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Effect of Processing Conditions on Hydrothermal Synthesis of Dendritic PbSe

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Abstract: PbSe dendritic structures have been synthesized by a facile hydrothermal route in glycerol solution without surfactant. Temperature, time, and Pb^{2+} source play a major role in controlling the morphology and shape evolution of the product. The obtained products were characterized by X-ray power diffraction (XRD), scanning electron microcopy (SEM) and transmission electron microscopy (TEM). This simple synthesis technique for the growth of various nano- and microstructures opens a new route to prepare hierarchical structures of a variety of semiconducting materials in a large quantity. The possible formation mechanism for products with various structures are presented, which is mainly based on the variation of the ratio (*R*) of the growth rates along the <100> direction and <111> direction.

Key words: PbSe; dendrite; hydrothermal method

Materials with different sizes and morphologies give us opportunities in exploring their physical and chemical properties in terms of their application. During the past few years, considerable interests have been focused on the design of rational methods for synthesizing high-ordered inorganic semiconductor crystals with specific sizes, shapes and hierarchies because of their potential application in designing novel materials and devices in various fields[1]. As an important narrow-band gap IV-VI group semiconductor, PbSe is an attractive material characterized by a large bulk exciton Bohr radius (46) nm, eight times larger than that of CdSe[2], which results in a strong confinement of the electron-hole pair and large optical nonlinearity[3]. PbSe can be potentially applied in near-IR luminescence, infrared detector, Pb^{2+} ion selective sensors, optical switching device application and so on [4-7].

Over the past few years, various methods, including radiation[8], photochemical method[9], sonochemical method[10], microwave assisted preparation[11], solution-based method[12], and so on, have been reported to synthesize PbSe nanostructures with different shapes, snowflakes[13], hyperbranches[14], multipods[15], dendrites[16], and hierarchical superstructures[17]. In all of the morphologies, dendrities have attracted much attention in recent years due to their intersection morphology and potential applications. The dendrites of metals, chalcogenides, and macromolecules[18-22] have been successfully obtained by a variety of methods.

In this work, we reported the preparation and characterization of novel PbSe dendritic structures through a facile hydrothermal process in the absence of surfactant. To the best of our knowledge, this is the first time to synthesize a large amount of PbSe dendrites. Keeping other conditions the same, only by changing the concentration of NaOH from 1 mol/L to 8 mol/L, the dendrites can be formed. The possible growth mechanisms for the cubes and dendrites structures of PbSe were discussed on the basis of transmission electron microscopy (TEM) and scanning electron microscopy (SEM) analysis from the temperature-dependence.

1 Experiment

All the reagents used are of analytical grade and purchased from Shanghai Chemical Reagent Co. In a typical experiment, $Pb(NO_3)_2$ was dissolved into a certain amount of glycerol and H_2O (60 mL); then NaOH solution was put into the mixed solution; at last, selenourea (CH_4N_2Se) was discharged into the solution to form a homogeneous solution. After being vigorously stirred for 1 h, the mixed solution was put into a Teflon lined autoclave of 100-mL capacity and maintained at 120 ℃ for 24 h and then allowed to cool to room temperature. The resulting black product was collected by filtration,

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washed several times with water and ethanol, and then dried at 50 ℃ for 4 h. Summary of the experimental results indicating the influences of the concentration of NaOH and reaction temperature, time on the shape formation of PbSe crystals are listed in Table 1.

The phase purity of the as-synthesized products were examined by XRD using Bruker X-ray diffractometer (Model D/max-3A, Cu Kα, λ= 0.154 18 nm, German). The scan rate of 0.06 °·s^{-1} was applied and the patterns was recorded in the 2θ range of 10 °~80 °. The surface morphology of the prepared products was studied with a scanning electron microanalyzer (SEM, JSM-5910, Japan). EDS was carried out on a Hitachi S-4700 equipped with energy dispersive X-ray Spectrometer. The TEM studies were carried out on transmission electron microscopy (TEM, JEM-100 CXII, Japan) apparatus with accelerating voltage of 200 kV.

2 Results and Discussion

X-ray diffraction (XRD) analysis was used to examine the crystal structure of the products. The XRD pattern of the as-synthesized PbSe dendrites (S3) is shown in Fig.1. All the diffraction peaks can be indexed to the cubic rock salt structure of PbSe with lattice constant a=0.613 505 nm, which is in good agreement with the literature value (JCPDS No 78-1903), and no impurity phase can be detected. The strong and sharp peaks indicate that PbSe dendrites are highly crystalline. A strong 200 peak indicates that the products on a Si substrate have a preferential orientation in the <100> direction. The product morphology was determined by scanning electron microscopy (SEM). Fig.1b is a typical SEM image of the products, clearly showing that PbSe possesses a dendritic structure. Examining numerous SEM images of the samples prepared at 120 ℃ for 24 h, we found almost all the particles are dendrites. It indicates that well-defined PbSe through careful examination of the structure of a single particle (Fig. 1c) with dendritic structures can be obtained under the present experimental conditions. The growth of the dendrites is rather unique. The individual PbSe dendrites have three-dimensional (3D) structures with one trunk (long axis). The nanorods of branch are parallel to each other and in the same plane. A higher magnification of SEM image can clearly show their 3D structures, as demonstrated in Fig. 1c. The length of the trunk and the diameter of the branches of the PbSe dendrites are 5~10 μm, and 500 nm~1 μm, respectively.

2.1 Influence of the concentration of NaOH

In the present system, as soon as the concentration of OH^- was increased to above 1, XRD shows that the patterns of PbSe began to appear, indicating the formation of PbSe. Therefore, to

Table 1 Summary of the experimental results indicating the influences of the concentration of NaOH and reaction temperature, time on the shape formation of PbSe crystals

Sample	Pb^{2+} source	Concentration of NaOH/mol·L^{-1}	Temperature/℃	Time/h
S1	$Pb(NO_3)_2$	1	120	24
S2	$Pb(NO_3)^2$	2	120	24
S3	$Pb(NO_3)_2$	3	120	24
S4	$Pb(NO_3)_2$	6	120	24
S5	$Pb(NO_3)_2$	8	120	24
S6	$Pb(NO_3)_2$	3	100	24
S7	$Pb(NO_3)_2$	3	160	24
S8	$PbCl_2$	3	120	24
S9	$Pb(Ac)_2·3H_2O$	3	120	24
S10	$Pb(NO_3)_2$	8	200	24
S11	$Pb(NO_3)_2$	8	200	48
S12	$Pb(NO_3)_2$	8	120	48

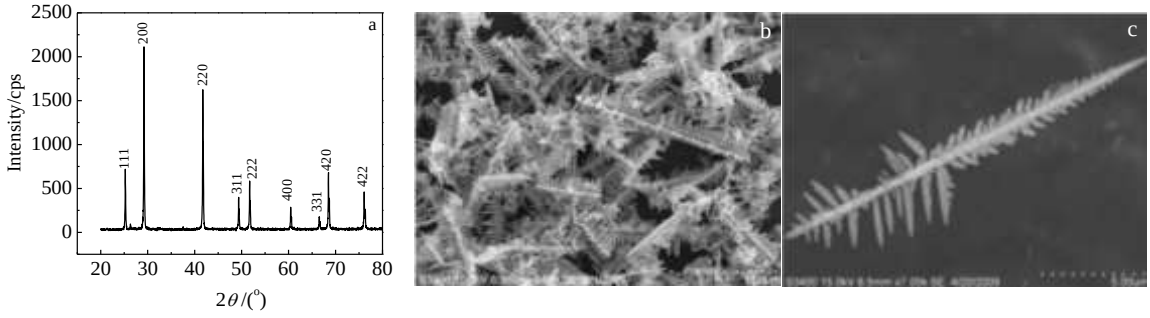


Fig.1 XRD pattern of the as-prepared samples of the PbSe dendrites hierarchitectures (a), low-magnification SEM image showing PbSe dendritic structures (b), higher magnification SEM image showing their 3D dendritic structure (c)

investigate the morphological evolution process of the PbSe crystals, the concentration of OH^- was changed from 1 to 2, 3, 6, 8 mol/L under otherwise the same experimental conditions; a serial of PbSe morphologies including cubes, dendrites came out. The morphologies of the corresponding products are shown in Fig.2. When the concentration was 1 mol/L, the morphology was irregular (S1). As the ratios increase to 2 mol/L, the dendritic structures began to appear, with a few sheets structure (S2). While the concentration reached 3 mol/L, a large amount of dendritic structures were found (S3). However, when the concentration was 6 mol/L, the cubic structure bean to appear (S4); when the concentration continued to increase into 8 mol/L, the morphology changed completely into cubes (S5). When the concentration further increased, the XRD shows that the major diffraction peaks of PbSe disappear, which is not shown in the Fig1a. The above result shows that the concentration of OH- varies, the morphology will change greatly. It is the most influential factor in our experiment. And we can control the major morphology through controlling the concentration of OH-. It is worth noting that the as-obtained dendrites will not disband under irradiation of strong ultrasonic wave, indicating that this morphology is very stable. From the above results, we reasonably believe that shape-controlled synthesis of PbSe crystals can be readily achieved through the delicate control of the reaction concentration of OH- in our case.

2.2 Effects of temperature

Comparative experiments were carried out, in which other parameters were kept constant, to investigate the influence of temperature on the formation of PbSe crystals. As shown in Fig.3, the concentration of OH- was chosen to be 3 mol/L. The major morphologies were dendrites. However, different temperature has different morphologies. Fig.3 clearly shows the shape evolution process of the products by varying the reaction temperature. Fig.3a shows the SEM image of PbSe prepared at 100 ℃, indicating the formation of PbSe dendrites, but it goes with impurities, which is shown in XRD. When the temperature was elevated to 120 ℃, perfect dendrites began to appear, with an average edge length of 5 μm as shown in Fig. 3c. Increasing the temperature to 160 ℃, the obtained products (Fig. 3d) are dendrites with side branch broken off. Through the magnified SEM image of an individual PbSe (inset), we can see that the branches have been broken off. The shape was not changed greatly when the reaction temperature was elevated to 200 ℃. From the aspect of the temperature, we can see that the dendrites can be formed perfectly when the temperature was 120 ℃. And when the temperature didn't attain that, there were some impurities in the product. On the other hand, when the temperature exceeded 120 ℃, the morphology would be destroyed by the superfluous energy.

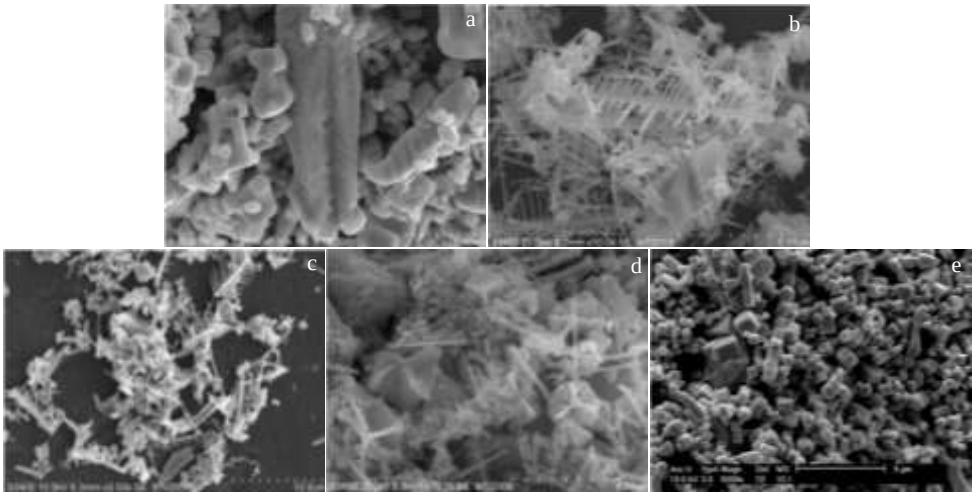


Fig.2 SEM images of samples synthesized by processes with different ratios of OH^- to Pb^{2+} (a) S1, (b) S2, (c) S3, (d) S4, and (e) S5

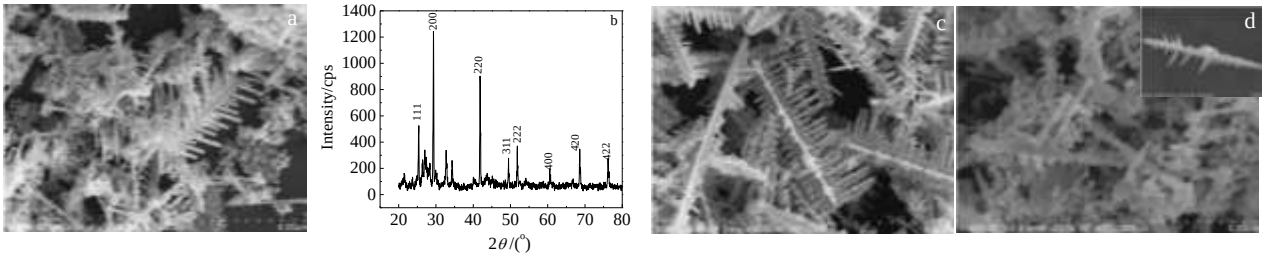


Fig.3 SEM image (a) and XRD pattern (b) of S6; SEM images of S3 (c) and S7 (d)

2.3 Effects of Pb^{2+} ion source

To explore the influence of Pb^{2+} sources on the morphologies of final PbSe products under otherwise same reaction conditions, $PbCl_2$ and $Pb(Ac)_2·3H_2O$ were used as Pb^{2+} sources instead of $Pb(NO_3)_2$. When $PbCl_2$ was adopted, a large amount of dendrites are presented in Fig.4a, which is almost similar to the products when the Pb^{2+} ion source was $Pb(NO_3)_2$. On the other hand, when $Pb(Ac)_2·3H_2O$ was used as the Pb^{2+} source, the branches begin to form another dendrites, which is shown in Fig.4b. Above results demonstrate the morphology of product depends on the types of Pb^{2+} source to a certain extent. Therefore, we can control the subtle feature of dendrites, for example, the feature size or shape of the branches.

2.4 Effects of solvent glycerol

The solvent glycerol played a key role in the formation of the unusual leaflet PbSe crystals, according to Fig.5. We can see that dendrite can form well when glycerol exists. If glycerol weren't added into the solvent, the viscosity of the whole system was very low, and the product reunited quickly, and it wasn't favorable to form structures with uniform shape On the other hand, glycerol was beneficial for forming crystal, which needs further research.

2.5 Formation mechanism

In the approach to construct dendritic structure, the formation of PbSe is based on the combination of Pb^{2+} and Se^{2-}. While in the case of NO_3^-, only Se^{2-} coordinates with Pb^{2+}, which might favor the quicker growth of the (111) faces. This phenomenon can be attributed to the different interactions between anions and Pb^{2+}. During the growth process, the adsorption rate of Se^{2-} on different planes of PbSe nuclei may be affected by the anions. The formation of PbSe crystals involves formation and growth processes of PbSe nuclei. It is well known that selenourea can decompose at certain temperature to produce H_2Se. And the reaction of H_2Se and Pb^{2+} occurs to produce PbSe nuclei. The possible chemical process for the formation of PbSe can be summarized as follows:

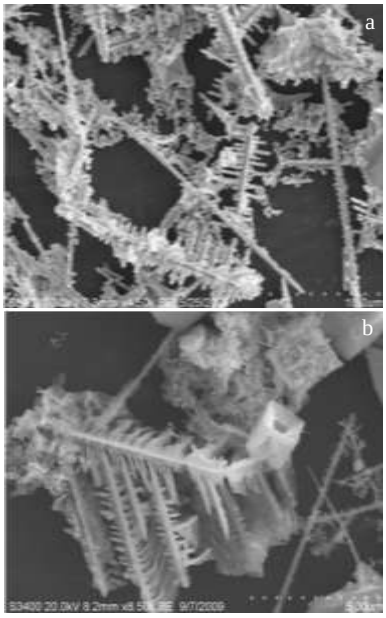


Fig.4 SEM images of different Pb^{2+} sources S8 (a) and S9 (b)

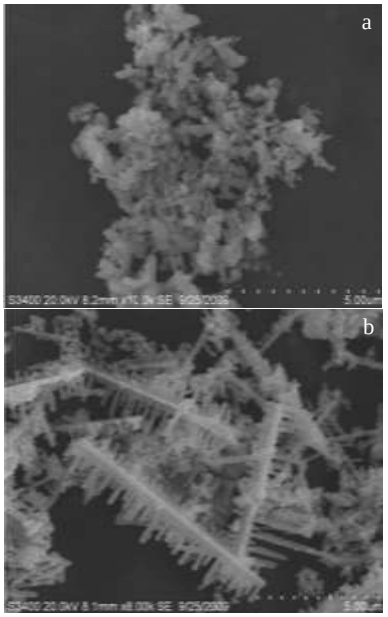
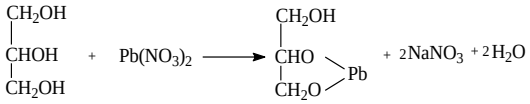


Fig.5 SEM images of glycerol of different amounts: (a) 0 mL and (b) 25 mL

$$NH_2CSeNH_2+2H_2O\rightarrow 2NH_3+H_2Se+CO_2 \quad (1)$$

$$Pb^{2+}+H_2Se\rightarrow PbSe+2H^+ \quad (2)$$

In the alkaline glycerol/water solution system, glycerol acts as a complexing reagent to form the complex, $Pb(C_3H_6O_3)$; NaOH provides an alkaline environment for the $Pb(C_3H_6O_3)$, which sharply decreases the free Pb^{2+} concentration in the solution and slows down the speed of the following reaction for the formation of PbSe crystals. The whole reaction process can be summarized as follows:

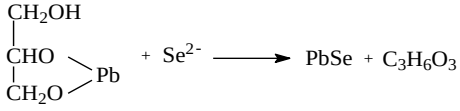


(3)

Slow reaction rate is favorable for crystallization as well as for the separation of the growth step and the nucleation step.

$$NH_2CSeNH_2+H_2O\rightarrow 2NH_3+H_2Se+CO_2 \quad (4)$$

$$H_2Se\rightarrow Se^{2-}+2H^+ \quad (5)$$



(6)

3 Conclusions

In summary, we have presented a simple hydrothermal process for preparing unusual 3D PbSe dendritic microstructures. It

has been found that the concentration of NaOH plays important roles in the formation of well-defined PbSe dendritic microstructure; at the same time, we investigate influence of the reaction parameters on the shape of PbSe dendrites. A possible mechanism for the formation of PbSe dendrites has been proposed. However, the exact mechanism for the formation of PbSe dendrites is still not fully understood and further studies are needed to explain the observed phenomena. The experimental results clearly show that the PbSe microstructures prepared in the present study are good crystal and have some specific optical properties. Our study may provide a new method for direct growth of dendritic microstructures and related materials.

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水热法合成树枝状 **PbSe** 的影响因素研究

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摘　要：在无表面活性剂条件下，以甘油为溶剂采用简易水热法，合成了树枝状结构 PbSe。水热温度、时间以及 Pb 源对 PbSe 形貌调控及形状影响很大。得到的 PbSe 分别用 XRD、SEM、TEM 进行了表征。这一合成方法为高通量制备不用纳米结构及微观形貌的半导体纳米材料开辟了一条崭新的技术路线。同时也探讨了不同微观形貌 PbSe 的形成机理，表明 PbSe 形貌主要取决于晶面<100>和<111>的生长速率比（R）。

关键词：PbSe；树枝状；水热法

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