersing CdSe nanocrystallites in distilled water.

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RESULTS AND DISCUSSION

A typical XRD pattern of as-prepared nanocrystalline CdSe is shown in Fig. 1. All peaks in the XRD pattern can be indexed to the hexagonal cell of CdSe with the cell constants $a = 4.300$ Å, $c = 7.010$ Å, which are close to the report values (9). The grain size of the sample, which is calculated from the half-width of diffraction peaks using the Scherrer equation, is about 7 nm. Further evidence for the formation of CdSe and the purity of the sample can be examined by the XPS measurement of the product. No obvious peaks of metal or metal oxide, sodium ion, and chloride are observed in the survey spectra and the compositions of the products are close to the formulae of CdSe.

Figure 2 is a typical TEM image of the nanocrystalline CdSe. In the figure, one can see that the nanocrystalline CdSe grains are homogeneous and granular with the average size of around 7 nm, which accords well with XRD results.

The quality of the product is influenced by several factors, such as solvents, reaction temperature, and heating time. In this experimental process, a slightly excessive amount of sodium is essential to ensure the quality of CdSe. The excessive sodium is removed by absolute ethanol in the washing procedure. Otherwise, if the selenium powder is excessive, it is difficult to remove from the final product and there are strong reflection peaks of selenium in the XRD patterns of the product, which greatly decreases the purity of the product. The optimum condition for synthesizing the pure phase of CdSe is 120°C for 6 h. However, it is found that a temperature higher than 160°C or a time longer than 12 h has no influence on the yield and quality of the products, but results in an increase in the particle size. Lower temperature or shorter time leads to an incomplete reaction.

Different solvents were tested in our experiments and the results revealed that the selection of solvents is the most important and influential factor on the quality of nanocrystalline CdSe. Ethylenediamine was chosen as solvent because its N-chelating behavior makes it a strong donor ligand, and it plays an important role in the formation of nanocrystalline CdSe grains. The possible growth mechanism of CdSe is that ethylenediamine binds to and stabilizes the Cd(II) and produces a chelate compound. The solubility of $CdCl_2$ in ethylenediamine increased while Cd(II) tended to enter and disperse in the solution, which increases the activity of Cd(II), promotes the reactions, and controls the nucleation of CdSe. This makes the reaction temperature and grain size decrease greatly, and furthermore the solvothermal method is totally different from the solid-state reactions. If the reaction takes place in other solvents, such as benzene, toluene, or tetrahydrofuran, which have no chelation, a pure nanocrystalline CdSe semiconductor cannot be obtained. Using these solvents, greater amounts of reactants

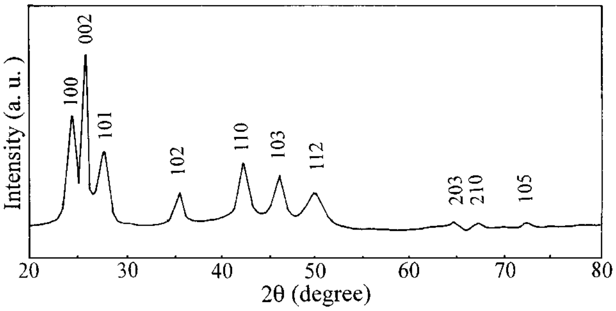

FIG. 1. XRD pattern of the nanocrystalline CdSe.

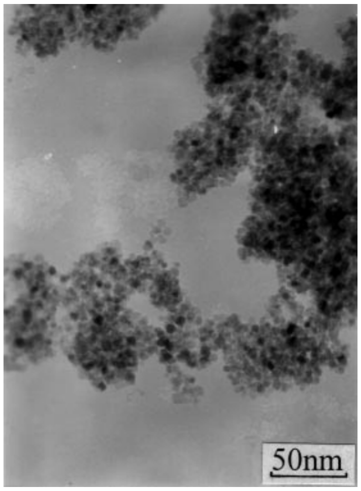

FIG. 2. TEM microphotograph of the nanocrystalline CdSe.

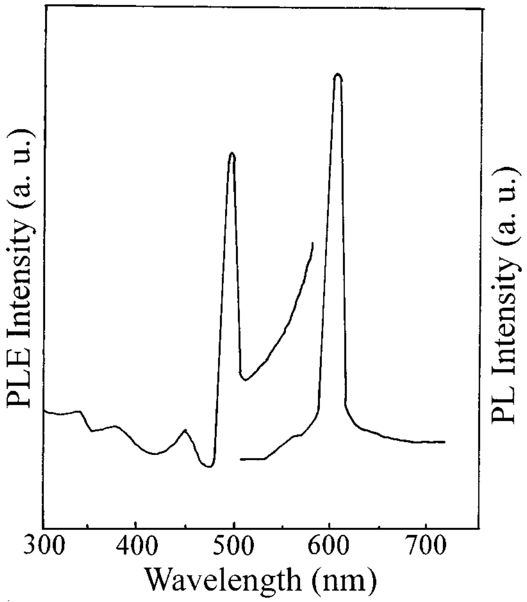

FIG. 3. PL spectra of the nanocrystalline CdSe.

remained unreacted in the final products even under much higher temperature and longer time, and the quality of the resulting products was low.

Figure 3 shows the room temperature photoluminescence spectrum of the 7-nm diameter CdSe crystallites and compares it with its excitation spectrum. The PL spectrum consists of one sharp emission feature at 600 nm, which has an obvious blue shift compared with that of bulk materials (10, 11), indicating its quantum confinement. The sharp emission feature suggests the highly monodisperse samples. The blue shift of the lowest excited state energy can be attributed to the quantum size effect, due to the confinement of electrons and holes. The 0.3-eV blue shift in the PL spectrum is in good agreement with its effective Bohr radius of exciton of 4.5 nm.

CONCLUSIONS

In summary, 7-nm CdSe semiconductor was synthesized at 120°C for 6 h through solvothermal process. This one-step method was carried out under quite milder conditions. Ethylenediamine was used as a solvent and it mediated the formation of CdSe grain. As-prepared CdSe was characterized by XRD, TEM, and XPS and the results revealed that the CdSe particles were granular and homogenous with an average size of about 7 nm. No impurities were detected. Photoluminescence spectra of the 7-nm CdSe showed a 0.3-eV blue shift compared with that of the bulk materials, indicating its quantum confinement.

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