Sonochemical synthesis and characterizations of monodispersed PbSe nanocrystals in polymer solvent

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Abstract

A sonochemical method was applied to the preparation of monodispersed nanocrystalline PbSe in the presence of polyethylene glycol solvent. The nanocrystals were analyzed by X-ray diffraction (XRD), FT-IR, X-ray photoelectron spectra (XPS), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). It was found that the polyethylene glycol (PEG) as both a reducing agent and dispersant played an important role in the formation of monodispersed PbSe nanocrystals.

1. Introduction

In the past decade, there has been a growing interest in the synthesis and characterization of selenides due to their unique properties in electronics, magnetism and optics, and wide applications in various fields such as sensors, laser materials [1], thin film polarizers [2], thermoelectric cooling materials [3] and IR detectors [4]. Emphasis has been devoted to the preparation of selenides in the nanophased form. This is due to the modern trend of miniaturization, on the one hand, and the unique properties associated with the nanostructure, on the other. Unfortunately, there is an immense delay in the development of synthetic methods for the preparation of these compounds. Several methods have been known for the preparation of selenides such as chemical bath deposition [5], molecular beam epitaxy [6], vacuum deposition, and photoirradiation [7]. Generally, all these reactions mentioned above require high temperatures and pressure, or the use of toxic gaseous and sensitive precursors and it is difficult to grow nanocrystalline materials under such conditions.

Currently, the sonochemical method has been used extensively to generate novel materials with unusual properties, since they form particles of a much smaller size and higher surface area than those reported by other methods. The chemical effects of ultrasound arise from acoustic cavitation, that is, the formation, growth, and implosive collapse of bubbles in a liquid. The implosive
collapse of the bubbles generates a localized hotspot through adiabatic compression or shock wave formation within the gas phase of the collapsing bubble. The conditions formed in these hotspots have been experimentally determined, with transient temperatures of ~5000 K, pressures of 1800 atm, and cooling rates in excess of $10^{10}$ K/s [8–11]. Ultrasound offers a very attractive method for the preparation of nanosized materials and has shown very rapid growth in its application to materials science due to its unique reaction effects. Recently, a few reports [12–18] have described the preparation of metallic and main group chalcogenides conditions under solvothermal conditions using ethylenediamine as a solvent. These reactions are conducted in autoclaves, with temperatures kept in the range 12–200°C and requiring relatively high pressures. Among the disadvantages of the solvothermal reaction, we can mention the high pressure, the prolonged reaction time (from few hours to days), and the solvent incorporation into the product. Gedanken et al. have extended this methodology and successfully applied the polyol method to the synthesis of a variety of chalcogenides using microwave or ultrasonic irradiation [19–20]. In the present paper, we report a sonochemical method for the preparation of monodispersed nanocrystalline PbSe in polyethylene glycol solvent. The method is known for polyol process [21–25]. However, the exact mechanism of this reaction is poorly understood. According to Ref. [16], the reduction is based on the decomposition of polyol and the temperature is a dominant factor in affecting the reactivity. In these reactions, the temperature influences three factors: (1) reducing potential of polyol compound; (2) rupture and creation of chemical bond; and (3) diffusion. It is well known that polymer is a kind of good material in the preparation of nanoparticles. Because polymer can be used as a dispersant and stabilizer to promote the formation of nanoparticles, using polymer as solvent in the reaction, smaller and monodispersed nanocrystalline materials may be obtained. To the best of our knowledge, it is the first time that polyethylene glycol was chosen as a reducing agent and dispersant solvent in sonochemical synthesis of PbSe semiconductor nanocrystals. The nanocrystals were analyzed by X-ray diffraction (XRD), FT-IR, X-ray photoelectron spectra (XPS), transmission electron microscopy (TEM) and differential scanning calorimetry (DSC). It was found that the polyethylene glycol (PEG) played an important role in the formation of PbSe nanocrystals. On the one hand, PEG, like some other polyol solvent, such as ethylene glycol and triethylene glycol, can act as a reducing agent, and on the other hand it is a dispersant which prevents the generated nanocrystals agglomerating together.

2. Experimental procedure

2.1. Materials

All the reagents used in the experiment were of the analytical purity. Pb(Ac)$_2$ and Se powder were purchased from Shanghai Second Chemical Re- gent Factory (China), and polyethylene glycol(400) was purchased from Huakang Sci-Tech Company (China).

2.2. Instruments

The XRD patterns were recorded on a Shimad- zu X-ray diffractometer XD-3A (Cu K$_\alpha$ radiation, $\lambda = 0.15418$ nm). The TEM images were obtained employing a JEOL-JEM 200CX instrument, working at 200 KV accelerating voltage. The XPS measurements were performed on ESCALAB MKII instrument, using non-monochromatized Mg K. X-ray was used as the excitation source. Infrared absorption spectra (FT-IR) were recorded on AVATAR 360 made in NICOLET Co. using a computer-interfaced EZ OMNIC system. Differential scanning calorimetry (DSC) was carried out on Perkin Elmer Pyris1, using argon or nitrogen as a purging gas while the scanning rate was 10°C/min.

2.3. Preparation of PbSe nanocrystals

In a typical procedure, a mixture of about 0.45 g Pb(Ac)$_2$·3H$_2$O ($\sim 1.2 \times 10^{-2}$ mol), 0.09 g Se ($1.1 \times 10^{-3}$ mol) powder and 100 ml PEG-400 were
introduced into a 150 ml round-bottom flask. The solution was irradiated with a high-intensity ultrasonic probe (Xinzhi JY92-2D, Ti-horn, 20 KHz, 80 W/cm²) immersed directly in the solution. The reaction was conducted for 60 min under the ambient air. At the end of the reaction, black precipitates occurred. The precipitate was centrifuged and washed with distilled water and acetone, dried under vacuum at room temperature for 4 h. The final products were collected for characterizations.

3. Results and discussion

3.1. XRD studies

The XRD pattern of the as-prepared PbSe nanocrystals is shown in Fig. 1, which matches well with the literature (JCPDS card No. 6-0354). The crystalline size is calculated to be about 45 nm according to half-width of the diffraction peaks using Debye–Scherer equation.

3.2. TEM measurements

The morphology of the as-prepared nanocrystals was observed by TEM. Monodispersed PbSe nanocrystals can be clearly observed in the TEM image of the product (Fig. 2). The shape of the nanocrystals is irregular, but most of them are close to sphericity. The size is ranging from 20 to 40 nm, which is consistent with the XRD result. We also observed that on the surface of the nanocrystals, there is an absorptive layer. Because of nanoparticles' high surface-to-volume ratio and shortage of complexing on surface, they show a relatively strong absorption compared with the same bulk material. There are two main absorptions between sorbent and absorbed phase. One is physical absorption and the other is chemical absorption, namely the combination through chemical bond and the latter is much more stronger than the former [26–27]. In our experiments, PEG-400 was used as a dispersant in order to prevent PbSe nanoparticles from gathering. The major forces between PEG and PbSe are attributed to the formation of O–Se chemical bond.

Through chemical bond, PEG molecule was absorbed on the surface of the PbSe nanoparticles, which became the micronuclei in the solvent. Because of this absorption effect, PbSe nanoparticles could be kept away from each other and as a result, aggregation was not observed.

3.3. FT-IR investigation

Fig. 3 shows the FT-IR spectrum of pure PEG and PEG absorption on the surface of products. Comparing the two spectra, two interesting changes were observed. In Fig. 3(a), ν (~3343 cm⁻¹) corresponded to the stretching vibration of associated hydroxyl while the corresponding vibration of associated hydroxyl in Fig. 3(b) was shifted to a higher frequency, namely ν (~3423 cm⁻¹). It is well known that if hydrogen bonding was formed between PEG and PbSe, the vibration ought to be moved to a lower frequency and the stronger the strength of associated hydrogen bonding, the lower the frequency will be moved to. So it is impossible for the formation
of hydrogen bonding between PbSe and PEG. The reason that the O–H group moves to a higher frequency is the formation of chemical bond between O and Se, which led to the vibration force constant and the bond energy of O–H increased and vibration of the associated hydroxyl occurred at a higher frequency. Another change which aroused our interest was $\nu$ ($\sim 1109$–$1014 \text{ cm}^{-1}$) in Fig. 3(a), which corresponded to the asymmetric stretching vibration of C–O–C. Due to the vibrational coupling effect of C–O–C, the peak was split. In Fig. 3(b), the vibrational coupling of C–O–C almost disappeared. As we mentioned above, oxygen in C–O–C also formed chemical bond with Se in PbSe, therefore, it strongly influenced the vibrational coupling of C–O–C group. In short, PEG played its dispersive role by modifying the surface of PbSe nanocrystals.

### 3.4. XPS measurements

The PbSe nanocrystals were also characterized by XPS to study its composition and purity (Fig. 4). The binding energies obtained in the XPS analysis were standardized for specimen charging using C 1s as the reference at 284.60 eV. The peaks at 142.20 and 62.45 eV corresponded to Pb 4f and Se 3d of PbSe, respectively. The peak areas of the Pb and Se cores are measured and an

![Fig. 3. FT-IR spectra: (a) commercial PEG-400 (b) product.](image)

![Fig. 4. The XPS of as-prepared PbSe: (a) Pb 4f; (b) Se 3d; and (c) survey.](image)
average composition of PbSe\textsubscript{0.84} was given. Another information obtained from the XPS is that there is a large number of C and O in the products, which provides another proof demonstrating the existence of organic compound on the surface of PbSe nanoparticles. In the XPS spectrum, no other impurities were found, such as Pb 4f of PbO (138.85 eV), or Se 3d of SeO\textsubscript{2} (59.8 eV).

### 3.5. DSC investigation

DSC was carried out using argon as a purging gas; the scanning rate was 10°C/min. Three endothermic peaks were observed in Fig. 5. The first peak appears at 196.378°C, which corresponds to the decomposition of PEG. The second peak was measured at 221.160°C, which corresponds to the eutectic reaction PbSe + Se → PbSe + liquid. The peak disappeared when the sample was cooled and reheated again because of the small amounts of Se and its evaporation. XRD measurements did not detect the unreacted Se due to its relative low sensitivity. As for the last peak, we cannot make a sure conclusion without further studies.

### 4. Conclusions

In summary, monodispersed PbSe nanocrystals have been successfully prepared sonochemically by using PEG as the solvent. This method is proved to be simple and efficient without complicated operation and instruments. It may also be extended to the preparation of some other selenides nanocrystals.

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### References


