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Inorganic Chemistry Communications 7 (2004) 1014-1016

INORGANIC CHEMISTRY COMMUNICATIONS

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One-step fabrication of selenium and tellurium tubular structures

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Received 28 May 2004; accepted 5 July 2004 Available online 10 August 2004

Abstract

Single-crystal Se and Te tubular structures have been synthesized in one step by a hydrothermal method and characterized by means of X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and selected-area electron diffraction (SAED). The hollow prismatic morphology of the tubular structures has been revealed and explained based on the nucleation and growth mechanism of the highly anisotropic crystal structures of Se and Te. © 2004 Elsevier B.V. All rights reserved.

Keywords: Hydrothermal synthesis; Selenium; Tellurium; Tubular structure

One dimensional materials have attracted much attention due to their importance in mesoscopic physics and potential applications in fabricating novel nanoelectronic, optoelectronic, electrochemical, and electromechanical devices [1-4]. Selenium and tellurium are of special interests because they possess versatile properties such as high photoconductivity, catalytic activity toward organic hydration and oxidation reaction, intrinsic chirality, high refractive indices and large birefringence, relatively large piezoelectricity and thermoelectricity, nonlinear optical responses [5-7], and a high reactivity toward a wealth of chemicals that can be exploited to convert into other one-dimensional functional materials like Ag₂Se [8] and CdSe [9]. So far, Se nanowires and nanorods [10], Se or Te nanotubes [11,12] and Se/Te alloy nanorods [13] have been generated through different approaches, e.g., refluxing method, sonochemical method and physical evaporation approaches [14-16]. However, the above-mentioned methods involved long

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period processes, high temperature or complex multistep processes to grow appreciable quantities of nanostructures. On the other hand, the fabrication of Se nanotube has not been fully investigated with only one example which involved a two-step approach [11]. Herein, we report a simple hydrothermal method to fabricate Se and Te tubular structures in one-step at low temperature (50–180 °C).

Different from the above-mentioned known preparations of Se and Te nanostructures [14–16], we used sodium selenite (Na₂SeO₃) or sodium tellurite (Na₂TeO₃) as the Se or Te sources and water as the sole solvent. Ammonia or alkali is not necessary in our experiment because Na₂SeO₃ or Na₂TeO₃ can dissolve in water to form clear alkalescent solution (pH = 8).

In a typical procedure, 2 mmol Na₂SeO₃ or Na₂TeO₃ was dissolved in 33 ml distilled water and 0.2 ml hydrazine hydrate (N₂H₄ · H₂O, 50%) was added by stirring. The resulting clear solution was transferred into a 40 ml Teflon-lined autoclave and heated to a given temperature for a certain time. After cooling to room temperature naturally, the depositing precipitate was collected and washed with distilled water and absolute ethanol for several times, and then dried at 60 °C for 4 h. The

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^{1387-7003/\$ -} see front matter © 2004 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2004.07.003

size and the morphology of Se and Te were characterized by SEM (JSM-6330F, operating at 10 kV) and TEM (JEOL-2010, operating at 180 kV). The XRD patterns for the structural measurements were recorded on a D/Max-IIIA diffractometer with Cu K α radiation ($\lambda = 1.54056$ Å) at a scanning rate of 0.07° s⁻¹ for 2 θ ranging from 10° to 70°.

Fig. 1 shows the powder XRD patterns of Se and Te products which were obtained via hydrothermal process at 90 °C for 48 h and at 150 °C for 12 h, respectively. All peaks in the patterns can be indexed to hexagonal phases of Se and Te. The lattice parameters were calculated as a = 4.3659 Å, c = 4.9606 Å for Se (Fig. 1(a)), and a = 4.4573 Å, c = 5.9221 Å for Te (Fig. 1(b)), which are in good agreement with the reported values of Se



Fig. 1. X-ray diffraction patterns of the samples of Se and Te tubular structures: (a) Se microtubes synthesized at 90 °C for 48 h; (b) Te nanotubes synthesized at 120 °C for 12 h.

(a = 4.3662 Å, c = 4.9536 Å, JCPDS 06-0362) and Te (a = 4.4579 Å, c = 5.9270 Å, JCPDS 36-1452), respectively. Compared to the standard XRD patterns, the (100) peaks in Figs. 1(a) and (b) are much stronger, possibly indicative of the $\langle 001 \rangle$ oriented growth of trigonal Se and Te tubular structures.

Typical micrographs of the two as-prepared products are shown in Fig. 2, which clearly illustrate tubular structure of prismic morphology for both Se and Te: Se microtubes with average width of 1 µm and length nearly up to 10 µm; Te nanotubes with width from 100 to 700 nm and length nearly up to 5 µm. It can be seen from the SEM images that the inner aperture of Te nanotubes is much larger than that of Se microtubes, and the wall of Te nanotubes is thinner than that of Se microtubes. The average length of Te nanotubes is shorter than that of Se microtubes. In Fig. 2(a), some spherical particles can be observed. This indicates that the initial forms of Se and Te were spherical particles, from which the nanotubes were assembled due to the highly anisotropic structures of trigonal Se and Te consisting of helical chains of covalently bound atoms. A similar growth procedure was reported for Se nanotube in a two-step method [11]. From Fig. 2(b), we can also see that many nanotubes are broken, probably owning to the fact that the walls of Se and Te nanotubes were packed from abovementioned spiral chains which bind to each other merely through van der Waals interactions [10], remarkably different from other tubular structures made of sheet-like building blocks [16].

TEM images shown in Figs. 3(a) and (b) also confirm the tubular structures of Se and Te. The sharp spots of the selected-area electron diffraction patterns (SAED, see the insets to Figs. 3(a) and (b)) show that both of Se and Te tubular structures are single crystalline phase with growth direction along the *c*-axis as indicated by the arrows in Figs. 3(a) and (b).

The exact mechanism for the formation of Se and Te tubular structures is still not fully understood, however,



Fig. 2. SEM images of Se and Te tubular structures: (a) Se microtubes obtained at 90 °C for 48 h; (b) Te nanotubes obtained at 120 °C for 12 h.



Fig. 3. TEM and SAED images of Se and Te tubular structures: (a) TEM images of Se microtubes obtained at 90 °C for 48 h; (b) TEM images of Te nanotubes obtained at 120 °C for 12 h.

the first step of Se or Te tubular structures growth might be described as the following reaction:

$$\begin{split} &Na_2 \text{SeO}_3(\text{or } Na_2 \text{TO}_3) + N_2 \text{H}_4 \\ &\rightarrow N_2 \uparrow + \text{Se} \downarrow (\text{or } \text{Te} \downarrow) + \text{H}_2 \text{O} + 2\text{NaOH} \end{split}$$

Sodium selenite or sodium tellurite was reduced to Se or Te by N_2H_4 at low temperature in the hydrothermal conditions, and then Se or Te particles aggregate partly and grow into hollow structures in suitable environment. It is well known that the highly anisotropic crystal structure is the primary factor for the formation of one-dimensional nanostructures [17,18]. As far as the trigonal Se and Te are considered, they have highly anisotropic crystal structures composed of infinite helical chains of covalently bound atoms parallel to the *c*-axis, which are connected together through van der Waals forces [10]. Such an inherently anisotropic structure gives Se and Te a tendency to grow toward [001] direction. In addition, we found that the reaction temperature, hydrothermal conditions and the reducing agent were also important in the formation of Se and Te tubular structures. The Se microtubes can be obtained at a lower temperature with longer reaction time compared to the Te nanotubes. For example, Se tubular structures were obtained at 70-110 °C for 48 h (or even at 50 °C when prolonging the reaction time), while Te nanotubes were obtained at 100-180 °C for just 12 h. We could not get Se tubular structures but red-black solution when the temperature was higher than 140 °C, which is due to the fact

the Se is more active than Te [19]. More detailed investigation is underway to understand the exact mechanism for the formation of Se and Te tubular structures by this method.

In summary, we have succeeded in synthesizing tubular structures of Se and Te by hydrothermal method in one-step process without templates or surfactants. According to their possible nucleation and growth mechanism, this simple and convenient method may be applied to other inorganic materials with highly anisotropic crystal structures. Furthermore, the properties such as melting point, band gap and magnetoresistance (MR) effect of Se and Te tubular structures might show promise for fruitful exploration of their technological applications.

Acknowledgements

The financial supports of NNSF of China, NSF of Guangdong Province, and the RFDP of Higher Education are greatly appreciated.

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