

PVP存在下液液界面生长法制备硒纳米线

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Preparation of Selenium Nanowires by Liquid-liquid Interface Growth in the Presence of Polyvinylpyrrolidone

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Abstract: Nanowires of trigonal selenium were synthesized in large-scale by two step processes: reaction in homogeneous solution and growth at liquid-liquid interface. Polyvinylpyrrolidone was used as a soft template in the synthesis.

Key words: selenium nanowires; interface growth; polyvinylpyrrolidone

0 Introduction

Selenium (Se) is well known for its photoelectrical and semiconductor properties and has been successfully used in solar cells, rectifiers, photographic exposure meters and xerography^[1]. It could be expected that the unique structure and the quality of one-dimensional (1D) Se nanostructures, such as wires, rods, and tubes, would introduce new kinds of applications, or enhance the performance of the existing devices^[2]. In addition, 1D Se nanostructures have been used as the templates for the synthesis of other 1D nanostructures^[3] and converted into 1D nanostructures of selenide functional materials, such as ZnSe, CdSe, and Bi₂Se₃^[4]. So, 1D Se nanostructures have recently received considerable attention. Some chemical meth-

ods, due to their low cost and potential application for large-scale production, have been used to prepare 1D Se nanostructures^[2,5,6].

Generally, in chemical synthesis, the formation and the growth of nanostructures are conducted in the same bulk phase. Recently, some nanoparticles or nanostructures have been prepared in a mixed Langmuir monolayer at the gas-liquid interface^[7,8]. Faget^[9] reported an approach that the silica precursors were placed in two phases and mesoporous silica film was prepared at the liquid-liquid interface. Patil^[10] prepared CdSe thin films by liquid-liquid interface reaction technique in which the reaction of precursors and the formation of thin films were all at the interface. In this work, Se nanowires were prepared by two step processes. Firstly, the uniform Se nanoparticles were

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formed by homogeneous reaction in polyvinylpyrrolidone (PVP) aqueous solution. Then the Se nanowires rapidly grew up at the oil-water interface because of the high reactant concentration at the interface. PVP, a nonionic polymer, can stabilize and control the growth of nanoparticles and has been used to prepare various nanoparticles, such as copper spherical nanoparticles^[11], silver nanowires^[12] and Se spherical nanoparticles^[13]. In this note, PVP was used as a soft template for the preparation of large-scale nanowires of trigonal Se.

1 Experimental

1.1 Materials and instruments

PVP (M.W.=40 000) were purchased from Aldrich (Milwaukee, WI, USA). Analytical grade elemental Se and sodium sulfite were obtained from Shanghai Chemical Reagent Company (China). Materials were used as received without further purification. Na_2SeSO_3 solution was obtained by dissolving an appropriate amount of Se powders in saturated sodium sulfite solution as indicated in reference^[14]. TEM (Transmission Electron Microscopy, TEOL JEM-100SX), SEM (Scanning Electron Microscopy, Hitachi X-650) and XRD (X-Ray Diffractometer, MXP18AHF) were used to characterize products.

1.2 Preparation of Se nanoparticles

The synthesis was carried out at room temperature unless otherwise stated. In a typical procedure, 25 mL $0.01 \text{ mol} \cdot \text{L}^{-1}$ Na_2SeSO_3 and 25 mL 0.1% PVP water solution were mixed thoroughly under stirring in order to achieve good dispersion of SeSO_3^{2-} in PVP matrix. Then two synthesis processes were performed. First process was an aqueous solution reaction: 5 mL $3 \text{ mol} \cdot \text{L}^{-1}$ HCl solution was dropwise added into Na_2SeSO_3 /PVP mixture solution under stirring and the reaction solution was aged for 2 h. Second process was liquid-liquid interface growth: 10 mL *n*-butanol was added into the reaction solution under stirring and this mixture was aged for 6 h after the formation of butanol-water interface. The products were separated by centrifugation and characterized.

2 Results and discussion

Fig.1a shows the SEM image of the final products obtained in optimal conditions ($3 \text{ mol} \cdot \text{L}^{-1}$ HCl, 0.1%

PVP). From the image, it can be seen that uniform Se nanowires were obtained. The crystallization and the purity of Se nanowires are shown in Fig.1b. All the diffraction peaks in the XRD pattern could be indexed as the trigonal phase of Se. From this XRD pattern, it can be concluded that the Se nanowires were highly pure in chemical composition. The lattice constants were calculated as $a=0.437 \text{ nm}$, $c=0.495 \text{ nm}$, which corresponds well to those of the trigonal phase ($a=0.434 \text{ nm}$, $c=0.495 \text{ nm}$) reported in the literature^[15].

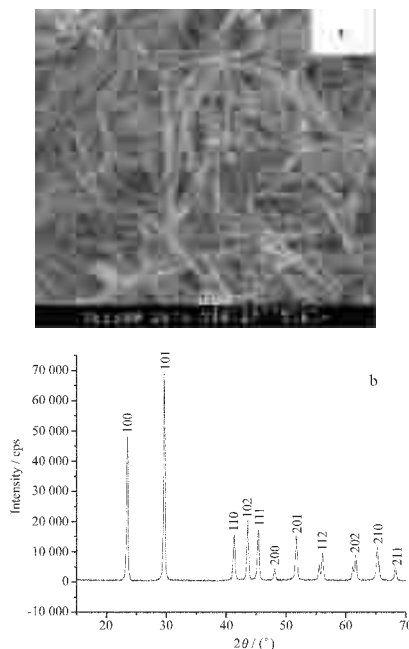
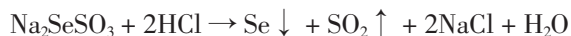


Fig.1 Patterns of Se nanowires
(a) SEM image; (b) XRD patterns

The morphology of the first products obtained in homogeneous reaction process was sensitive to the concentration of precursors as reported in reference^[16,17]. Furthermore, the morphology of the first products would affect or determine the shape of final products.

2.1 Homogeneous reaction process

In this process, the following reaction would occur in Na_2SeSO_3 /PVP mixture solution with the addition of HCl solution:



Based on the color change from colorless to orange colloid of the solution, we could infer that the amorphous Se nanoparticles were formed^[4] through a homogeneous nucleation process. These Se nanoparticles were prevented from aggregation into larger ones due to the presence of PVP molecules.

2.1.1 Effect of HCl concentration

HCl concentration influenced the morphology of the products obtained in this process. At low HCl concentration ($1 \text{ mol} \cdot \text{L}^{-1}$), the Se nanoparticles obtained were mainly amorphous spheres (as shown in Fig.2a). When HCl concentration increased to $3 \text{ mol} \cdot \text{L}^{-1}$, Se nanorods were obtained (as shown in Fig.2b). At higher HCl concentration ($5 \text{ mol} \cdot \text{L}^{-1}$), the products obtained were amorphous spherical nanoparticles again. HCl concentration affected the speed of the elemental Se release and the structure of PVP molecules. With $3 \text{ mol} \cdot \text{L}^{-1}$ HCl, the speed of the release of elemental Se would be suitable for the crystallization of nanoparticles. On the other hand, PVP molecules with linear structure could adsorb the hydrophobic nanoparticles and induce an epitaxial growth of nanoparticles under this condition. Thus, Se nanorods were produced. At $5 \text{ mol} \cdot \text{L}^{-1}$ HCl, the reaction occurred so fast that elemental Se as-produced did not have enough time for crystallization, leading elemental Se to grow in various directions and to form spherical nanoparticles. In addition, the excess hydriions bonded with oxygen atoms in the lactam structure of PVP could weaken the function of PVP. On the contrary, the strong adsorption of PVP on Se nanoparticles could hinder the crystallization and growth of nanoparticles at low HCl concentration. Thus amorphous spheres were produced at $1 \text{ mol} \cdot \text{L}^{-1}$ HCl.

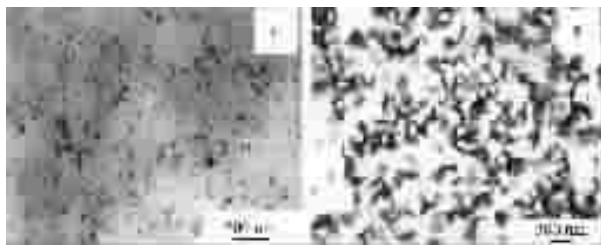


Fig.2 TEM patterns of products obtained in the first process

(a) $1 \text{ mol} \cdot \text{L}^{-1}$ HCl; (b) $3 \text{ mol} \cdot \text{L}^{-1}$ HCl

2.1.2 Influence of PVP concentration

PVP concentration also influenced the morphology of the products in the first process. When PVP concentration decreased to 0.02%, Se nanoparticles congregated rapidly. If PVP concentration increased over 0.5%, Se spherical nanoparticles were produced. This is because that the stereo molecular structure of PVP in high concentration would transfer itself from linear to net-like^[18] in favor of the formation of Se

spherical nanoparticles.

2.1.3 Influence of temperature

When the temperature was increased over $50 \text{ }^{\circ}\text{C}$, Se spherical nanoparticles were only obtained with $3 \text{ mol} \cdot \text{L}^{-1}$ HCl concentration. Fig.3 shows the interesting TEM image of the products directly taken from the reaction solution at $60 \text{ }^{\circ}\text{C}$. From Fig.3a, it can be seen that the Se spherical nanoparticles distributed in dense-branching morphology. If the adsorptive PVP on the product was removed by washing, the dense-branching morphology disappeared. This result suggested that there were some action forces among the PVP molecules and Se nanoparticles. We thought that action forces would include the hydrogen bond of PVP inter-molecules and the adsorption of PVP molecules on Se nanoparticles. In addition, the annealing of amorphous materials could favor the formation of the dense-branching morphology^[19]. Torsten et al.^[20] obtained the similar networks by specific interactions between PVP and the gold clusters. The result had shown that the hemispherical nanoparticles could be formed at $60 \text{ }^{\circ}\text{C}$ (as shown in Fig.3b), if the Na_2SeSO_3 concentration was reduced to $0.005 \text{ mol} \cdot \text{L}^{-1}$. The reason for this is still under investigation.

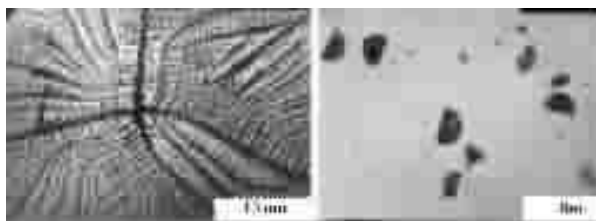


Fig.3 TEM patterns of products obtained in aqueous solution reaction process at 60°C

(a) $0.01 \text{ mol} \cdot \text{L}^{-1}$ Na_2SeSO_3 ;

(b) $0.005 \text{ mol} \cdot \text{L}^{-1}$ Na_2SeSO_3

2.2 Interface growth process

In this process, two transparent layers were formed after *n*-butanol was added into the reaction solution. The Se nanoparticles suspended at the interface between the two layers. For $3 \text{ mol} \cdot \text{L}^{-1}$ HCl concentration, the Se short nanorods produced in first process could grow into uniform Se nanowires by aging oil-water mixture at room temperature (the products as shown in Fig.1). The mechanism of interface growth could be suggested as follows. In *n*-butanol/water mixture solution, the PVP molecules absorbed Se nanorods were drawn into the interface of the oil-

water and formed the Gibbs film. Similar to Langmuir film, the Gibbs film could possess fiber structure under high interface pressure^[21]. The Se nanorods absorbed by PVP molecules would array parallel due to the spatial limit and grow into Se nanowires in terms of the fiber structure. The growth of Se nanorods could be accelerated at the interface due to the relatively high reactant concentrations. The result indicated that few Se nanowires were produced by interface growth if the products obtained in the first process were amorphous Se nanoparticles. This fact revealed that the interface process could not transfer amorphous Se directly to trigonal Se.

3 Conclusion

Using PVP as soft template, the synthesis was performed by two step processes: the reaction in homogeneous solution and the growth at liquid-liquid interface. The present technique would be useful for the synthesis and self-organization of other nanoparticles.

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