

抗坏血酸为还原剂制备 Se 纳米线

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Preparation of Selenium Nanowires Using Ascorbic Acid as Reductant

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A novel route has been developed to synthesize selenium nanowires based on ascorbic acid as reductant. The diameter of selenium nanowires can be controlled by the synthetic temperature. The as-obtained samples were characterized by XRD, SEM. The growth mechanism was also discussed.

Keywords: amorphous selenium semiconductor chemical synthesis ageing

0 Introduction

One-dimensional nanostructures such as nanowires, nanorods, or nanotubes have been the subject of intensive research due to their potential use as active components or interconnects in fabricating nanoscale electronic or electromechanical devices^[1]. They also represent an excellent system for investigating the dependence of optical, electrical transport, electrochemical, and mechanical properties on size confinement^[2,3]. One-dimensional materials, in contrast to zero-dimensional nanostructures, have been relatively unexplored, primarily due to the synthetic challenge in producing high quality materials of controlled

size^[4].

As one of the most important photoelectric and semiconductor materials, selenium nanocrystals have critical applications, such as in rectifiers, solar cells, photographic exposure meters and Xerography^[5]. Selenium also has a high reactivity towards a wealth of chemicals that can be potentially exploited to convert into other functional materials such as Ag₂Se, CdSe^[6-8]. Selenium exists in a number of crystalline structures, the principal ones being trigonal, consisting of helical chains, and the less stable monoclinic consisting of Se₈ rings, and the amorphous selenium consisting of a mixture of disordered chains. The transformation ener-

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gy from amorphous to trigonal crystal phase is $6.63 \text{ kJ} \cdot \text{mol}^{-1}$. Recently, there have been some reports on the synthesis of selenium nanowires. For example, Abdelouas et al. reported their work on using protein cytochrome c_3 reducing selenate to make selenium nanowires^[9]. Zhang's group synthesized monoclinic selenium nanowires by decomposition of selenodiglutathiones^[10]. Recently, Byron Gates and co-workers reported the controlled synthesis of high-quality selenium nanowires by ageing amorphous selenium in the dark, and the amorphous selenium was prepared by the reaction of hydrazine and selenious acid^[11–13]. Hydrazine is extremely toxic, pyrophoric and explosive at elevated temperatures, more than one week synthesis time is too long. Due to these reasons, the hydrazine-related schemes have some limitations to their practical applications. We report here that hydrazine can be replaced by ascorbic acid. Surprisingly, in a way, this new synthetic scheme works better than the hydrazine-related ones; and the synthesis time is also very short.

1 Experimental

A typical synthesis was as follows. 0.128 g of selenious acid was added into a round-bottom flask equipped with a condenser, containing 20 mL of anhydrous ethylene glycol, distilled water, absolute ethanol, respectively. Then the solution was heated to a certain temperature for 1 h. In a separate beaker, 0.400 g of ascorbic acid was dissolved in 5 mL solvent by sonication, and then this transparent solution was rapidly transferred (using a pipette) into the above solution under continuous stirring. After 30 minutes, the mixture was cooled to room temperature. Finally, the resultant sample was centrifuged, and washed with distilled water and absolute alcohol, dried in air before further characterization.

The crystal structure and composition of the obtained sample were analyzed by X-ray diffraction (XRD) on a Japan Rigaku D/MAX-2400 X-ray diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=0.154178 \text{ nm}$), at a scanning rate of $0.02^\circ \cdot \text{s}^{-1}$ in the 2θ range of 20° to 80° . The morphology and size were characterized

by a JSM-5600LV scanning electron microscopy.

2 Results and Discussion

Fig.1(a) shows XRD patterns of the selenium prepared in ethylene glycol system at 70°C . The diffraction peaks indicate that as-obtained sample was consisted of the different shape. Thus, we inferred that the selenium nanoparticles were the mixtures of the different shape. Fig.1(b) and (c) show the XRD patterns of selenium prepared at temperature 110°C and 130°C respectively. These diffraction peaks are indexed to trigonal phase.

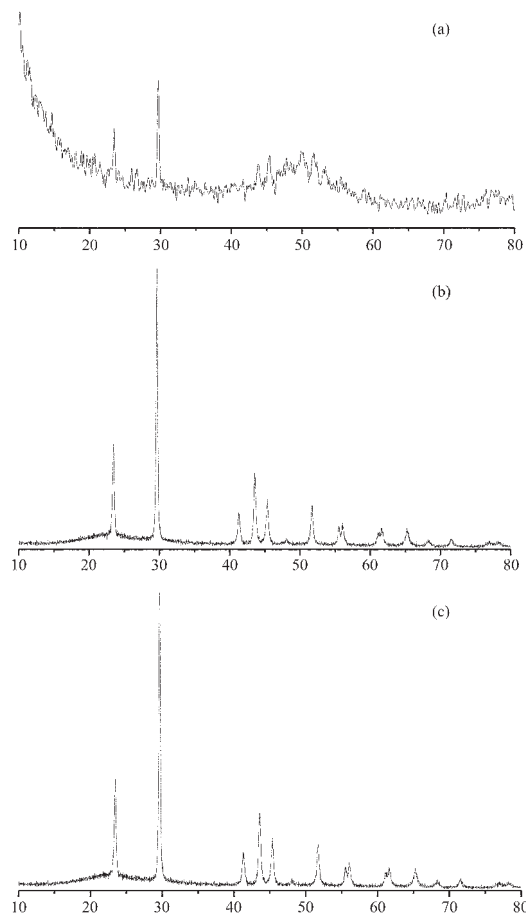


Fig.1 XRD patterns of selenium particles prepared using ethylene glycol as solvent at (a) 70°C ; (b) 110°C ; (c) 130°C

Fig.2(a) confirms the above-mentioned inference, the morphology of selenium prepared in ethylene glycol at 70°C was wire-like (60 nm in diameter, more than $10 \mu\text{m}$ in length) mixed with spherical (2 μm in diameter). Seleniums prepared at temperature 110°C

and 130 °C both display pure wire-like shape (120 nm or 150 nm in diameter, 10 μ m or 5 μ m in length, respectively). Selenium prepared in ethanol system at 70 and 130 °C (solvothermal reaction) as shown in Fig.3 (a) and (b) display similar morphology as synthesized in ethylene glycol system. The selenium prepared in distilled water at 70 and 130 °C (hydrothermal reaction) as shown in Fig.3(c) and (d) both display spherical morphology. The following conclusion can be drawn: The morphology of the obtained products varied from wire-like mixed with spherical products to pure wire-like with increasing temperature (in ethy-

lene glycol and ethanol system), and the diameter of nanowires is increased significantly; the length is decreased.

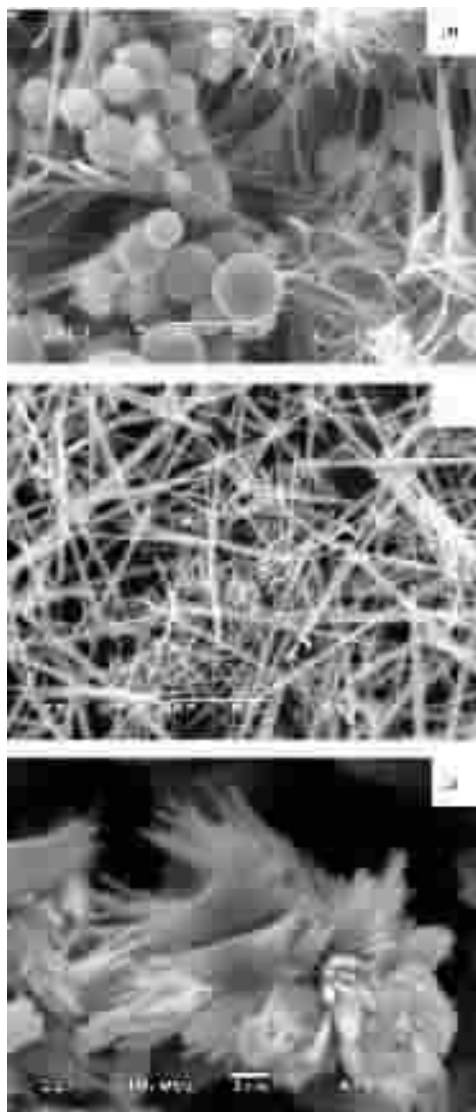


Fig.2 SEM images of selenium particles prepared using ethylene glycol as solvent at (a) 70 °C; (b) 110 °C; (c) 130 °C

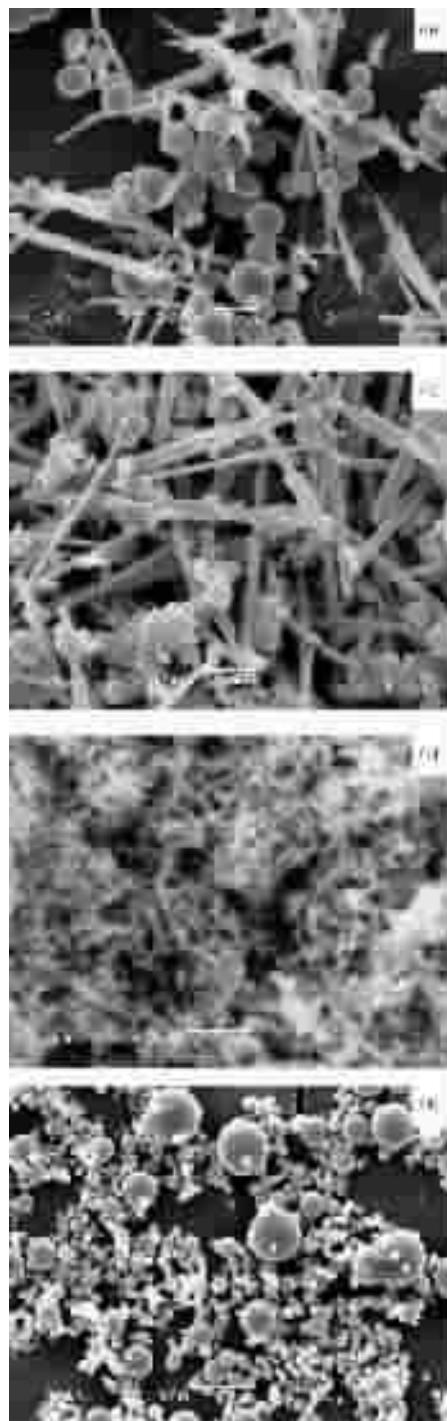


Fig.3 SEM images of selenium particles prepared in ethanol system at 70 °C (a, b) and 130 °C; and in water system at 70 °C and 130 °C (c, d)

After ascorbic acid was injected into reaction system, the appearance of brick-red color immediately

indicated the formation of amorphous selenium nanoparticles. So the growth of trigonal selenium followed two distinct paths as the previous reports^[12,13]. The first step was the formation of amorphous selenium from reaction solution; the following step was the growth on seeds of trigonal selenium generated in the same reaction solution through homogeneous nucleation. Due to high free energy in contrast to trigonal phase, the amorphous selenium will be transferred into the trigonal selenium as a result of Rayleigh instability^[14]. The transformation from amorphous to trigonal is an endothermal process, higher temperature may facilitate this transformation, so selenium prepared at higher temperature displays pure trigonal phase. On the basis of Gates's studies, the elevated temperature caused the amount of dissolved selenium to increase, so the diameter of nanowires is increased significantly with increasing temperature.

The selenium particles, trigonal phase (not shown), prepared at 130 °C in water system displayed pure spherical shape, indicating that the solvent just like temperature also played a critical role in the formation of nanowires. Gates's studies indicated the growth of trigonal selenium from the slow dissolution of amorphous colloidal selenium. The dissolution rate of amorphous colloidal selenium was determined by the solvent property and reaction temperature. Only when the reaction was carried out in ethylene glycol or ethanol at temperature above 110 °C, was the dissolution rate quick enough for the growth of selenium along the c-axis of trigonal phase, so the helical nature could be obviously reflected in the resultant morphology (wire-like). The dissolution rate in water system is so slow that a nearly spherical shape that minimizes surface area is favored^[15]. The dissolution rate in ethylene glycol or ethanol at 70 °C, was so slow that the resultant sample displayed wire-like mixed with spherical morphology. According to this growth mechanism, the growth rate in ethylene glycol is the fastest, the following is in ethanol, and the third is in water.

3 Conclusions

In summary, a simple and short reaction time method has been developed to synthesize selenium nanowires. Both reaction temperature and solvent played important roles in the formation of nanowires. It was also found that this synthesis method could be used to synthesize tellurium, the alloy of selenium and tellurium.

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