Selenium nanowires and nanotubes synthesized via a facile template-free solution method

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1. Introduction

Over the past decade, one-dimensional (1D) nanostructures such as nanorods, wires, belts, and tubes have been the focus of intensive research owing to their unique physical and chemical properties as well as fascinating potential applications in electronic and photonic nanodevices [1–3]. Until now, a variety of synthetic strategies including electrodeposition [4], laser-assisted catalytic growth [5], template-assisted (anodic aluminum oxide, carbon nanotubes, porous membranes, and surfactants) and template-free synthesis [1], sonochemical fabrication [6], solution-phase route [7], and CVD (chemical vapor deposition) [8] have been developed for the synthesis of 1D nanostructures. Among all these methods, the solution-phase route seems more promising for producing 1D nanomaterials in terms of low cost, process simplicity and high-yield production.

As an important elemental semiconductor, selenium has been extensively studied due to its particular physical properties such as high photoconductivity ($\approx 8 \times 10^4$ S cm$^{-1}$), piezoelectricity, thermoelectricity, and nonlinear optical responses [9]. In addition, it has a relatively low melting point ($\approx 490$ K) and glass-transition temperature (304 K), high solubility in various solvents like CS$_2$ and N$_2$H$_4$, and a high reactivity toward a variety of chemical reagents [10]. Therefore, it has been widely used in many attractive fields, such as solar cells, semiconductor rectifiers, medical diagnostics, xerography, and also as starting material for the fabrication of other functional materials [10,11].

Selenium exists in several allotrope forms including trigonal, monoclinic and amorphous phase. Among all the selenium allotropes, trigonal selenium (t-Se) is one of the most thermodynamically stable phases and its anisotropic crystal structure contains covalently bonded Se atoms that are helically arranged in infinite chains. It has been reported that t-Se is apt to grow into 1D nanostructure because of its unique chains of atom that is favor of the synthesis of selenium nanowires [6,7,9,12–17], nanorods [18–20], nanotubes [21–27], nanobelts [14,28,29] and so on [30,31]. Typically, Xia’s group successfully employed solution refluxing method and Xie and co-workers reported the controlled synthesis of 1D t-Se microstructures using SeO$_2$ and polyvinylpyrrolidone (PVP) by a photothermal assisted method [21]. Li et al. obtained t-Se tubular selenium by reducing selenious acid with hydrazine hydrate in different solvents accompanying a sonochemical treatment [23]. However, most of these methods were involved in the use of...
solution was under constant stirring for 20 min, the beaker dissolved in 100 mL water hosted in a 250 mL beaker. After the resonance peak centered at 234 cm$^{-1}$ was employed during the entire synthetic process, and “solid-solution-solid” mechanism for the formation of these Se nanowires time is enough. In water system and at high temperature, t-Se crystallizes with t-Se nuclei to grow into nanowires when the aging process can be greatly accelerated using ultrasonic-assisted current synthetic route.

In this work, we selected glucose as a safe reducing agent and Na$_2$SeO$_3$ as selenium source to prepare amorphous selenium ($\alpha$-Se) particles and single crystal t-Se. These $\alpha$-Se particles may dissolve in absolute ethanol at room temperature, and then re-crystallize with t-Se nuclei to grow into nanowires when the aging time is enough. In water system and at high temperature, t-Se nanotubes are the dominate product. No surfactant or template was employed during the entire synthetic process, and “solid-solution-solid” mechanism for the formation of these Se nanowires and nanotubes has been proposed based on the experimental results.

2. Experimental

2.1. Materials

Sodium selenide (Na$_2$SeO$_3$) and glucose were purchased from Sigma–Aldrich and used as received without further purification.

2.2. Preparation of t-selenium nanowires and nanotubes

In a typical procedure of synthesizing Se nanowires, 0.52 g Na$_2$SeO$_3$ and 2 g glucose were dissolved in 320 mL water hosted in a 500 mL beaker. After mixing for 20 min under vigorous magnetic stirring, the beaker containing the mixture solution was sealed and maintained in an electric oven with temperature set at 85°C for 4 h in an electric oven. After the reaction, the black-gray product was collected quickly by centrifugation and washed several times with de-ionized water, and finally dried at 40°C in air for 10 h.

2.3. Characterizations

Powder X-ray diffraction (XRD) measurements were performed on a Bruker D8 focus diffractometer with Cu K$\alpha$ radiation ($\lambda = 0.15406$ nm) at a scan rate of 4°/min in the 2$\theta$ range from 20° to 80°. SEM images were obtained using a field emission scanning electron microscope (FESEM, JEOL JSM6700F). Transmission electron microscopy (TEM and HRTEM) images as well as the corresponding selected-area electron diffraction (SAED) patterns were obtained using a JEOL JEM2100F instrument at an accelerating voltage of 200 kV. The Raman spectra were measured from 100 to 800 cm$^{-1}$ at room temperature using the 514-nm line of an Ar$^+$ laser with a power level of 20 mW (RM1000-Invia, Renishaw).

3. Results and discussion

The crystal structure of the obtained Se nanowires was characterized by X-ray diffraction (XRD) and Raman spectroscopy. Fig. 1a shows the typical XRD pattern. All the diffraction peaks could be indexed as trigonal phase of selenium with lattice constants of $a = 4.367$ Å and $c = 4.956$ Å, which were in good agreement with the reported data (JCPDS card No. 06-0362, $a = 4.3682$ Å and $c = 4.9536$ Å). At the same time no other peaks of crystalline impurities were detected. Compared to the peaks in the standard pattern of t-selenium, the intensities of the (1 0 0) and (1 1 0) diffraction peaks were greatly enhanced, which indicated that these Se nanowires had been preferentially grown along the [0 0 1] direction. Fig. 1b presents the Raman spectrum of the as-prepared Se nanowires. The strong resonance peak at 234 cm$^{-1}$ is a characteristic signature of trigonal selenium, which can be assigned to the stretching vibration of helical selenium chains ($A_1$ mode). The peak at 139 cm$^{-1}$ corresponds to the transverse optical phonon mode ($E$ mode). Another two peaks at 432 and 456 cm$^{-1}$ can be attributed to the second-order spectra of t-Se. In comparison, the characteristic Raman resonance absorption band for $\alpha$-selenium and monoclinic selenium are centered at 264 and 256 cm$^{-1}$, respectively, which are not observed in this spectrum. Combining the results of XRD and Raman spectrum analysis, it can be concluded that well-crystallized t-Se was obtained via the current synthetic route.

The morphology and microstructure of the Se nanowires was investigated by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The typical SEM image is shown in Fig. 2a, which demonstrates that these selenium nanowires are produced with large quantities and have a width of 70–100 nm as well as their length up to tens of micrometers. By

![Fig. 1. XRD pattern (a) and Raman spectrum (b) of the t-Se nanowires obtained in absolute ethanol solution with aging time of 7 days at room temperature in darkness. The resonance peak centered at 234 cm$^{-1}$ in Raman spectrum is a characteristic stretching mode of t-selenium.](image-url)
careful observation, some of the Se nanowires have a slight bend and seem to be flexible probably due to their remarkable long length. Fig. 2b is a representative TEM image, which shows that these Se nanowires are straight with smooth surface and uniform with an average width of about 70 nm, consistent with the SEM observation. In order to investigate the microstructure of the nanowires, an individual selenium nanowire was selected for the high-resolution TEM (HRTEM) observation and selected-area electron diffraction (SAED) characterization. The HRTEM image in Fig. 2c reveals that the fringe spacing of the crystal planes perpendicular to the long axis direction of the nanowire is about 0.50 nm, which is close to the (0 0 1) lattice spacing of t-Se. The discrete SAED spots (Fig. 2d) indicate a well-crystallized single crystal, which can be well indexed to trigonal selenium along [1 1 0] zone axis. Both the HRTEM and SAED results indicate that the t-selenium nanowires have a preferential [0 0 1] growth direction along their long axis, which are in good agreement with the analysis of the XRD pattern.

During the entire synthetic procedure, the less stable amorphous selenium (α-Se) colloidal nanoparticles were initially generated in the solution. As the beaker containing the reactants was heated in an oven and before the solution temperature was increased to the target of 85 °C, the color of the solution changed to brick-red, which indicated that the α-Se formed at this stage. Fig. 3a and b shows the typical SEM and TEM images of the obtained nanoparticles, from which we can find that these α-Se colloidal nanoparticles exhibit perfect spherical shape with monodispersed size of about 280 nm. The XRD pattern shown in the inset of Fig. 3b further confirmed that all these selenium colloidal nanoparticles were in the amorphous phase.

Several experiments with different aging time were carried out to investigate the detailed growth process of t-Se nanowires. After the amorphous Se colloidal nanoparticles were redispersed in the absolute ethanol for 1 day, some spherical α-Se particles began to collapse into irregular shapes (due to the dissolution process of α-Se) as shown in Fig. 3c and d. Close inspection found that some collapsed particles jointed together and a small fraction of protruding granules generated on its surface. The SAED pattern (Fig. 3e) demonstrated that these granules are crystalline. When the dispersed solution was aged at room temperature for prolonged time, amorphous Se nanoparticles partially dissolved into the ethanol solution and generated high reactive selenium atoms, which would re-crystallize and form crystalline t-Se nuclei when the concentration of these free selenium atoms was high enough. The nuclei could be precipitated out and deposited on the surface of the collapsed α-Se colloidal particles, and this dissolution process could continue until all the α-Se was completely converted to more stable t-Se. Here, absolute ethanol was served as an important medium for the phase transformation. If water was used instead of ethanol for aging the α-Se for even more than three weeks, no t-Se nanowires could be obtained and the dispersion of α-Se preserved brick-red all the time. It might be due to the much greater solubility of selenium in ethanol than in water at room temperature [12,13].

When the aging time was prolonged to 3 days, some irregular particles combined with some t-Se nanowires were obtained (Fig. 3f). These nanowires have a mean width of 70–100 nm and length of only a few micrometers. It was also observed that most of the t-Se nanowires grow with one end on the surface of irregular particles, where the t-Se seeds were produced and deposited in the previous stage. It can be concluded that the nanowires grow in situ where the crystalline seeds were located, and the continuous feeding of selenium atoms onto the crystalline seeds led to the formation of linear nanostructures due to its anisotropic crystal structure. It has been reported that the diameter of these t-Se nanowires was defined by the lateral dimensions of the
nanocrystalline seeds and an increase in the growth time only led to the formation of longer nanowires at the expense of α-Se colloidal nanoparticles [9]. The same results were obtained in our study. When the aging time of dispersed solution was increased to one week, most of the amorphous selenium particles disappeared and the t-Se nanowires became longer along their longitudinal axis. Compared with the nanowires obtained with aging time of 3 days, the nanowires achieved at this stage almost preserved the same width as before while the length could be up to tens of micrometers (Fig. 2a). When the transformation from α-Se to t-Se was complete, further extension of the aging time could not obviously increase the length of the nanowires. At room temperature, the process of phase transformation may proceed slowly due to the insufficient energy supply. However, the relatively slow reaction favors separating the growth from the nucleation step, which, in turn, can provide enough time for the anisotropic growth of the product and lead to the final formation of t-Se nanowires.

Based on the results of a series of experiments, it was interesting to find that Se nanotubes could be produced if we aged the initial reactant system continuously at high temperature (e.g., 85 °C). After the brick-red α-Se colloidal nanoparticles were generated in the solution, the reaction was allowed to continue instead of cooling down the reactants and collecting the α-Se

Fig. 3. (a) SEM image of a-Se nanoparticles obtained initially in 320 mL water containing 0.52 g Na₂SeO₃ and 2 g glucose. (b) TEM image of single a-Se nanoparticle. XRD pattern in the inset demonstrates the amorphous phase. (c) SEM image and (d) TEM image of Se product prepared in absolute ethanol with aging time of 1 day at room temperature. (e) The SAED pattern of the circled part in (d), suggesting the crystal structure of small t-Se granules. (f) SEM image of Se product prepared in absolute ethanol with aging time of 3 days at room temperature.

Fig. 4. (a) SEM image of Se nanowires and hemi-nanotubes obtained from the reaction at 85 °C for 15 h with 320 mL water containing 0.52 g Na₂SeO₃ and 2 g glucose. The inset shows the typical hemi-tube structure and the scale bar of 300 nm. (b) Low-magnification and (c) magnified SEM images of Se nanotubes obtained from the reaction at 85 °C for 4 h with 100 mL water containing 1.03 g Na₂SeO₃ and 3 g glucose. White arrows in (c) and the magnified view of the white circled part in the inset show the open tubular structure. (d) TEM image of the obtained t-Se nanotubes. (e) HRTEM image and (f) SAED pattern of single t-Se, suggesting the growth along [001] direction.
nanoparticles. As the SEM image is shown in Fig. 4a, when the sample was synthesized at 85°C for 15 h with the concentrations of starting materials unchanged, the products included Se nanowires and scroll-like hemi-nanotubes, combined with a few particles. Generally, the reaction rate can be greatly enhanced when the concentrations of reactants are substantially increased. In order to complete the reaction in shorter time, we both increased the concentration of Na₂SeO₃ and reduced the solvent volume simultaneously as described in the synthetic process of t-Se nanotubes in the experimental section. In such case, large-scaled Se nanotubes could be obtained with the reaction time of 4 h and typical SEM images are shown in Fig. 4b and c. The tubular characteristics of the 1D nanostructure can be clearly seen in an enlarged SEM image (Fig. 4c). By careful observations, these nanotubes have a diameter ranging from 180 to 350 nm. The TEM image (Fig. 4d) shows that the Se hollow nanotubes are approximately 80–120 nm in thickness of walls and 250–320 nm in outer diameter. The SAED pattern (Fig. 4e) taken from an individual nanotube indicates its single crystallinity. The fringe spacing observed in the HRTEM image (Fig. 4f) is about 0.50 nm, consistent well with interplanar spacings of the (0 0 1) lattice planes of t-Se, which implies that the Se nanotube is a single crystal and also grows along the [0 0 1] direction.

To understand the entire growth process of such nanotubes, series of experiments on various growth stages of t-Se nanotubes were carried out in details. As shown in Fig. 5a, α-Se colloidal nanoparticles with various sizes (100–400 nm) were generated before the temperature of the solution increased to 85°C. The broad size distribution probably results from the high concentration of initial reactants. These α-Se colloidal nanoparticles would partially dissolve in the following stage with increasing temperature owing to their instable phase, and produced t-Se crystal seeds for the subsequent growth of 1D nanostructure. As a matter of fact, the phase transformation energy from amorphous selenium to trigonal selenium is only 6.63 kJ/mol, hence, a slightly increase in temperature will lead to achieve the phase conversion [32].

Clearly shown in Fig. 5b, some partially dissolved nanoparticles with rough surface and a few nanotubes with length within 1.5 μm and different diameters could be obtained when the reaction time was prolonged to 100 min. It was reasonable that much more α-Se was obtained when the concentrations of original reactants were obviously increased, and thus, more t-Se seeds with hexagonally or trigonally facetted shapes could be transformed from the less stable α-Se particles. Also, some of the t-Se seeds might join together leading to the increase in their lateral dimensions, which influenced and determined the diameters of the 1D nanostructure. Therefore, the diameters of the resultant 1D Se nanostructure exhibited various values. The continuous addition of Se atoms to the t-Se seeds would preferentially occur at the circumferential edges of hexagonally or trigonally faceted seeds, resulting in the formation of t-Se nanotubes [14]. In comparison, when the concentration of t-Se seeds was not high enough, only a small amount of them partially joined together and probably produced some scroll-like hemi-nanotubes (Fig. 4a). This result also confirms that the long t-Se nanotubes develop from very short ones, instead of plane-scroll mechanism. By increasing the reaction time to 2.5 h or above, longer Se nanotubes could be obtained accompanied with the gradual disappearance of nanoparticles (Fig. 5c and d). Similar to the preparation of t-Se nanowires in the room temperature, the nanotubes would not grow longer once the amorphous selenium nanoparticles were completely converted into trigonal selenium.

According to the above detailed investigations about the growth process of Se nanowires and nanotubes, a “solid-solution-solid” growth process was proposed as shown in Fig. 6. Firstly, the α-Se colloidal nanoparticles were generated in the synthetic system (step a or b). In fact, according to Stranski rule, during the crystal growth process, the least stable phase usually precipitates first because it is favored kinetically, then this metastable phase is transformed into a more thermodynamically stable phase [33]. Based on our observations in the series of experiments, it is understood that the α-Se nanoparticles would be transformed into t-Se seeds, which served for the subsequent
growth of 1D nanostructures. At room temperature, the solubility of α-Se in the ethanol is much larger than that in pure water and crystal growth rate is slow, leading to final formation of t-Se nanowires (step c and thereafter). While at higher temperature of 85 °C with and higher concentrations of initial reactants, t-Se nanowires combined with some scroll-like hemi-nanotubes (step d) or nanotubes (step e and thereafter) were formed.

In addition, the glucose maybe also plays a vital role in the formation of such nanotubes or scroll-like hemi-nanotube in this study, because glucose serves as not only a reducing reagent but also a structure-directing reagent. Our present understanding of the detailed reason to the formation of different final products related to the various concentrations of t-Se seeds is still limited, and further investigation is in progress.

4. Conclusions

In summary, t-Se nanowires with width of 70–100 nm and length up to tens of micrometers were synthesized in absolute ethanol at room temperature, while t-Se nanotubes with outer diameter ranging from 180 to 350 nm could be obtained at 85 °C in water system. HRTEM and SAED analyses indicate that these 1D t-Se nanostructures grow along [0 0 1] direction. A “solid-solution-solid” growth process was proposed based on the SEM and TEM observations of the samples obtained at different stages. Amorphous Se nanoparticles were generated initially and then would transform into crystal seeds for the subsequent growth of nanowires or nanotubes. At room temperature, a-Se nanoparticles dispersed in ethanol can transform into t-Se nanowires owing to the higher solubility of a-Se and slower growth rate of t-Se. In contrast, at 85 °C and with higher concentrations of reactants, t-Se nanotubes are easily achieved probably because of the faster growth speed and the in-situ formation from t-Se seeds with hexagonally or trigonally faceted morphology.

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