

Rapid communication

# Template synthesis of heterostructured polyaniline/ $\text{Bi}_2\text{Te}_3$ nanowires

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## Abstract

Heterostructured polyaniline/ $\text{Bi}_2\text{Te}_3$  nanowires have been prepared by chemical and electrochemical reactions on a porous alumina template. Its morphology and structure have been studied by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and electron probe microanalysis. The microscope analysis reveals that  $\text{Bi}_2\text{Te}_3$  is well enveloped in polyaniline tubules in pores of alumina template. This microscopic material shows possible application in microthermoelectric device.

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**Keywords:** Polyaniline;  $\text{Bi}_2\text{Te}_3$ ; Nanowires; Heterostructures

## 1. Introduction

Interest in the development of new inorganic/organic hybrid materials with composition modulated on the nanometer scale has grown rapidly in recent years due to wide range of potential applications in microelectronics, display technologies, catalysis and sensors. Among the different strategies to synthesize nanoscopic material reported in the literature, template synthesis is an elegant approach [1]. It was reported that nanowires of metals, semiconductors and conducting polymers have prepared by using commercial membranes as templates [2]. One advantage of template synthesis is its versatility arising from a possibility of joining up components with inorganic and organic materials [3]. During recent years, thermoelectric materials aiming at thermoelectric refrigerator applications have attracted much attention. Bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) is considered to be the best material to date for near room-temperature thermoelectric applications [4]. More recently, conducting polyaniline are thought to be another kind of potential thermoelectric materials [5,6], due to much lower thermal conductivity [7]. In addition, the polymer is

inexpensive, flexible and fit for some special uses. If polyaniline can be compounded with  $\text{Bi}_2\text{Te}_3$  in form of nanowires, the electronic transport properties of the composite should be better than those of polyaniline, and thermal conductivity of the composite should be much lower than that of  $\text{Bi}_2\text{Te}_3$ . Moreover, recent theoretical studies suggest that nanostructured thermoelectric materials with quantum confinement of electrons and holes could enhance the efficiency of these materials significantly above that of bulk values [1,8]. Therefore, polyaniline compounded with  $\text{Bi}_2\text{Te}_3$  in form of nanowires is an excellent candidate material for thermoelectric applications.

In this work, we extended the method of template synthesis with chemical and electrochemical two-step deposition to the fabrication of polyaniline/ $\text{Bi}_2\text{Te}_3$  nanowire heterostructures. In other word, we use chemically or electrochemically deposited polyaniline as second-order template to electrochemically deposit bismuth telluride. The target product is bismuth telluride encapsulated in polyaniline nanotubules. The composition and crystallinity of these structures were determined by transmission electron microscopy (TEM), scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and powder X-ray diffraction (XRD).

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## 2. Experimental section

Alumina filters made by Waterman Inc. with a thickness of 60  $\mu\text{m}$  were used as template for the synthesis of polyaniline/ $\text{Bi}_2\text{Te}_3$  nanowire heterostructures. Aniline was distilled prior to use. All the other reagents were used without further purification.

Typical polyaniline chemical template synthesis: Porous alumina template was immersed into the solution of 0.3 M aniline in 1 M HCl and subsequently (after about 20 min) an equal volume of 0.1 M  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (oxidant) and 0.3 M *p*-toluene sulfonic acid, sodium salt in 1 M HCl acid was added. After 1 h of polymerization at room temperature the substrate was removed, rinsed with the 1 M HCl acid solution and deionized water.

Typical polyaniline electrochemical template synthesis: A silver film with thickness of about 1  $\mu\text{m}$  was evaporated onto one side of the alumina template to serve as a working electrode for electrodeposition. Templates were immersed into electrolyte solutions of 0.3 M aniline and 1 M HCl for 2 h, then the electropolymerization was performed, at room temperature, in a conventional cell used with a Pt disk as counter electrode. Polymerization was accomplished galvanostatically at a current density of 11.2  $\text{mA cm}^{-2}$ ; a total of 1.6 C of charge was passed. A drastic color change to dark green was observed in alumina template.

Typical  $\text{Bi}_2\text{Te}_3$  electrochemical template synthesis: We use the same setup of polyaniline electrodeposition for  $\text{Bi}_2\text{Te}_3$  electrochemical template synthesis. Electrodeposition was conducted at  $-1.85$  V with the template as the working electrode, Pt disk as the counter electrode, from solutions of 0.075 M  $\text{Bi}^{3+}$  and 0.1 M  $\text{HTeO}_2^+$  in 1 M  $\text{HNO}_3$ . After 15 min, the  $\text{Bi}_2\text{Te}_3$  deposit filled the pores and began growing across the top surface of the template, causing the template color to change from dark green to gray.

The deposited specimens were mechanically polished to remove the surface coating layer for study in the forward XRD analysis. XRD measurement was carried out using a Rigaku Rint2000A diffractometer. EPMA analysis carried out using Shimadzu EPMA-8705QH<sub>2</sub> calibrated with tellurium and bismuth standards. For SEM imaging, the alumina templates were immersed in 6  $\text{mol L}^{-1}$  aqueous NaOH for 10 min to remove a part of alumina. A field-effect gun digital scanning microscope (JSM-6700F) with an accelerating voltage of 10 KV was used to characterize the polyaniline/ $\text{Bi}_2\text{Te}_3$  heterostructures. To study individual nanowires by TEM, alumina templates have been removed by aqueous NaOH.

## 3. Results and discussion

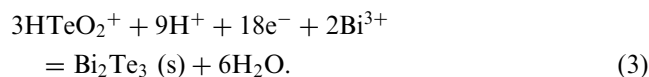
We used chemical or electrochemical deposition to synthesize polyaniline nanotubules. Fig. 1 shows SEM

images of porous alumina templates and polyaniline nanowire array composite. Fig. 1A indicates the size of pores of template is between 100 and 200 nm. Before the polymerization began, it is always essential that the template had been immersed into monomer solution for adequate time of monomer diffusion in narrow pores of template. Polyaniline nanowire arrays were fabricated in alumina template with sufficient polymerization time (Fig. 1B). In contrast, while polyaniline were synthesized (either chemically or electrochemically) within the pores of alumina template in proper reaction time, for the polyaniline preferentially nucleates and grows on the pore walls [2]. As a result, tubules of polyaniline were obtained (Fig. 1C and D). Prolonged reaction time of polymerization will close up tubules ultimately to form solid fibrils (Fig. 1B). Tubules of polyaniline were our target product for next step to fill  $\text{Bi}_2\text{Te}_3$  within it; therefore, controlling reaction time is of importance to improve the yield of tubules in deposition of polymerization reaction. Comparing chemical deposition with electrochemical deposition for fabricating tubules of polyaniline, we found electrochemical deposition of polyaniline is advantageous in two points. One is easy to transport the template filled with polyaniline to next electrochemical deposition of  $\text{Bi}_2\text{Te}_3$ . Secondly, the chemical deposition of polyaniline would be easily affected by temperature, stirring, reaction time, and were prone to form solid fibrils, while the electrochemical reaction is much easier to be controlled by voltage and current density to produce desired tubules.

Electrodeposition of  $\text{Bi}_2\text{Te}_3$  was performed in a glass cell containing  $\text{Bi}^{3+}$  and  $\text{HTeO}_2^+$  ions, acid solution at room temperature. Conducting polyaniline tubules work as second-order template and working electrode. Acid doped polyaniline in good conducting state guaranteed the electrochemical reaction to proceed successfully. Electrochemical reaction sequence to form  $\text{Bi}_2\text{Te}_3$  film from aqueous solution containing  $\text{Bi}^{3+}$  and  $\text{HTeO}_2^+$  ions has been proposed by previous reports [9,10]. In present experiment, we used the same aqueous solution system and the possible reaction sequence of the formation of  $\text{Bi}_2\text{Te}_3$  nanowires could be described as follows. Firstly, metallic Te could be reduced from  $\text{HTeO}_2^+$  ion by Eq. (1), and then  $\text{Bi}^{3+}$  ions receive electrons on the Te precipitates to form  $\text{Bi}_2\text{Te}_3$  alloy by Eq. (2):



Thus, the overall reaction could be expressed as



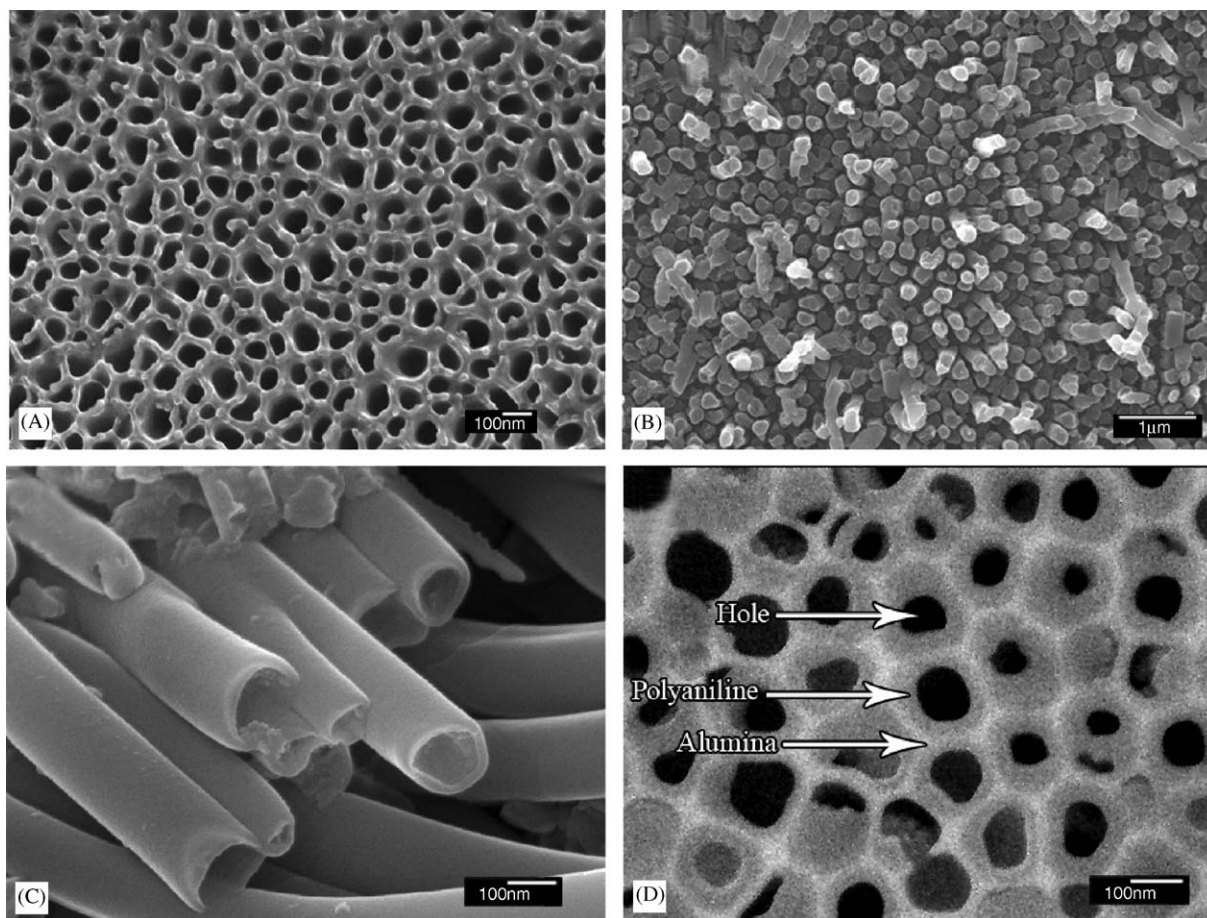


Fig. 1. SEM images of template and polyaniline nanowire array composite. (A) Empty alumina template; (B) 2.5 h polymerization with chemical deposition, alumina templates have been removed by aqueous NaOH; (C) 1 h polymerization with chemical deposition, alumina templates have been removed by aqueous NaOH; (D) cross-sectional view of electrochemically deposited polyaniline in template.

EPMA analysis of heterostructured nanowires confirmed the Bi:Te stoichiometry of 2:3 as expected for  $\text{Bi}_2\text{Te}_3$ . The error associated with EPMA is within 5 at%.

A powder XRD pattern for the product polyaniline/ $\text{Bi}_2\text{Te}_3$  composite with alumina template shown in Fig. 2 compares well to the known pattern for  $\text{Bi}_2\text{Te}_3$  (Powder Diffraction File 15-0863). The [110] peak is much stronger than expected for polycrystalline  $\text{Bi}_2\text{Te}_3$ , indicating strong texturing in  $\text{Bi}_2\text{Te}_3$  nanowire [11–13]. The wire axis is [110] meaning the  $\text{Bi}_2\text{Te}_3$  cleavage planes are parallel with pore canals in alumina template; moreover,  $\text{Bi}_2\text{Te}_3$  wires grow preferentially with the [110] planes which is the best orientation for the thermoelectric properties. The reason for the behavior of growing is related with highest electrical conductivity of perpendicular planes of [110].

To probe microscopic polyaniline/ $\text{Bi}_2\text{Te}_3$  nanowire heterostructures, we use two approaches of TEM and FESEM for characterization; both of them definitely confirmed the existence of polyaniline/

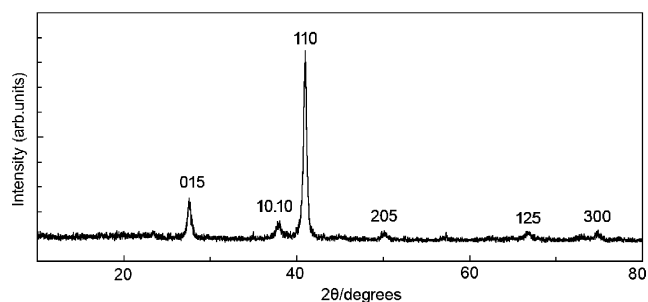


Fig. 2. X-ray diffraction pattern of a filled polyaniline/ $\text{Bi}_2\text{Te}_3$  template. The high intensity of the 110 peak indicates preferred orientation; the wire axis is [110].

$\text{Bi}_2\text{Te}_3$  heterostructures. The TEM image of polyaniline/ $\text{Bi}_2\text{Te}_3$  nanowire heterostructures is shown in Fig. 3A. Polyaniline is amorphous and transparent, while  $\text{Bi}_2\text{Te}_3$  is dark and opaque. From TEM images,  $\text{Bi}_2\text{Te}_3$  wire was well encapsulated by polyaniline tubules.

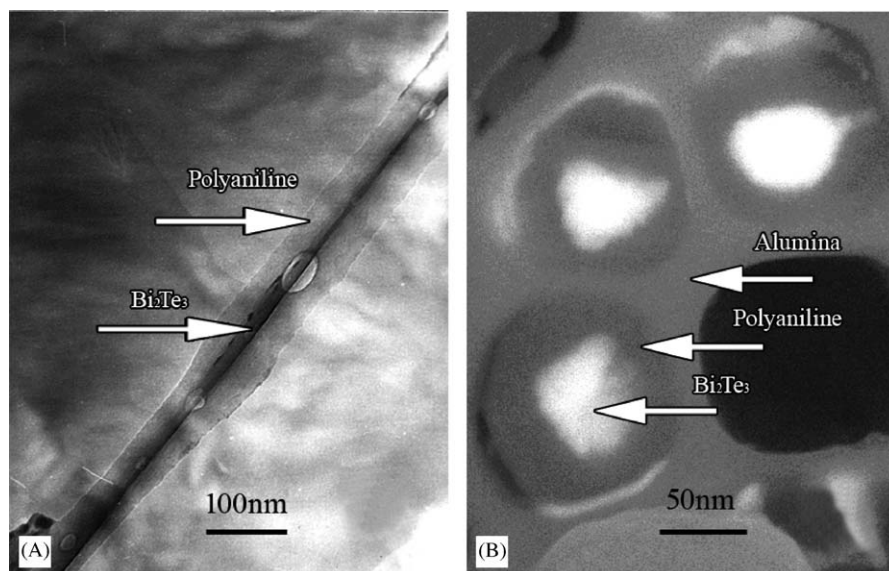


Fig. 3. Microscopic images of  $\text{Bi}_2\text{Te}_3$  nanowires encapsulated in polyaniline nanotubules. (A) Bright-field TEM images of nanowire heterostructures; (B) cross-sectional FESEM view of the wire heterostructures in alumina template.

Another evidence of the special heterostructures is SEM image. These SEM specimens were prepared by cross-section polisher. From Fig. 3B, in intersection images of specimens, it shows three polyaniline/ $\text{Bi}_2\text{Te}_3$  heterocyclic compositions over small regions. Bismuth telluride of proximate 100 nm diameter nanowires shows off-white, while polyaniline tubules having proximate 30 nm thin wall show gray in SEM image, due to the large difference in atomic weight.

In summary, we have succeeded in the fabrication of polyaniline/ $\text{Bi}_2\text{Te}_3$  nanowire heterostructures into alumina template by means of chemical as well as electrochemical deposition from aqueous solution. We found that using polyaniline tubules produced by electrodeposition as template to electrodeposite  $\text{Bi}_2\text{Te}_3$  wires is a good path to synthesize heterostructured polyaniline/ $\text{Bi}_2\text{Te}_3$  nanowires. EPMA analysis confirms chemical composition of bismuth telluride nanowires. Characterizations of XRD indicate that the deposited  $\text{Bi}_2\text{Te}_3$  wires are highly textured in the [110] direction. Furthermore, SEM and TEM analyses show that the heterostructures of  $\text{Bi}_2\text{Te}_3$  are well enveloped in polyaniline tubules in pores of alumina template. Due to quantum confinement and a strong contribution from interface effect, the novel structure of polyaniline/ $\text{Bi}_2\text{Te}_3$  composition we prepared may be a promising candidate material for thermoelectric device.

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