

Bi₂Te₃ Nanorods: Preparation, Reaction Mechanism and Electrochemical Property

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Abstract. A rapid chemical method has been developed for the synthesis of the Bi₂Te₃ nanorods with hexagonal crystalline phase. The method is based on the template-engaged synthesis in which the Te nanowires were used as template reagents. On the basis of a series of experiments and characterizations, the effect factors and the formation mechanism of the Bi₂Te₃ nanorods were discussed. Furthermore, the electrochemical property of the Bi₂Te₃ nanorods was determined by the voltammetric technique.

1. Introduction

Chalcogenides of V–VI groups (especially V₂VI₃-type) are useful semiconductors, which found applications in television cameras with photo-conducting targets, infrared spectroscopy, electronic and optoelectronic devices, and thermoelectric devices.[1] Recently, the bismuth chalcogenides have attracted much attention due to their interesting properties and great potential applications.[2,3] As a kind of chalcogenides, bismuth telluride has much more technological prospects.[4] Generally, antimony telluride bulk material was prepared by the solid reaction between elemental Bi and Te using microwave irradiation. Compared with the conventional bulk materials, nanomaterials have attracted considerable attention due to their distinctive geometries, novel physical and chemical properties, and potential applications in numerous areas such as nanoscale electronics and photonics. Going with the increasing interest in the nanostructured materials and nanodevices, a number of methods for the synthesis of the bismuth telluride nanomaterials with different morphologies have been developed. Bismuth telluride nanorods were synthesized in a hydrothermal system. It was especially important that bismuth telluride film was prepared by the electrodeposition method. [5] Although it is a challenge to fabricate antimony telluride into nanostructured materials that could be applied to design various nanodevices, some strategies for the synthesis of antimony telluride nanostructures have been devised.[6] In this paper, Bi₂Te₃ nanorods were prepared by a rapid chemical reaction route, in which the Te nanowires as-obtained were used as template reagents. In addition, for their thermoelectric applications, the electrochemical property of the Bi₂Te₃ nanorods was studied by the voltammetric technique.

2. Experimental Section

The reagents are of analytical grade and were used in experiments without further purification. The Te nanowires that would be used as the template reagents were prepared as described in the literature. With the Te nanowires as-obtained, Bi₂Te₃ nanorods were typically synthesized as follows. First, under magnetic stirring, 0.1mmol (0.0485g) Bi(NO₃)₃·5H₂O was added into 10 mL deionized water. Then, 0.15mmol (0.0192g) Te nanowires was added into 20 mL deionized water. After ultrasonic



irradiation at room temperature for 30 min, the Te nanowires solution was added into Bi (NO₃)₃ solution. Finally, 4 mL hydrazine (N₂H₄·H₂O) was added into the reaction solution under magnetic stirring for 2h. The mixed solution was added into a Teflon-lined stainless steel autoclave (50 mL), the vessel was immediately closed tightly and heated to 160 °C, and kept at this temperature for 5 h. The reaction took place at an autogenic pressure depending on the amount of distilled water added. After cooling the sample to room temperature, the product was obtained by centrifuge-separating and water washing the gray-black precipitate formed in the solution.

The products as-obtained were characterized by scanning electron microscopy (SEM, X—650, HITACHI), X-ray diffraction (XRD, Japan Rigaku D/max-RA X-ray diffractometer, with graphite monochromatized CuKα₁ radiation, λ= 0.15406 nm), X-ray photoelectron spectroscopy (XPS, ESCALAB MKII, UK, AlKα 1486.6 eV).

The electrochemical behavior of the products was studied by potential scan voltammetry on an electrochemical system (Lanlike, Tianjin, China). The electrochemical cell was made up of a given electrolyte solution and a three-electrode system. Prior to voltammetry experiment, the surface of CPE was polished with fine paper and the electrolyte solution was degassed with N₂. The potential scan rate was 50 mV/s for all electrochemical experiments, except the situation specialized.

3. Results and Discussion

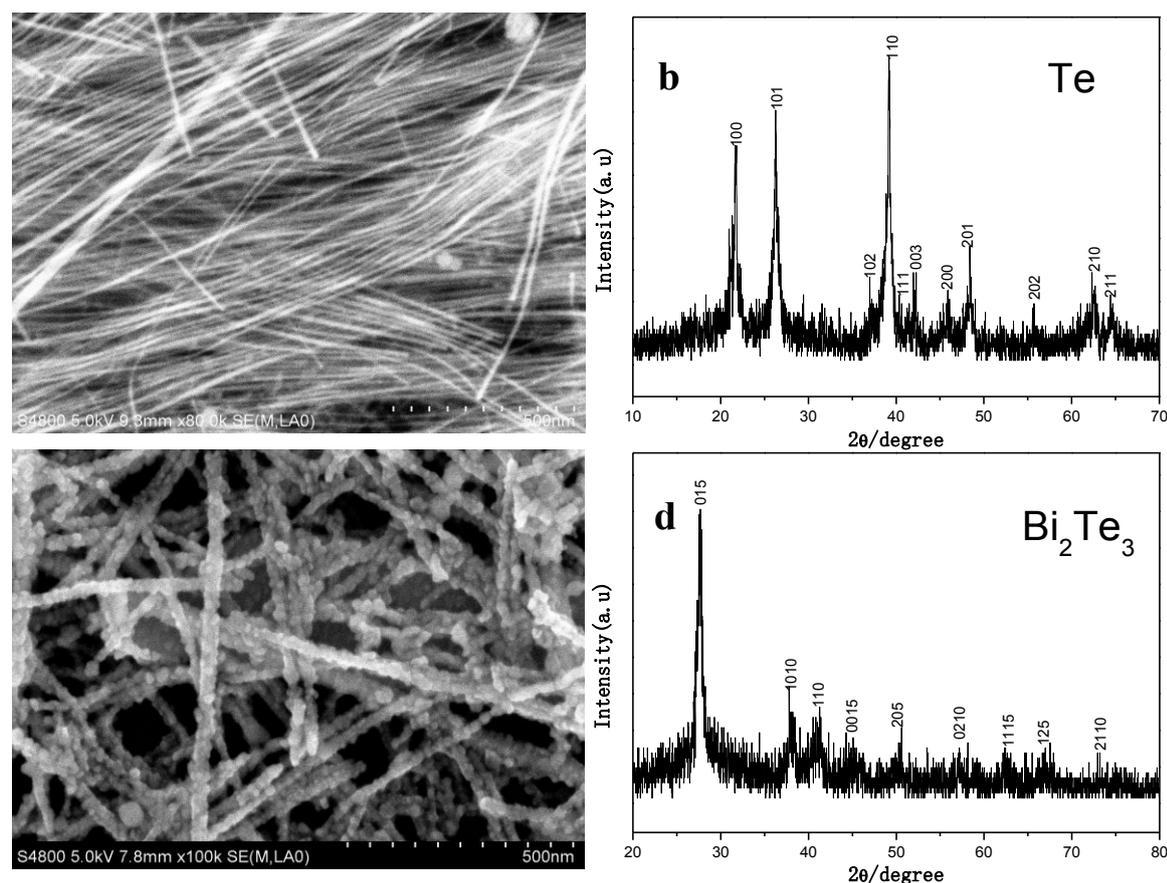


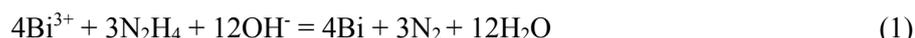
Figure 1. SEM images and XRD patterns of the Te template (a and b) and Bi₂Te₃ product (c and d).

The SEM image (Figure 1a) for the as obtained Te product discloses its rod-like morphology. The XRD pattern (Figure 1b) indicates that the Te product is composed of a hexagonal crystalline phase whose unit cell constants are $a = 0.4450$ nm and $c = 0.5996$ nm, corresponding well to those in the literature (JCPDS Card, No.36-1452). Figure 1c shows the plate-like morphology of the typical Bi₂Te₃

product, which's crystalline phase was determined by XRD (Figure 1d). Clearly, all of the diffraction peaks on the XRD pattern can be indexed to the hexagonal Bi_2Te_3 phase, and the unit cell constants calculated from the diffraction peaks are $a=0.4388\text{nm}$, $c=3.0867\text{nm}$, which are consistent with those in the literature (JCPDS Card, No.82-0358).

3.1. Reaction Mechanism.

In synthesis, the Bi_2Te_3 nanorods were produced by the reaction of Te nanowires with neonatal Bi particles. The Te nanowires were prepared in advance and the Bi particles were formed in solution by the follow reactions:



The experimental results show that the freshly formed Bi particles had a high reactivity and could readily start the synthesis reaction with Te nanowires. In synthesis, the neonatal Bi particles were first formed, since the Bi^{3+} was gradually reduced to elemental Bi by hydrazine ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$). As a result, the neonatal Bi particles could be continually supplied to react with Te nanowires. Through the topotactic transformation of Te templates, the Bi_2Te_3 nanorods were formed by the diffusion of Bi atom into the Te nanowires. Similarly, the silver chalcogenides have been prepared by this template transformation mechanism. Due to the change of atom radius and bond length in the conversion of Te to Bi_2Te_3 , the shape of the product transformed from straight to curve nanorods. In the interest of probing into the effect of the atom ratio in precursors on the product, a series of experiments were performed (Figure 2). As above, in typical synthesis, pure Bi_2Te_3 nanorods were obtained with the 1:1.5 atom ratios of Bi and Te in the precursors. When this ratio is decreased, the Te/ Bi_2Te_3 or Bi/ Bi_2Te_3 composites were obtained, which had been confirmed by the XRD patterns. This phenomenon indicates that pure Bi_2Te_3 nanorods could be obtained by the complete reaction of the Bi and Te atoms in the precursors, as performed in typical synthesis.

3.2. Electrochemistry

Figure 3a shows the experimental results of linear scan voltammetry by carbon paste electrode (CPE) modified with the Bi_2Te_3 nanorods. Consulting the results reported about the electrochemistry of Bi_2Te_3 particles, we attribute three anodic peaks on curve I, namely, peaks 1 (at 0.08 V), 2 (at 0.40 V), 3 (at -0.65 V) and 4 (at -1.14 V), to the oxidation of the Bi_2Te_3 nanorods

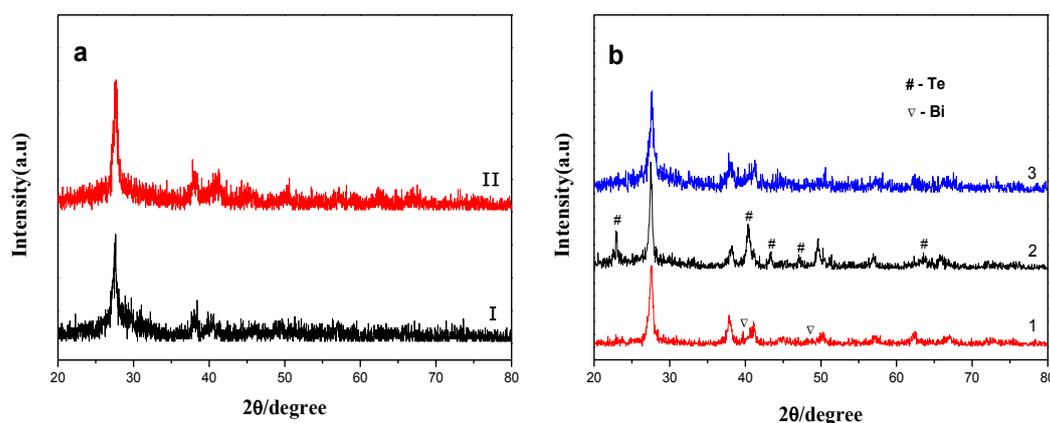


Figure 2. The XRD patterns of the products: (a) with different reaction temperature: 120°C (I); 160°C (II); (b) with different atom ratios of Bi and Te in the precursors: (1)2.0:1.5 ; (2) 1.0:3.0; (3) 1.0:1.5.

($\text{Bi}_2\text{Te}_3 - 6\text{e} \rightarrow 3\text{Te}^0 + 2\text{Bi}^{3+}$), the oxidation of Te ($\text{Te}^0 - 4\text{e} \rightarrow \text{Te}^{4+}$), the reduction of Te^{4+} ($\text{Te}^{4+} + 4\text{e} \rightarrow \text{Te}^0$), and the reduction of Bi^{3+} ($\text{Bi}^{3+} + 3\text{e} \rightarrow \text{Bi}^0$), respectively. Figure 3b shows the successive cyclic voltammograms of the Bi_2Te_3 nanorods. From the first cyclic voltammogram, it can be seen that

the peaks 1-4 are similar to that in Figure 3a and can be designated as above. Obviously, anodic peak 1 (at 0.40V) in the first cycle voltammogram is high and then fell off in the second and third cyclic voltammograms. As designated for Bi₂Te₃ nanorods, peak 1 is assigned to the oxidation of Bi₂Te₃ nanorods, and peak 5 formed in subsequent cycles is attributed the oxidation of Bi⁰ (Bi⁰ - 3e⁻ → Bi³⁺) that had been produced by the reduction of Bi³⁺ in the first cyclic voltammogram (behaving as peak 5 in Figure 3b).

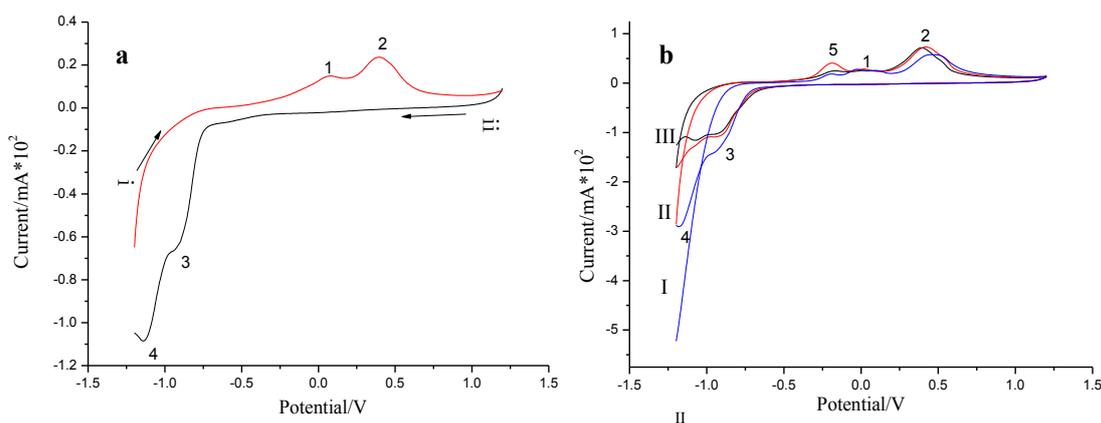


Figure 3. The voltammograms of Bi₂Te₃ nanorods in 0.10 M KNO₃: (a) the positive-going scan voltammogram (curve I) and the negative-going scan voltammogram (curve II); (b) three successive cyclic voltammograms.

4. Conclusion.

In summary, the Bi₂Te₃ nanorods with hexagonal crystalline phase were rapidly prepared by the template-engaged synthesis in which the Te nanowires were used as template reagents. It was found that the neonatal Bi could readily react with Te in a hydrothermal system, and the pure Bi₂Te₃ nanorods could be obtained with a 1.0:1.5 atom ratio of Bi and Te in the precursors. In addition, the electrochemical property of the Bi₂Te₃ nanorods was studied by the voltammetric technique in different conditions. Importantly, the as-prepared Bi₂Te₃ nanorods might be useful in various nanodevices, and the present electrochemical property of CdTe nanoribbons is potentially practicable to other nanostructures.

5. Acknowledgment.

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6. References

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