

Preparation of PbSe nanoparticles by electron beam irradiation method

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Abstract. A novel method has been developed by electron beam irradiation to prepare PbSe nanoparticles. 2 MeV 10mA GJ-2-II electronic accelerator was used as radiation source. Nanocrystalline PbSe was prepared rapidly at room temperature under atmospheric pressure without any kind of toxic reagents. The structure and morphology of prepared PbSe nanoparticles were analysed by X-ray diffraction, transmission electron microscope and atomic force microscope. The results indicated that the obtained materials were cubic nanocrystalline PbSe with an average grain size of 30 nm. The optical properties of prepared PbSe nanocrystalline were characterized by using photoluminescence spectroscopy. The possible mechanism of the PbSe grain growth by electron beam irradiation method is proposed.

Keywords. Lead selenide; nanoparticle; electron beam; irradiation.

1. Introduction

Recently, the synthesis of binary metal selenides of group IV has been investigated intensively for their unique semiconducting properties as narrow-bandgap semiconductors and their extensive commercial applications such as thermoelectric cooling materials, optical filter, optical recording materials, solar cell materials, superionic materials, sensor and laser materials (Mongellaz *et al* 1994; Wang *et al* 1999; Lakshmikumar and Rastogi 1994). Many methods have been used to prepare metal selenides including solid-state reaction (Bonnear *et al* 1991), self-propagating high-temperature synthesis (Parkin 1996), sonochemical method (Zhu *et al* 2000a), electrochemical method (Xu *et al* 2000), organometallic precursors (Murray *et al* 1993) and chemical bath deposition (Yamamoto *et al* 1998) and so on. Finding a convenient, mild, and efficient method for the preparation of nanocrystalline selenides attracts considerable attention.

Lead selenide is a narrow gap semiconductor with unique electrical, optical and magnetic properties. It has important applications in many fields, such as IR detectors and Pb²⁺ ion-selective sensors (Yamamoto *et al* 1998; Dashevsky *et al* 2002). PbSe has been prepared by various methods such as chemical bath deposition (Ding *et al* 2002), vacuum deposition (Das *et al* 1990), electro deposition (Saloniemi *et al* 1998), sonochemical method (Zhu *et al* 2000a), microwave heating (Zhu *et al* 2000b), sol-

vothermal (Xie *et al* 2000) and hydrothermal (Wang *et al* 2001). However, these methods usually require high temperature, long reaction time, or toxic reagents.

In this paper, we report an electron beam irradiation method to synthesize PbSe nanoparticles by a very simple reaction. 2 MeV 10mA GJ-2-II electronic accelerator was used as radiation source. Pb(Ac)₂ and Se powder reacted under different radiation doses, and the optimal experimental conditions were studied. Nanocrystalline PbSe was prepared rapidly at room temperature under atmospheric pressure without any kind of toxic reagents. The structure and morphology of prepared PbSe nanoparticles were analysed by X-ray diffraction (XRD), transmission electron microscope (TEM) and atomic force microscopy (AFM). The sizes of the crystallites as prepared were estimated by Debye–Scherrer formula according to XRD spectrum. The optical properties of prepared PbSe nanocrystalline were characterized by using photoluminescence spectroscopy, and the bandgap energy of nanocrystalline PbSe was obtained by using the equation of Bardeen (Bardeen *et al* 1956). The advantages of this process are that it is a simple, fast, efficient method without the use of any toxic reagent for producing nanoparticles.

2. Experimental

2.1 Materials

Lead acetate (Pb(Ac)₂·3H₂O), Se powder, polyvinyl alcohol (PVA), potassium hydroxide (KOH), and isopropyl

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alcohol (IPA) (all from the Shanghai Chemical Factory, Shanghai, China) were used for the preparation of PbSe.

2.2 Preparation of PbSe nanoparticles

First, 0.2 mol/L $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ aqueous solution, 10 ml, was dispersed adequately in 5 ml 5 wt% polyvinyl alcohol. 0.157 g Se powder and 28 g KOH was put into 40 ml distilled water and reacted adequately. Subsequently, the compound was added slowly into Pb^{2+} solution with churning up continuously. 3 ml IPA was added and dispersed adequately, which acted as scavenger of oxidative radicals (OH^\cdot). Then the mixed solution was put into sealed plastic bag. A GJ-2-II electronic accelerator (Shanghai Xianfeng Co. Ltd) was used to generate electron beams at 2 MeV 10 mA conditions. The prepared solutions were irradiated under electron beam at different doses. Figure 1 shows the process of electron beam irradiation. After irradiation, the suspension colloids were

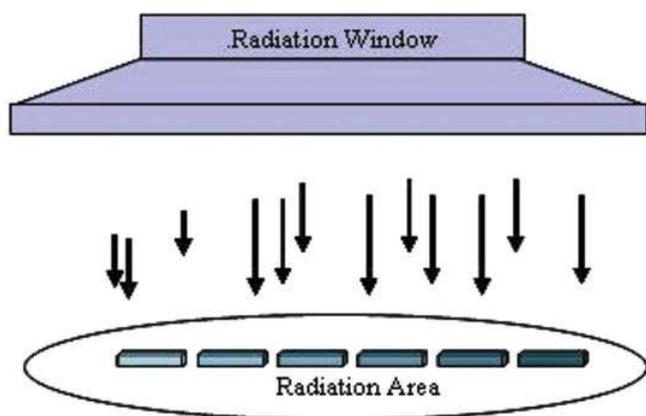


Figure 1. Schematic illustration of electron beam radiation process.

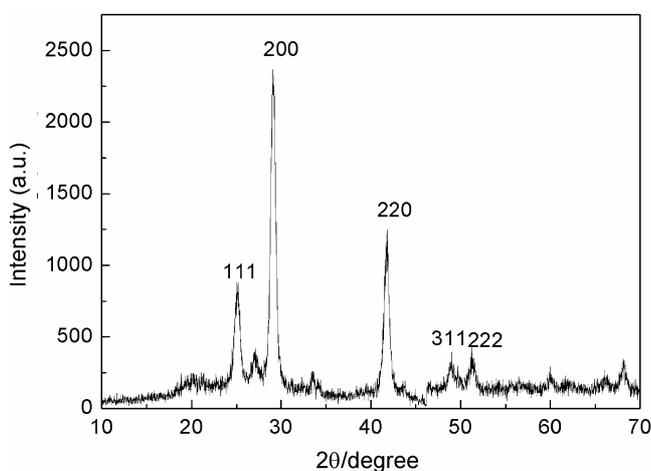


Figure 2. XRD pattern of as-prepared PbSe nanoparticles under 350 kGy irradiation dose.

kept for several hours to allow precipitation. A black precipitate was collected and washed with anhydrous ethanol and then distilled water to remove by-products. The final product was dried in vacuum at 60°C for 1 h.

2.3 Characterization

The XRD pattern was recorded on a Rigaku D/Max-2200 X-ray diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), employing a sampling width of 0.02° in the 2θ range from $0-70^\circ$. The crystallite size was calculated from the X-ray diffraction spectrum using the Scherrer equation. To examine the morphology and particle size of the products, TEM and selected area electronic diffraction (SAED) image were taken on a Hitachi H-800, using an acceleration voltage of 200 kV. In order to study the fine structure of the powder, the surface morphology of the powder was also examined by a Nanofirst-3000 AFM. Photoluminescence spectroscopy (Shanghai Analysis Instrument Plant 970CRT) was used to observe the optical properties.

3. Results and discussion

Figure 2 shows the XRD pattern of PbSe obtained under 350 kGy irradiation dose. The XRD peaks were at $2\theta = 24.88^\circ, 29.10^\circ, 41.82^\circ, 49.02^\circ$ and 51.26° . All peaks corresponded to the reflections of the cubic structure of PbSe (JCPDS 06-0354). No impurity XRD peaks such as PbSeO_3 and Pb were detected. The broadening of the peaks indicated that the particles were of nanometer scale. The cell constant, $a = 6.122 \text{ \AA}$, calculated from the XRD pattern of as-prepared nanocrystalline PbSe was consistent with the reported value, $a = 6.124 \text{ \AA}$. The grain size of the sample, which was calculated from the half-width of the diffraction peaks using the Scherrer equation, was about 24 nm.

TEM micrograph gives the morphology of the nanocrystallites. Figure 3(a) shows the TEM micrograph of as-prepared PbSe nanoparticles under 350 kGy irradiation dose. The particles were homogeneous and spherical. The sample was agglomerated slightly, but a few separated particles still could clearly be observed in the image. The particle size ranged from 20–40 nm. This result was in good agreement with XRD result. The selected area electron diffraction (SAED) pattern in figure 3(b) furthermore indicated that the nanocrystalline PbSe had a good crystallinity. The SAED pattern obtained from these particles showed three faint rings with d values of 3.06, 2.16 and 1.41. These values corresponded to the reported d values of 3.06 (2 0 0), 2.17 (2 2 0) and 1.40 (3 3 1), respectively (JCPDS 06-0354).

AFM was also used to investigate the morphology and roughness of a nanometer-order of magnitude in an area up to $1 \mu\text{m}^2$. Figure 4(a) shows the representative AFM

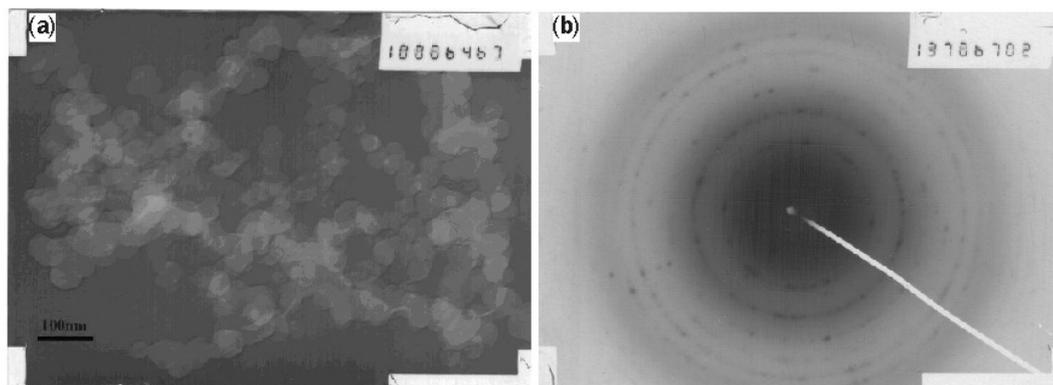


Figure 3. (a) TEM micrograph of as-prepared PbSe nanoparticles and (b) SAED pattern of as-prepared PbSe nanoparticles under 350 kGy irradiation dose.

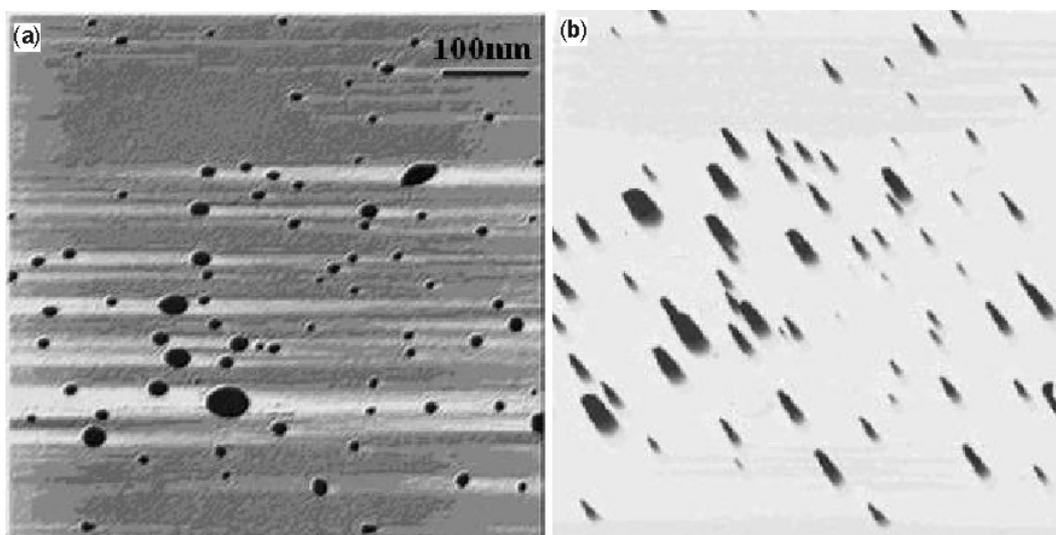


Figure 4. (a) Representative AFM image of as-prepared PbSe nanoparticles and (b) the three-dimensional AFM image of as-prepared PbSe nanoparticles under 350 kGy irradiation dose.

image of PbSe nanoparticles under 350 kGy irradiation dose. It could be seen that the powders were spherical with a mean size of about 30 nm. Figure 4(b) is a three-dimensional AFM image of the same sample. All island-like grains were strongly elongated in one direction, and were dispersed uniformly.

Semiconductor nanoparticles generally exhibit threshold energy in the optical absorption measurement due to the size-dependent bandgap structure, which is reflected by the blue shifting of the absorption edge with decreasing particle size. Figure 5 shows the photoluminescence spectra of as-prepared nanocrystalline PbSe dispersed in anhydrous ethanol and unirradiated mixed solution. The spectrum showed the emission spectrum under PL excitation at 300 nm with the range of 390–500 nm at a scan rate of 50 nm/min. There was no obvious PL peak on the spectrum of unirradiated mixed solution, but the strong PL peak of as-prepared nanocrystalline PbSe was de-

tected around 420 nm. In order to determine the bandgap of as-prepared nanocrystalline PbSe, the equation of Bardeen *et al* (1956) was used. The equation relates the absorption coefficient, A , with incident photon energy, $h\nu$, as: $Ah\nu = K(h\nu - E_g)^{n/2}$, where $n = 1$ and 4 for the direct and indirect band transitions, respectively. The bandgap energy of PbSe nanocrystalline was obtained as 2.79 eV. The bandgap energy of as-prepared nanocrystalline PbSe was larger than bulk PbSe (0.29 eV). The optical absorption showed a clear blue shifting due to the size quantization of nanomaterials.

The effects of irradiation dose on the formation of PbSe nanocrystalline were discussed. PbSe nanoparticles were obtained under different irradiation doses (250 kGy, 300 kGy, 350 kGy, 400 kGy). The structure of as-prepared products was analysed by X-ray diffraction. Figure 6 shows the XRD patterns of products obtained under different irradiation doses. XRD patterns of samples obtained

under 250 kGy and 300 kGy irradiation doses indicated that the samples were a mixture, and the samples consisted of PbSe and PbSeO₃. XRD pattern of sample obtained under 400 kGy irradiation dose indicated that the sample was also a mixture, and the sample consisted of PbSe and Pb. The as-prepared sample under 350 kGy irradiation dose is proved to be pure PbSe. Irradiation dose played an important role in preparing PbSe nanocrystalline.

The possible mechanism of the PbSe grain growth by electron beam method is described as follows. When Se powder reacted with OH⁻, SeO₃²⁻ and Se²⁻ were formed. Irradiation of water by electronic accelerator produces the hydrated electrons, e_{aq}⁻ (Woods et al 1994). Because the

standard electrochemical potential of hydrated electron e_{aq}⁻ is -2.77 V and the standard potential of SeO₃²⁻/Se²⁻ is -0.37 V, SeO₃²⁻ could be reduced to Se²⁻ by hydrated electron. Then Pb²⁺ and Se²⁻ could form PbSe. As a solvent, PVA played an important role in the nucleation of nanocrystalline PbSe. Before electron beam irradiation, PVA binds with Pb²⁺ to form the chelate complex, which made Pb²⁺ disperse adequately in the solution. While irradiating, the chelate bond was disrupted by the high energy of electron beam, then Pb²⁺ was released, which controlled the nucleation of PbSe.

When the samples were prepared under 250 kGy and 300 kGy irradiation doses, SeO₃²⁻ could not be reduced to Se²⁻ completely. Some SeO₃²⁻ might react with Pb²⁺ to form PbSeO₃. When the samples were prepared under 400 kGy irradiation dose, plus e_{aq}⁻ could react with Pb²⁺, and Pb²⁺ was reduced to Pb (the standard electrochemical potential of Pb²⁺/Pb -0.126 V).

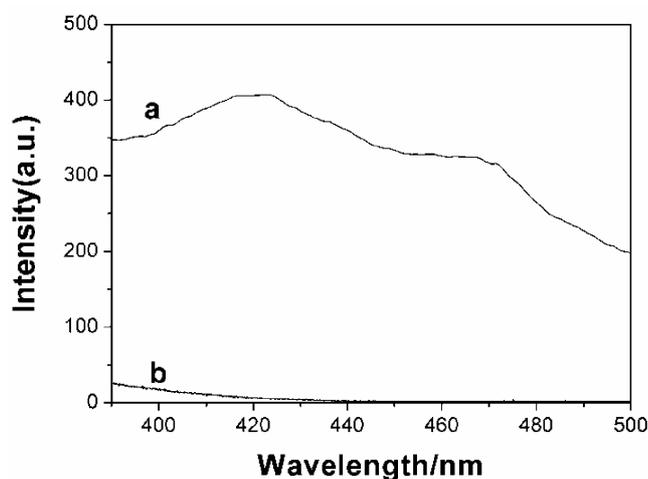


Figure 5. a. Photoluminescence spectra of as-prepared PbSe nanoparticles under 350 kGy irradiation dose and b. unirradiated mixed solution.

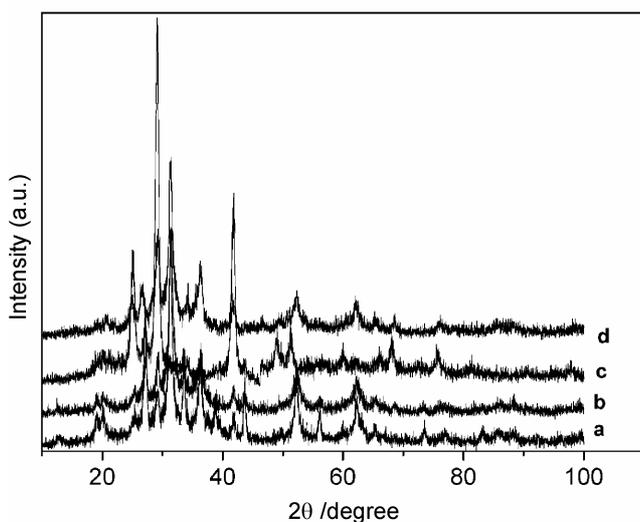


Figure 6. XRD pattern of as-prepared PbSe nanoparticles under different irradiation doses: a. 250 kGy, b. 300 kGy, c. 350 kGy and d. 400 kGy.

4. Conclusions

In summary, PbSe nanoparticles have been prepared by electron beam irradiation method. This one-step facile route was carried out rapidly at room temperature. XRD, TEM and AFM results revealed that the obtained particles were cubic PbSe nanoparticles. As-prepared PbSe nanoparticles were dispersed uniformly with spherical shape morphology and with a diameter range of 20–40 nm. PL spectrum showed the blue shifting of the absorption edge, which were due to small size effects of nanocrystalline PbSe. The advantages of this process exhibited that it was a simple, fast, efficient method without any kind of toxic reagent for producing nanoparticles. This method could be used to prepare other metal selenides such as SnSe, CdSe and ZnSe.

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