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Ionic Liquids Tailoring Trigonal Selenium Microrods under Solvothermal Conditions

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Abstract

An ionic liquids(ILs)-assisted solvothermal synthesis route has been proposed to preparing high-purity trigonal selenium (t-Se) microrods using sodium selenite and hydrazine hydrate as starting materials. The as-obtained samples are characterized by the X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. By choosing ionic liquids employed in the synthesis of t-Se, the aspect ratio of the as-synthesized Se microrods could be tailored. Furthermore, possible formation mechanism of t-Se microrods was rationally proposed. BF4- anions were found to play crucial roles in the formation of t-Se microrods, and the chain length of ILs had important effect on the determining the aspect of t-Se microstructures. This method may provide a new idea for the direct growth of inorganic nanomaterials with various morphologies by choosing anions and cations of ionic liquids.

Keywords: Ionic liquids; Solvothermal synthesis; Crystal growth; Selenium

Introduction

In recent years, room temperature ionic liquids (RTILs) have received significant attention as potential effective green solvents for a host of different applications.[1-4] RTILs, composed entirely of organic cations and organic or inorganic anions, display attractive physicochemical properties such as negligible vapor pressure even at elevated temperatures, excellent thermal and chemical stability, low toxicity and excellent salvation, etc. Furthermore, as the physicochemical properties of RTILs strongly depend on the species of cations and anions, the alternation of anions allows to finely tune the physicochemical properties of ILs, such as viscosity, solvation, hydrophobicity and melting points. These features play key roles in manipulating the application of RTILs, which allows RTILs to be easily designed for specific reaction systems.[5]

Until now, the advantages of RTILs in inorganic synthetic procedures have been realized and received increasing intention. RTILs have been utilized as electrolytes for electrosynthesis,[6] templates for hydro/solvothermal synthesis,[7-10] excellent media for microwave-assisted method,[11] structure-directing agents of sol-gel methods modified with ionic liquids,[12] solvents for ionothermal synthesis,[13, 14] etc. Trigonal selenium (t-Se), as an important elemental semiconductor, has found applications in rectifiers, solar cells, photographic exposure meters, and xerography. In addition, t-Se also has a high reactivity towards numerous chemicals that can be potentially exploited to convert selenium into other functional materials such as CdSe, ZnSe, and Ag_2Se etc.[15] It is reasonable to assume that the availability of one-dimensional (1D) selenium nanowires will introduce new types of applications or enhance the performance of currently existing devices, as a result of size restriction. In the past several years, 1D t-Se, such as nanowires, nanotubes and nanobelts, has been fabricated through a few solution-phase approaches, especially assisted by soft templates [16-25], e.g., beta-cyclodextrin, beta-carotene, cytochrome c(3), nonionic surfactants, SDS, CTAB, PVA and cellulose. In this work, we have successfully synthesized t-Se microstructures by employing different ionic liquids as soft templates, and investigated the effects of different imidazolium cations and BF_4^- anion on the growth of t-Se microstructures, respectively.

Experimental Section

Synthesis of t-Se samples

All of the reagents employed were commercially available and used as received without further purification. Typically, Na_2SeO_3 (0.13 mmol)and [bdmim]BF_4 (5 mmol) were first dissolved

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in 25 mL of the mixed solution of water and ethanol with equal volume rate, respectively. Next, hydrazine hydrate (0.05 mL, 80 wt% content) was added to the solution under constant stirring for 10 min. Then the mixture was transferred into a Teflon-lined stainless steel autoclave of 30 mL capacity, maintained at 145 ºC for 20 h, and then cooled to room temperature naturally. A black precipitate was filtered off and washed with distilled water and absolute ethanol for several times. Finally the product was dried in vacuum at 60 ºC for 4 h.

The syntheses of samples 2–5 were identical with that of sample 1 except that the additives were different. The detailed synthesis conditions were summarized in Table 1 (1-n-butyl-3-methylimidazolium tetrafluoroborate, abbreviated as [bmim]BF_4, 1, 2, 3-trimethylimidazolium tetrafluoroborate, abbreviated as [tmim]BF_4, 1-n-butyl-2, 3-dimethylimidazolium tetrafluoroborate, abbreviated as [bdmim]BF_4).

Table 1. Summary of the experimental results indicating that the influence of the additive on the shape and size of t-Se morphologies

Sample number	Additive	Morphology	Average diameter (μm)	Average length (μm)
1	0.5 mmol [bdmim]BF_4[a]	Microrods	0.5	30-40
2	0.5 mmol [tmim]BF_4[b]	Microrods	2	30-40
3	0.5 mmol [bmim]BF_4[c]	Microrods	0.5	30-40
4	0.25 mmol [tmim]BF_4	Microrods	2	25-35
5	1.5 mmol [tmim]BF_4	Microrods	1	30-40

Characterization

The X-ray powder diffraction patterns (XRD) of the products were recorded on a Rigaku D/max 2500V/PC X-ray diffractometer with Cu Kα radiation (λ=1.54056 Å), employing a scanning rate of 0.017° s^{-1} in the 2θ range from 20° to 70°. The scan electron microscopy (SEM) images were taken with a JSM 6700F field-emission scanning electron microscopy (FE-SEM).

Results and Discussion

XRD analysis of as-prepared samples

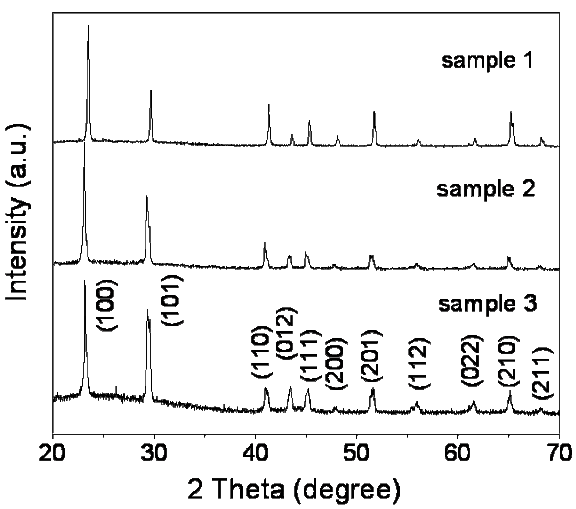

Fig. 1. XRD patterns of the samples prepared with three kinds of ionic liquids.

The XRD patterns of the samples prepared by using three kinds of different additives are shown in Fig. 1. Typical XRD patterns of microstructures, including sample 1 (microrods), sample 2 (microrods) and sample 3 (microrods) shown in parts a–c of Fig. 1, respectively. All of the diffraction peaks of the products can be readily indexed to a single phase of trigonal structured selenium (JCPDS cards no. 73-0465). No characteristic peaks are observed for the other impurities. It can be obviously seen in Fig. 1 that the intensity of the (100) peak is abnormally strong compared with the standard pattern of trigonal selenium (t-Se), which may be caused by the orientation growth of t-Se along [001] direction. The XRD results are in good agreement with the previous report,[26] which confirms the crystallinity and purity of as-obtained products.

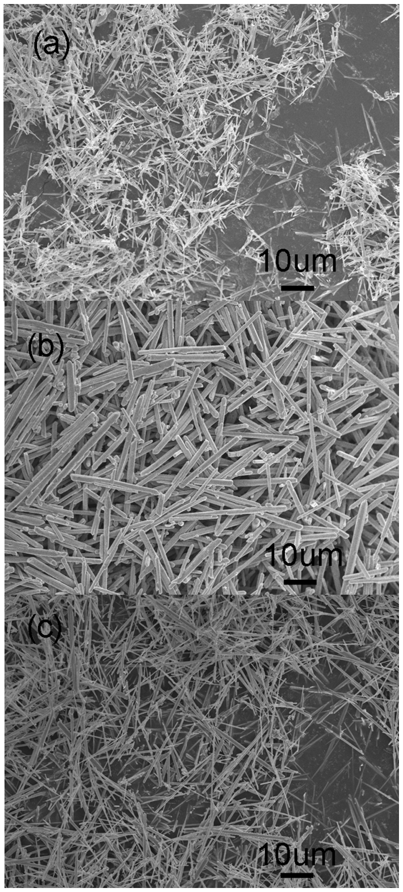

Fig. 2. SEM images of as-prepared products: (a) sample 1, (b) sample 2, and (c) sample 3.

Influence of ILs on the size and shape of t-Se

Samples 1 and 2 were synthesized under the same conditions except using two different ILs mentioned above as soft templates (Table 1). By comparing the sizes of two samples, we investigated the effect of the structure of ILs on the sizes of the final t-Se nanostructures. When [bdmim]BF_4 was introduced to the reaction system, uniform t-Se microrods with an average diameter of about 0.5 μm are obtained (Fig. 2a). If [tmim]BF_4 was introduced to the reaction system with the same reaction parameters, the length of t-Se microrods almost exhibits similarity, although the average diameter variation of microrods in (Fig. 2b) is large. This result indicates that the length of the chains at C-1 of imidazole ring of the ionic liquid affects the diameter of the final products; longer chains will hinder the 1D t-Se microstructures from growing thicker to a degree because of the steric hindrance effect. However, when [bmim]BF_4 was introduced to the reaction system with the same other reaction parameters, the morphologies of sample 3 (Fig. 2c) exhibit the similarity to sample 1. This result indicates that the methyl group at N of imidazole ring of the ionic liquid merely affects the sizes of final products.

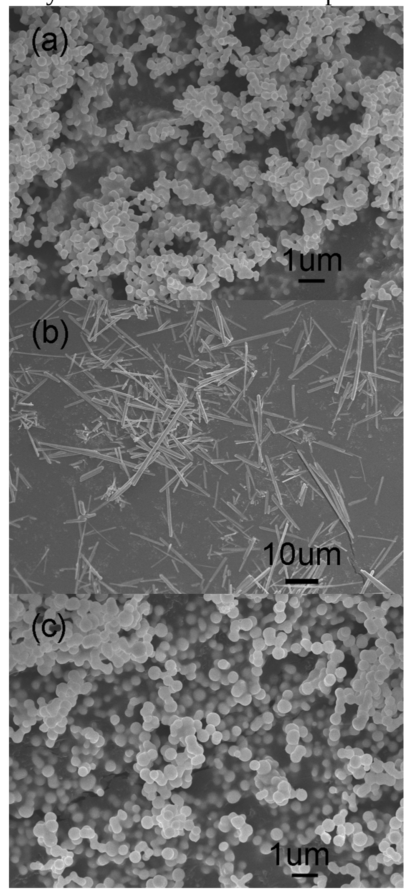

Fig. 3. SEM images of the products synthesized by adding different additives (a) without any additive, (b) $NaBF_4$, and (c) KF.

In order to investigate the influence of BF_4^- anions on the formation of t-Se microrods, a series of controlled experiments were done. Firstly, when the reaction was performed at the same condition except without adding any ionic liquid, the product is mainly consisted of microsphere (Fig. 3a), which has fairly dramatic differences, compared to that of sample1-3. Moreover, to better understand the effect of BF_4^- on the t-Se microstructures' growth, control experiments were also done under the same condition. By directly reducing Na_2SeO_3 by hydrazine hydrate in the existence of $NaBF_4$ (5 mmol), t-Se microrods (Fig. 3b) are obtained, suggesting that BF_4^- anions played an irreplaceable role for the preferential growing of t-Se microstructures. Moreover, considering the possible influence of fluorine ion hydrolysis from BF_4^- at high temperature,[27] controlled experiments were done under the same condition except adding an equal mount of KF instead of ionic liquid to reaction system. Only microspheres of t-Se are obtained, as shown in Fig. 3c. This result eliminates the possible influence of fluorine ion from hydrolysis of BF_4^- anions.

Influence of reaction temperature, reaction media and the amount of ILs on the morphologies of t-Se

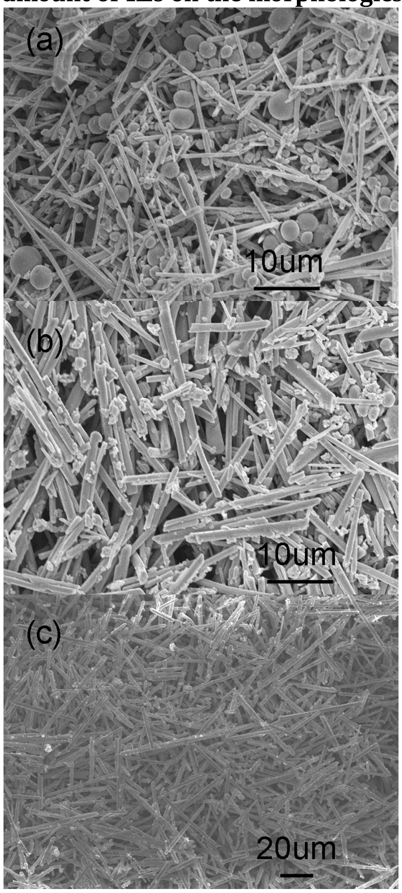

Fig. 4. SEM images of the products synthesized at: (a) 80 ºC, (b) 100 ºC and (c) 180 ºC.

To determine the effects of other experimental parameters (reaction temperature and reaction media) on t-Se materials under the IL-assisted solvothermal condition, we preformed a series of control experiments in which the experimental parameters were compared with those of Se microwires, unless otherwise stated. First, we found that the reaction temperature had a significant effect on the selenium morphology. When reaction was performed at 80 ºC, a mixture of microrods and microspheres were obtained (Fig. 4a). After reaction was conducted at 100 ºC, more microrods were produced and microspheres disappeared but still short microcrystals could be seen, shown in Fig. 4b. Improving the reaction temperature to 180 ºC resulted in more anisotropic growth. As shown in Fig. 4c, the product is almost consisted of microrods. Clearly, the reaction temperature palys a pivotal role in determining the morphology of Se product morphology.

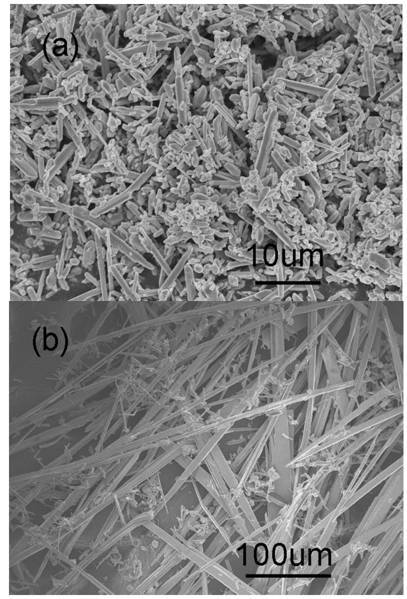

Fig. 5. SEM images of the products synthesized by using different solution of distilled water and alcohol with different ratio: (a) 3:1 and (b) 1:3.

Furthermore, it was found that the ratio of distilled water and ethanol also exerted a marked influence on the product shapes in this method. When the volume ratio of distilled water and ethanol is controlled to 3:1, irregular microrods are discerned (Fig. 5a). Increasing the ratio of distilled water and ethanol to 1:3 resulted in a mixture of microrods and microtubes (Fig. 5b), suggesting that the ratio of distilled water and ethanol is a critical factor in determining t-Se microphologies.

Proposed Mechanism

Systematic investigations of the formation mechanism of t-Se microstructures in the mixed solution with different ionic liquids are important for the morphology control of t-Se products, which up to now has not been reported in detail. To explore the formation mechanism of t-Se nanowires, it is necessary to consider the factors influencing crystal growth and the structure of the trigonal form of selenium. It is well known that the most important factor affecting crystal growth in a solution is the solubility of the solute.[28, 29] In our experiment, when the reaction was processed without any ionic liquids, it gave microspheres. However, we could get t-Se microrods when the BF_4^- based ionic liquid was added to the reaction system. From the dynamic point of view, the way of t-Se nucleation was changed by introducing BF_4^- based ILs to the reaction. The BF_4^- based ILs is known to be hydrophilic ionic liquid and is miscible with water. In the aqueous solution, the ILs could be dissociated into imidazolium cations and BF_4^- anions. The BF_4^- anion favours the formation of the t-Se microrods, due to its unique function as a bidentate ligand.[30] Moreover, it can be explained that the length of the chains at C-1 of imidazole ring of the ionic liquid affects the size of the final products, structurally. Longer chains will hinder the 1D Se microstructures from growing along the direction perpendicular to c-axis because of the steric hindrance effect, which countacts the van der Waals Forces between selenium helical chains.[31]

Conclusions

In conclusion, t-Se microstructures with different aspect ratio have been successfully synthesized by solvothermal methods with ILs. The structures of ILs were found to be crucial for determining the morphologies of final products. BF_4^- anions play key roles in the preferential growth of 1D t-Se microstructures. The chain length also affected the diameter of final products. This method may provide a new idea for the direct growth of inorganic micro/nanomaterials with various morphologies by designing different anions and cations of ILs.

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