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Direct solution-phase synthesis of Se submicrotubes using Se powder as selenium source

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ABSTRACT

The selenium submicrotubes were directly prepared using Se powder as selenium source by microwave-assisted method. Field-emission scan electron microscopy (FESEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD) were adopted to characterize the as-prepared products. The results of high-resolution transmission electron microscopy (HRTEM) and XRD pattern proved that the selenium submicrotubes were single crystalline in nature and [0 0 1] oriented. A possible growth mechanism of the selenium submicrotubes was proposed. The effects of the experimental conditions, such as alkaline concentration and solvent properties, on the morphology and dimension of the products have also been discussed.

1. Introduction

One-dimensional nanostructure materials such as nanotubes, nanorods, nanowires, nanobelts, and nanoribbons not only open new opportunities in the field of microelectronics but also provide models for studying the effect of dimensionality and size confinement on electrical, transport, and mechanical properties [1–3]. Selenium is an important semiconductor with indirect band gaps of 1.85 eV. It has a relatively low melting point (~490 K), catalytic activity toward organic hydration and oxidation reaction, intrinsic chirality, high refractive indices and a large birefringence. It also has interesting spectrum properties as follows: a photovoltaic effect, a high photoconductivity ($\sim 8 \times 10^4\ S\ cm^{-1}$), relatively large piezoelectricity and thermoelectricity, and nonlinear optical responses [4–7]. Due to trigonal selenium (t-Se) for its fundamental significance in potential applications in various fields, a wealth of excellent strategies has been devoted to the synthesis of trigonal selenium 1D nanostructures such as nanowires/nanorods [8–17] and nanotubes [18–24] in the past years. But Se submicrotubes seldom were reported. Recently, we obtained such Se submicrotubes during the preparation of Se nanowires.

In this work, single-crystal t-selenium submicrotubes are successfully fabricated by direct conversion of selenium powder via a simple microwave-assisted process. To the best of our knowledge, there is no report about the synthesis of selenium submicrotubes in ethylene glycol solution directly using selenium powder up to now. Furthermore, this route needs no template and is easy to scale up. The formation mechanism of the selenium submicrotube and the effects of the experimental conditions, such as alkaline concentration and solvent properties, on the morphology and dimensions of the products have been examined.

2. Experimental

All chemicals were of analytical grade and purchased from Nanjing chemical reagent Co., Ltd. and used as received. In a typical procedure, a mixture of 0.05 g Se powder, 1.20 g NaOH, and 20 ml ethylene glycol (EG) in a flask was heated for 5 min in a homemade microwave oven equipped with a refluxing system (frequency, 2.45 GHz; power, 800 W). The black precipitates were firstly cooled to room temperature. Then the black precipitates were centrifuged, washed with water and anhydrous ethanol in sequence. Finally, the products were dispersed in anhydrous ethanol for future characterization.

FESEM (LEO 1550). TEM (Tecnai G2 S-TWIN) equipped with an energy dispersive X-rays analysis (EDXA) using an accelerating voltage of 200 kV and XRD (SHIMADZU Cu Kα, λ = 0.1548 nm) were used to characterize the as-prepared products.

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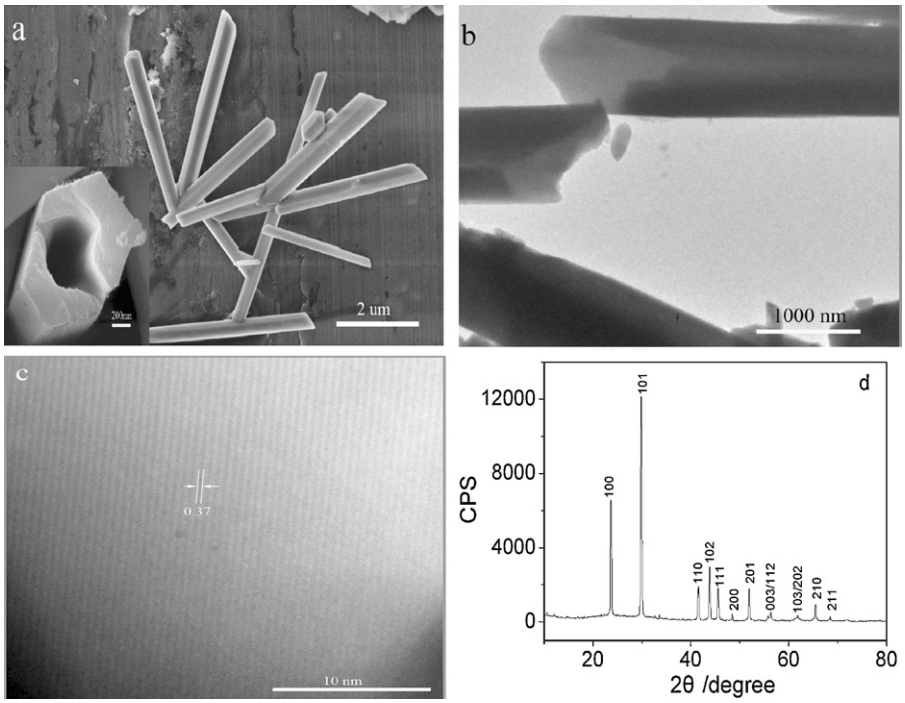

Fig. 1. Characterization of the product obtained with a typical experiment. (a) FESEM image of submicrotubes, the insert shows the hexangular mouth of a submicrotube. (b) TEM image of submicrotubes. (c) HRTEM image obtained from the edge of an individual submicrotube. (d) XRD pattern of the Se submicrotubes.

Selected-area electron diffraction (SAED) patterns were obtained on TEM at an acceleration voltage of 200 kV.

3. Result and discussion

The morphology of the obtained Se products was first characterized using FESEM and the typical FESEM image is displayed in Fig. 1a. From the low magnification FESEM observation, it is found that the as-prepared Se products are hollow tubular structure. The as-prepared submicrotubes are of 1–1.5 μm in outer diameter and 0.6–0.8 μm in inner diameter, and their length can be up to several micrometers. Higher-magnification FESEM image inserted in Fig. 1a clearly manifests the product's hexagonal tubular structure and the wall thickness of which is about 200 nm. TEM was further adopted to analyze the morphology and structure of the selenium submicrotubes. As shown in Fig. 1b, the selenium submicrotubes have an outer diameter of about 1 μm and an inner diameter of about 500 nm. The HRTEM images give further insight into the details of the crystal structure of the outer edge of the submicrotube. The clear crystal stripe in the HRTEM image shows that the submicrotube is highly crystalline. The distance of interplane perpendicular to the axis direction of the submicrotube is 0.37 nm calculated by the software, which is close to the (1 0 0) lattice plane of t-selenium. Fig. 1d provides a typical XRD pattern recorded in the 2θ range of 20–80° at a scanning rate of 5° min^{-1}. All of the diffraction peaks in the XRD pattern can be readily indexed to crystalline t-Se. The lattice constants (a = 0.435 nm, c = 0.496 nm) calculated from this XRD pattern correspond well to the values given in the standard card (JCPDS 06-0362). Compared to the standard card, the (1 0 0) peak in Fig. 1e is much stronger, it indicates that the t-Se submicrotube grow along the [0 0 1] direction. Obviously, the constant also agrees well with the fringe spacing (0.37 nm) observed in the HRTEM image (Fig. 1c). All of the above results confirm the selenium submicrotubes grow along [0 0 1] orientation [25–28].

Recently, the ultrasonic-assisted oriented attachment growth mechanism, [18–20] nucleation-dissolution-recrystallization growth mechanism [22] and the surfactant-directed growth mechanism [19] were used to explain the formation of t-selenium nanotubes. From our experimental observations, we believe that the formation of the t-selenium submicrotubes can be rationally expressed as 'disproportionation and reversal' mechanism. This mechanism has once been proposed to account for the formation Te, Se nanowires by Zhu and Zhou [26]. The route for the preparation of one-dimension Se submicrotube was developed on the basis of the following facts: firstly, Se could disproportionate easily in hot and condensed alkaline solution, and the so-called 'Se solution' was obtained. It was represented by Eq. (1). Secondly, when this 'Se solution' was cooled, the disproportionation reaction of Se reversed and Se recurred. It was illustrated by Eq. (2).

$$3Se + 6NaOH \rightarrow Na_2SeO_3 + 2Na_2Se + 3H_2O \quad (1)$$

$$Na_2SeO_3 + 2Na_2Se + 3H_2O \rightarrow 3Se + 6NaOH \quad (2)$$

It is found that the temperature plays an important role in dissolving Se powders. Without microwave irradiation, selenium particles still remain their ill-defined shape (Fig. 2a). It can be interpreted that the reaction of Eq. (1) will not carry on at a room temperature. A short time microwave irradiation can lead to the formation of selenium submicrotubes with some particles (Fig. 2b). Longer irradiation of microwave, i.e. higher temperature, favored the formation of the selenium submicrotubes (Fig. 2c). Conventional heating performed such as a hot oil bath, electric heater, or hydrothermal can obtained the similar results [26]. However, microwave heating is preferred for its great rapidity, simplicity, homogeneousness, and energy-saving considerations. The presence of this semiclosed tubular structure (Fig. 2d) indicates that the growth of the selenium submicrotubes along the c-axis based on strong covalent bonds is faster than that along the circumferential direction based on weak van der Waals interactions between selenium helical chains [23]. Based on this phenomenon, we can conclude that the hexangular submicrotubes were gradually formed by following a folding growth mechanism. The pattern