Morphology-controllable Solution Route to PbSe Micrometer-scaled Crystals

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Lead selenide micrometer-scaled crystals were synthesized via a simple morphology-controllable solution route with the reactions of lead nitrate and sodium selenosulfate in aq sodium hydroxide or ethylenediamine solution. Scanning electron microscopy images showed that cubic and spherical PbSe crystals were obtained by varying alkaline medium and $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio. The possible reaction mechanism is discussed.

Lead selenide crystals draw considerable interest because of their unique properties of semiconductor. A bulk PbSe has a narrow direct band gap (0.28 eV at 300 K), a relatively large effective Bohr radius ($a_B = 46$ nm), and an increase in Seebeck coefficient, which suggest that PbSe crystals can be used for optoelectronic and biophysical devices in the IR spectral regime,[1,2] in telecommunication applications,[2,3] and in thermoelectric devices.[4] Various methods have been adopted to prepare PbSe crystals including chemical bath deposition,[5,6] electrodeposition,[7] hydrothermal and solvothermal syntheses,[8,9] organometallic precursors thermolysis,[10] sonochemical method,[11,12] and soft template route.[3,13] Finding a convenient and mild route for fabrication of PbSe crystals with controllable morphology is still one of the desired goals to synthetic chemists and materials scientists.

Herein, a simple morphology-controllable solution route is reported to synthesis of cubic and spherical PbSe micrometer-scaled crystals with the reactions of lead nitrate and sodium selenosulfate in different aqueous alkali at low temperature. By varying the alkaline medium and $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio, the morphology of the products can be controlled. Compared with the above-mentioned methods, this approach, without additional complexing agent, surfactant, or template, is simple, convenient, and mild.

Lead selenide micrometer-scaled crystals with two types of morphologies were formed as follows. In a 100-mL conical flask, addition of 13 mL of 2 M aq NaOH solution to 5 mL of 0.5 M aq solution of $Pb(NO_3)_2$ formed a clear solution (pH = 14). Then 20 mL of 0.5 M aq Na_2SeSO_3 solution, prepared according to the literature,[14] was added. The mixture was maintained at 80 °C for 24 h. In another 100-mL conical flask, 5 mL of ethylenediamine (en) was added to 10 mL of 0.5 M aqueous $Pb(NO_3)_2$ solution to form a mixture. The pH value was adjusted to 10–11 by 1:10 (V:V) diluted acetic acid. Then 20 mL of 0.5 M aq Na_2SeSO_3 solution was added. The flask was sealed and kept at room temperature for 24 h. The final gray precipitates were filtered, washed with distilled water and absolute ethanol several times, and then dried in vacuum at 60 °C for 2 h. The detailed conditions of experiments including contrastive experiments and the morphology of the products are listed in Table 1.

X-ray powder diffraction (XRD) analysis was carried out on a MAX 18 AHF X-ray diffractometer (MAC Science) with Cu $K\alpha_1$ radiation ($\lambda = 1.54056$ Å). X-ray photoelectron spectra (XPS) were taken with a VG ESCALAB MKII X-ray photoelectron spectrometer using nonmonochromatized Mg $K\alpha$ (1253.6 eV) as the excitation source. Scanning electronic microscopy (SEM) images were performed on a KYKY 1010B scanning electron microscope.

Table 1. Experimental conditions and the morphology of the products

Sample	Alkaline solution	Molar ratio of $Pb^{2+}/SeSO_3{}^{2-}$	Morphology
1	NaOH	1:4	cube
2	NaOH	1:1	cube
3	en	1:2	sphere
4	en	2:1	rod

The XRD patterns of as-prepared PbSe of samples 1 and 3 are shown in Figure 1. All peaks can be indexed to cubic phase PbSe with no impurities detected. The calculated cell constants, $a = 6.121$ Å for sample 1, and $a = 6.110$ Å for sample 3, are consistent with the reported value ($a = 6.124$ Å, JCPDS Card No.6-0354), respectively. The corresponding sharp peaks of XRD patterns suggest that the samples are well crystallized.

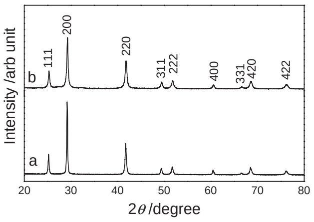

Figure 1. XRD patterns of sample 1 (a) and 3 (b) of PbSe.

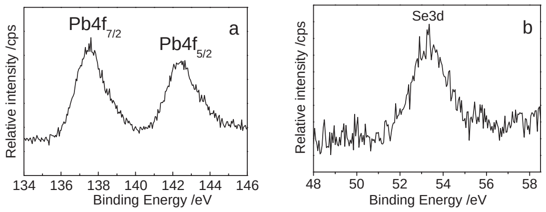

Figure 2. XPS spectra of sample 1 of PbSe.

The XPS surface analysis of sample 1 is presented in Figure 2. 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 137.60 and 142.55 eV (Figure 2a) are assigned to Pb ($4f_{7/2}$) and Pb ($4f_{5/2}$) of PbSe, respectively. The peak at 53.40 eV in Figure 2b corresponds the Se (3d) of PbSe. These results coincide with the reported data.[15]

Quantification of the peak areas gives the molar ratio of Pb to Se as 1:1.042, which is almost consistent with the stoichiometry of PbSe. The surface compositions analysis of sample 3 was also carried out by XPS. The result of XPS indicates that the molar ratio of Pb to Se is 1:0.636, which shows that the surface of sample 3 is rich in lead.

The SEM image (Figure 3a) shows that sample 1, prepared in aq NaOH solution with a $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio of 1:4, consists of cubic particles with 0.5–0.8-µm edges. As shown in Figure 3b, sample 3, prepared in aqueous en solution with a $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio of 1:2, displays spherical microstructures with diameters of 2.0–2.5 µm. And the particles are connected with each other.

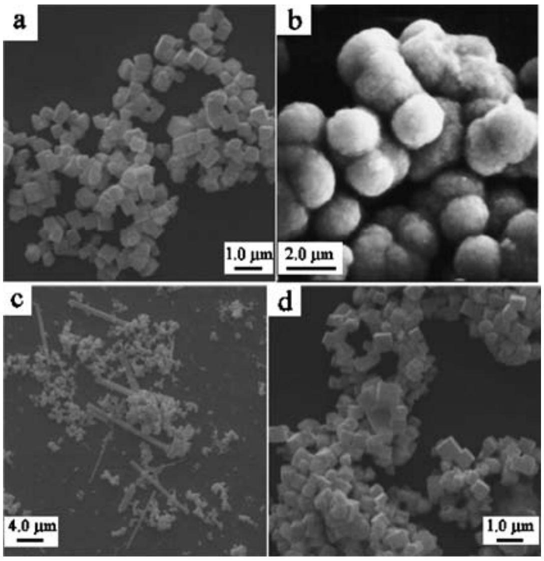

Figure 3. SEM images of PbSe crystals prepared in aq NaOH solution with a $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio of 1:4 (a) and 1:1 (d), and in aqueous en solution with a $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio of 1:2 (b) and 2:1 (c).

In the reaction systems, $SeSO_3{}^{2-}$ is used as a source of selenide ions owing to its hydrolytic decomposition in alkaline medium. Pb^{2+} can coordinate with OH^- or $SeSO_3{}^{2-}$ of the systems to form complexes. These complexes then combine with selenide ion to precipitate PbSe. These processes can be described as follows:

$$SeSO_3{}^{2-} + 2OH^- \rightarrow SO_4{}^{2-} + Se^{2-} + H_2O \quad (1)$$

$$[PbL_n] + Se^{2-} \rightarrow PbSe + nL \; (L = OH^- \text{ or } SeSO_3{}^{2-}) \quad (2)$$

In the formation of the products, the alkaline medium and the molar ratio of $Pb^{2+}/SeSO_3{}^{2-}$ have combined effect on crystal morphology. In ethylenediamine system (pH = 10–11), with the increase of the $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio from 1:2 to 2:1 keeping other conditions identical, the morphology of PbSe changed. Figure 3c shows SEM image of PbSe crystals obtained at $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio of 2:1. Compared with the SEM image of the products obtained at $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio of 1:2 (shown in Figure 3b), the shape of the PbSe crystals varied and PbSe rods appeared. At $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio of 1:2, lead selenosulphate complexes are formed in excess of selenosulphate.[14] Lead selenosulphate complexes act as intermediate species[3] that may control the formation of the spherical PbSe. At $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio of 2:1, $SeSO_3{}^{2-}$ is not enough to coordinate with Pb^{2+}. In this case, ethylenediamine can coordinate with Pb^{2+} to form $[Pb(en)_2]^{2+}$. $[M(en)_2]^{2+}$ (M = Pb, Cd) complex is believed to play an important role as an intermediate to form MSe nanorods or nanowires.[16,17]

However, in sodium hydroxide system (pH = 14), with the raise of the $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio from 1:4 to 1:1, the morphology of products did not vary. Figure 3d shows SEM image of the products obtained at $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio of 1:1. It is seen that the products still displayed cubic morphology when the $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio was changed from 1:4 to 1:1, indicating the change of $Pb^{2+}/SeSO_3{}^{2-}$ molar ratio in a range of 1:4 to 1:1 had little influence on the shape of PbSe at pH = 14. When the pH value is higher than 13, Pb^{2+} is coordinated by OH^- rather than $SeSO_3{}^{2-}$ to form $[Pb(OH)_n]^{2-n}$ complex.[11] This complex as an intermediate may favor the formation of PbSe cube.

Cubic and spherical PbSe micrometer-scaled crystals were synthesized via a simple morphology-controllable solution route in different alkaline medium without additional complexing agent, surfactant, or template under ambient air. Varying experimental conditions, such as alkaline medium and molar ratio of $Pb^{2+}/SeSO_3{}^{2-}$, could control the crystal morphology of the products. This method may be convenient and is expected to be applicable for preparation of other selenides. Further researches, such as the control of crystal size, are under progress.

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