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A rapid route for the synthesis of submicron Se and Te rod-like crystals

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Abstract

Submicron Se and Te rod-like crystals were successfully synthesized via a rapid polyol process by refluxing Na_2EO_3 (E=Se, Te) and $(NH_3)_2S_2O_3$ in ethylene glycol at 180 °C for 0.5 h under vigorous stirring. The obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscopy (TEM), and XPS procedures. Studies found that reaction time and temperature have great influences on the morphology of the final products.

Keywords: A. Element; B. Chemical synthesis; C. X-ray diffraction; D. Microstructure

1. Introduction

There has been much interest in one-dimensional nano-scale or submicron-scale materials due to their potential in mesoscopic physics and nanodevice technique. A variety of one-dimensional nano/submicron-structures have been successfully fabricated by various techniques including carbon nanotube confined reaction, arc discharge, laser ablation, physical evaporation, and chemical vapor deposition [1–5].

As important members of the semiconductor family, selenium and tellurium show unique physical and chemical properties, which provide them with the chances to widen the range of applications [6–9].

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During the last decades, there have been many reports on the solution routes to obtain Se and Te nanorods or nanowires [10–17]; however, very toxic reagents, complex procedures, or very long reaction time are usually needed to fulfill the synthesis of Se and Te nanorods and it is still a challenge to develop efficient route to synthesize Se and Te nanorods or submicron rods.

In the present work, we report on the successful synthesis of submicron Se and Te rod-like crystals via a simple polyol route, which has been widely used to synthesize metals, alloys, oxides, and chalcogenides nano- or submicron-structure materials [18–24]. The polyol route is very simple, rapid and efficient and provides us the new strategy to synthesize other important semiconductor materials.

2. Experiment

The polyol synthesis of submicron Se and Te rod-like crystals is carried out under air condition and the chemical reaction we employed can be formulated as the following equations:

$$Na_2SeO_3 + (NH_4)_2S_2O_3 \rightarrow Se + (NH_4)_2SO_3 + Na_2SO_3 \quad (1)$$

$$Na_2TeO_3 + (NH_4)_2S_2O_3 \rightarrow Te + (NH_4)_2SO_3 + Na_2SO_3 \quad (2)$$

In a typical procedure, 0.01 mol Na_2SeO_3 or Na_2TeO_3 and 0.01 mol $(NH_4)_2S_2O_3$ are added into a three-necked round-bottom flask, which is already filled with 50 mL ethylene glycol (EG). The flask is heated and refluxed at 180 °C for about 0.5 h under mechanical stirring. Cooled to room temperature, the precipitate is filtered and washes with absolute alcohol and distilled water sequentially, and then dry in vacuum at 60 °C for 3 h.

The phase purity of the products is examined by X-ray powder diffraction (XRD) using a Philips X-pert Pro Super X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscope (SEM) is performed on a Hitachi S-650 scanning electron microscope. Transmission electron microscopy (TEM) investigation is made on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV.

3. Results and discussion

All the peaks of XRD pattern shown in Fig. 1a could be indexed to the hexagonal phase Se with cell parameters comparable to the reported values (JCPDS Card. No. 73–465). Fig. 1b is the XRD pattern of as-obtained Te sample, in which the peaks can also be indexed to pure hexagonal Te phase. The refined cell constants are also in good agreement with the literature (JCPDS Card. No. 36–1452).

Fig. 2a is the SEM image of as-obtained Se sample. It can be seen that the sample consists of rod-like crystals of ca. 500 nm in diameter and length up to 15 μm. Further characterization of the obtained Se rod-like crystals is conducted by TEM (Fig. 2b), which shows a long Se rod-like crystal with diameter of about 450 nm, consisting with the SEM results. The corresponding selected area electron diffraction (SAED) pattern shows its single crystal nature. SEM image of as-obtained Te sample shown in Fig. 2d also reveals that the obtained Te sample is consisted of uniform rod-like crystals. The average diameter of

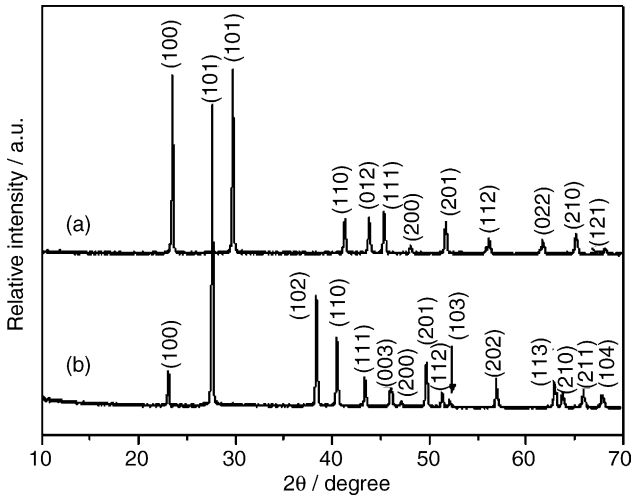

Fig. 1. XRD pattern of as-obtained samples. (a) Se; (b) Te.

these nanorods is ca. 400 nm and length ranges from 2 μm to 10 μm. TEM image and SAED pattern also show their single crystal nature (figures not shown here).

The product is also characterized by XPS for evaluation of its purity. The survey spectrum shows the presence of only Se or Te as well as C from reference and O impurity. Oxygen in the sample is likely due

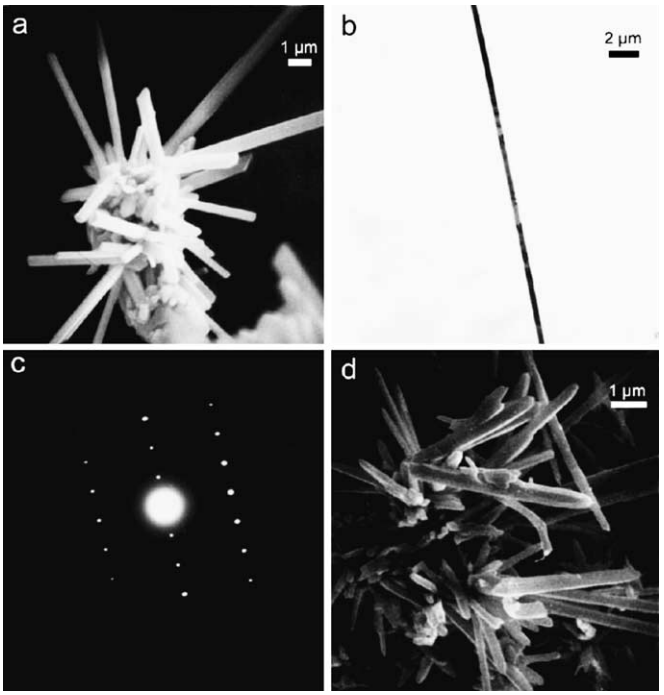

Fig. 2. (a) TEM image of submicron Se rod-like crystals; (b) TEM image of a single submicron Se rod-like crystal; (c) SAED pattern of (b); (d) SEM image of submicron Te rod-like crystals.

to exposure to the atmosphere since this ultrafine crystalline material exhibits a high surface-to-volume ratio. No obvious impurities are found on the surfaces of the samples, indicating that the as-obtained products are relatively pure.

In the formation of submicron Se and Te rod-like crystals, the feature of the present polyol route is the high boiling point of EG, which crystallizes the as-obtained products at relatively low temperature and short reaction time. We have systematically investigated the nucleation and growth process by conducting the same reaction at different temperature and different reaction time. To obtain pure crystallized submicron Se rod-like crystals, the reaction temperature should be no lower than 140 °C, otherwise no solid product was obtained. If the reaction was performed at 150 °C for 0.5 h, the yield of Se product was about 20% based on the calculation of Na_2SeO_3, and SEM observation shows that the product was short tube-like crystal just as shown in Fig. 3a. And high-magnified SEM shown in Fig. 3a inset clearly reveals the open tip of a single nanotube (the scale bar is 5 μm). From these images, it can be seen that the typical diameter of the tube-like crystal is about 5 μm and length is about 20 μm. And XRD study shows that the as-obtained samples are of relatively poor crystallinity. Conducted the same reaction at 195 °C for 0.5 h, the obtained solid product is characterized to be micrometer rod-like crystals with average diameter of ca. 5 μm and length of 30–100 μm just as shown in Fig. 3b. Our experiments showed that the higher the reaction temperature, the bigger the product diameter. Conducted the reaction at different reaction time has the similar results with that of reaction temperature: the longer the reaction time, the bigger the diameter. And when the reaction time was longer than 5 h, the diameter of the

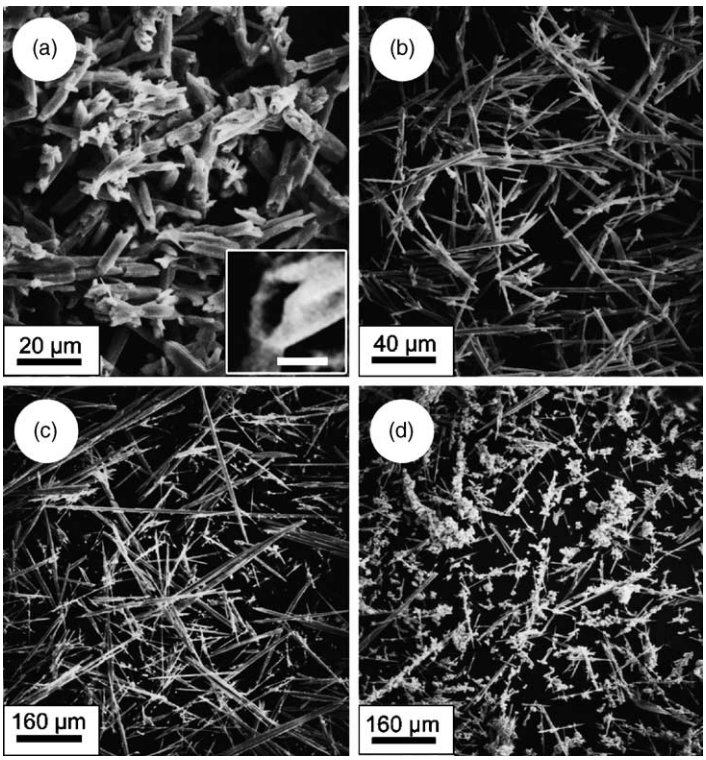

Fig. 3. SEM images of the as-obtained Se crystals under different reaction conditions: (a) 150 °C, 0.5 h; (b) 195 °C, 0.5 h; (c) 180 °C, 5 h; (d) 180 °C, without stirring.

obtained Se crystals was grown to about 10 μm and the length can be longer than 0.5 cm (Fig. 3c). The investigation of the growth of Te rod-like crystals has the similar results with that of Se.

Besides the influences of reaction temperature and reaction time, the stirring state also has great influence on the morphology of the final product. Without stirring, the as-obtained sample aggregated together and the diameter of the rod-like crystals can range from 100 nm to 10 μm while the length range from 200 nm to 300 μm (as shown in Fig. 3d). To obtain uniform submicron Se and Te rod-like crystals, the optimum condition is at 180 °C for 0.5 h under vigorous stirring.

4. Conclusions

In summary, submicron Se and Te rod-like crystals have been successfully synthesized by a rapid polyol process by refluxing the raw materials in ethylene glycol at 180 °C for 0.5 h. Studies found that the reaction temperature and time have great influence on the final products.

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