Sonochemical synthesis of taper shaped HgSe nanorods in polyol solvent

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Abstract

A new shape nanosized HgSe was synthesized in the presence of ethylene glycol, which was found to act as both reducing agent and be favorable to the formation of tapered HgSe nanorods. It was also observed that the ultrasonic power played an important role for the shape of the final products. X-ray powder diffraction, transmission electron microscopy and X-ray photoelectron spectroscopy were employed to characterize the HgSe nanorods. Other polyol solvents, such as diethylene glycol and polyethylene glycol 200, were also used to the preparation of HgSe nanoparticles. The possible mechanism of the formation of taper shaped HgSe nanorods was discussed.

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1. Introduction

In the past decade, there has been an increasing interest in semiconductors with nanosized dimensions in the light of their quantum size effect [1–3], especially in the field of semiconductors with one-dimensional (1D) structures, which are known to have many interesting physical properties and potential applications in optoelectronic devices [4]. Therefore, finding a fast and convenient way to synthesize one-dimensional semiconductors is a great challenge to materials researchers. Up to now, so many routes have been employed to the synthesis of 1D semiconductors, such as solution liquid solid growth, laser ablation, carbon nanotube-confined reaction, electrochemical fabrication, and nonaqueous solution synthesis [5–9]. Furthermore, importing sonochemical method into producing 1D structure greatly arouses the attention and interests of many scientists [10–12]. Our groups had successfully synthesized metal chalcogenide nanorods by a convenient sonochemical method under ambient air in aqueous solvent [13,14]. The polyol compounds, acting both as
solvent and reducing agent, have been widely used in the preparation of nanomaterials [15,16] and their basic reducing mechanism has been monitored and proved [15,17,18]. Here, we expanded the research to the synthesis of HgSe nanorod in polyol solvent by ultrasound irradiation. During the reaction, we found different polyol solvents, not only acting as reducing agent, but also influencing on the morphology of the final HgSe products.

2. Experimental procedure

2.1. Materials and instruments

All the reagents used in the experiment were of the analytical purity. Hg(Ac)$_2$ and Se powder were purchased from Shanghai Second Chemical Reagent Factory, China. Ethylene glycol (EG), polyethylene glycol 200 (PEG 200) and diethylene glycol (DEG) were purchased from Huakang Sci-Tech Company, China.

The X-ray diffraction (XRD) patterns were recorded on a Philips X-ray diffractometer X’Pert Pro MPD (CuK$_\alpha$ radiation, $\lambda = 0.15418$ nm). The transmission electron microscopy (TEM) images were obtained by employing a JEOL-JEM 200CX instrument, working at 200 kV accelerating voltage. The X-ray photoelectron spectra (XPS) measurements were performed on ESCALAB MKII instrument, using non-monochromatized Mg K$_\alpha$ X-ray as the excitation source.

2.2. Synthesis

In a typical procedure, mercuric acetate (~0.8 g) and selenium powder (~0.2 g) were placed in a round-bottom flask. EG, PEG 200 and DEG, about 50 ml, were added into the round-bottom flask. All of the solution was irradiated at a cycle of 27 s on and 3 s off with a high-intensity ultrasonic probe (Xinzhi JY92-2D, Ti-horn, 20 kHz, 80 W/cm$^2$) immersed directly in the solution. The reaction was conducted for 60 min under ambient air. The final black 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 discussions

3.1. Results of characterizations

The XRD patterns of the as-prepared HgSe nanocrystals are shown in Fig. 1. All the diffraction peaks located at (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0) and (3 3 1) can be indexed to be a pure cubic phase, which is in coincidence with the literature values (JCPDS card No. 8-469). No peaks of any other phases are detected, indicating the high purity of the products.

TEM images (Fig. 2a–d) show the as-prepared HgSe in different polyol solvents. In EG solvent (Fig. 2a), taper shaped HgSe nanorods with length in the range of 500 nm–30 μm and diameter of ca. 30–400 nm are found. Fig. 2b shows the single HgSe nanorod. The diameter of typical taper shaped HgSe nanorod is ca. 30–120 nm and length is ca. 1 μm. The inlet picture in Fig. 2b is the electron diffraction (ED) picture of a selected area of the as-prepared HgSe nanorod in EG solvent. The ED measurement shows that the product is single crystal. The rod-like HgSe is also found by employing DEG as solvent (Fig. 2c), but aggregated HgSe nanoparticles could be observed.
around the nanorod. However, only monodispersed HgSe nanoparticles are detected in PEG 200 solvent (Fig. 2d).

XPS measurements provide further information for the evaluation of the composition and purity of HgSe nanoparticles prepared in EG. The high-resolution XPS spectra taken for Hg (4f) and Se (3d) regions are shown in Fig. 3a and b, respectively. The two strong peaks at 100.60 and 54.55 eV correspond to Hg (4f) and Se (3d) accordingly. Peak areas of Hg (4f) and Se (3d) are measured and quantification of the peaks shows that the atomic ratio of the Hg:Se is approximately 56:44, indicating that the surface of the products are rich in mercury.

3.2. Discussion

During the preparation of HgSe, our research focuses on the mechanism of the formation of one-dimensional HgSe nanorod. In EG solvent, pure HgSe nanorod could be obtained (Fig. 2a). We speculate those EG molecules, not only act as solvent and reducing agent, but also act as a soft template to allow the HgSe growing in a certain direction. Li et al. had successfully synthesized CdS nanorod in ethylenediamine solvent by using cadmium metal powder and sulfur powder [19]. EG molecules, although their coordinate covalent bonds are relatively weaker compared with ethylenediamine, they could also form Hg²⁺ complex in the EG solvent and result in the formation of HgSe nanorod. To prove our assumption of the template mechanism, we chose DEG as solvent because it has the similar structure with EG. Rod-like HgSe are also obtained although some aggregated HgSe nanoparticles are found in the final products (Fig. 2c). The results further support the proposed template mechanism. However, when PEG 200 is used as solvent, only monodispersed HgSe nanoparticles could be obtained (Fig. 2d). We substitute polyethylene glycol 400
for PEG 200 and the same morphology of HgSe is found. That is to say, with increasing of the carbon chains, the morphologies of HgSe are changing gradually from rod to particles. We suppose that the increasing carbon chains can prevent the one-dimensional growth of HgSe. In our synthetic system, we observe that the power of ultrasound irradiation could also influence the formation of HgSe nanorod in EG solvent. If the power of ultrasound irradiation is up to 120 W/cm², all rod-like HgSe disappear and aggregated HgSe nanoparticles are found. It is well known that appropriate power of ultrasound irradiation could generate the enough temperature to guarantee the redox reaction to happen and that is the basis of the formation of HgSe [15]. However, the exorbitant power of ultrasound irradiation would destroy the coordinate covalent bond between Hg^{2+} and EG, thus results in the disappearance of HgSe nanorods.

4. Conclusions

In summary, we report a new synthetic method to prepared one-dimensional HgSe nanorods in polyol solvent by ultrasound irradiation. This convenient and fast method could be expanded to synthesize other desirable one-dimensional nanostructural materials.
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