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Facile synthesis and thermoelectric studies of n-type bismuth telluride nanorods with cathodic stripping Te electrode

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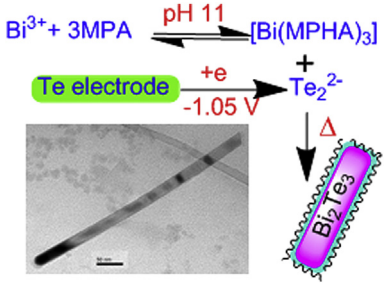
HIGHLIGHTS

- The n-type Bi_2Te_3 nanorods are prepared using an electrogenerated precursor.
- The rhombohedral structure of Bi_2Te_3 nanorods with the shell of Bi_2S_3 is demonstrated.
- Bi_2Te_3 nanorods show high thermoelectric performance.

GRAPHICAL ABSTRACT



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ABSTRACT

Bismuth telluride (Bi_2Te_3) nanorods (NRs) of n-type thermoelectric materials were prepared using an electrogenerated precursor of tellurium electrode in the presence of Bi^{3+} and mercapto protecting agent in aqueous solution under atmosphere condition. The optimal preparation conditions were obtained with ratio of Bi^{3+} to mercapto group and Te coulomb by photoluminescence spectra. The mechanism for generation of Bi_2Te_3 precursor was investigated via the cyclic voltammetry. The highly crystalline rhombohedral structure of as-prepared Bi_2Te_3 NRs with the shell of Bi_2S_3 was evaluated with high resolution transmission electron microscopy (HRTEM) and powder X-ray diffraction (XRD) spectroscopy. The near-infrared absorption of synthetic Bi_2Te_3 NRs was characterized with spectrophotometer to obtain information of electron at interband transition. The thermoelectric performance of Bi_2Te_3 NRs was assessed with the result of electrical resistivity, Seebeck coefficient, thermal conductivity, and the figure of merit ZT parameters, indicating that thermoelectric performance of as-prepared Bi_2Te_3 nanocrystals was improved by reducing thermal conductivity while maintaining the power factor.

1. Introduction

Bismuth telluride (Bi_2Te_3) nanocrystals are arguably desirable thermoelectric (TE) materials due to its attractive application in thermosiphon refrigeration, infrared detection and TE devices near room-temperature by utilizing the Seebeck effect [1]. The challenges to improve the performance of TE materials with high efficiency (defined by the dimensionless figure of merit, ZT) for practical realization stems from enhancing the electrical conductivity (σ) while suppressing the thermal conductivity (κ), according to $ZT = S^2\sigma T/\kappa$ [2], where S and T represent the Seebeck coefficient and the absolute temperature, respectively. A good TE material has high electrical conductivity and relatively low thermal conductivity: an "electron crystal, phonon glass" material [3]. One promising

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approach for improving the TE efficiency is to introduce nanophase heterostructures into bulk TE matrix for achieving this intuitively anomalous electron/phonon transport behavior [3]. Nanophase, such as nanopowders (metal, semiconductor, or nonconductor) or even nanosized cavities [4], are introduced into bulk TE materials, which can increase the grain boundary concentration, strongly scatter the long-wave phonons and reduce the lattice thermal conductivity. Consequently, considerable efforts have focused on nanostructured of Bi_2Te_3 such as quantum dots (QD) by Poudel [2] and Zhu [5], nanotubes by Wang [6], Zhao [7] and Chen [8], nanowires by Yu [9], nanoplates by Chen [8] and Fan [10] and superlattice thin films by Peranio [11] to significantly enhance TE efficiency via the quantum confinement effect resulting from enhanced electron density of states around Fermi level as the function of material dimension as well as the increase of phonon scattering effects from abundant hetero-interfaces [12,13].

So far, several techniques such as electrochemical deposition [14], hydrothermally synthesis [15], template-directed synthesis through the solvothermal route [9], standard solid-state reaction [16], galvanic displacement [17] and microwave assisted wet chemical method [5,10], have been successfully developed for the preparation of low-dimensional Bi_2Te_3 nanocrystals. Bi_2Te_3 have been widely studied along the adopting of different Te sources. Five types of Te precursors, namely Te powders [5–7,10], TeO_2 [8,15], and TeO_3^{2-} [9,18], $TeCl_4$ [19], and Tellurium(IV) ethoxide [$Te(OC_2H_5)_4$] [20] have been reported. When Te powders, $TeCl_4$ and TeO_2 were used, they must be either dissolved in hot organic trioctyl-phosphine oxide (TOPO) capping agent media, or synthesized in aqueous media under an inert atmosphere using $NaBH_4$ as a strong reducing agent. Although TeO_3^{2-} as an alternative Te source can be reduced for preparing Bi_2Te_3 nanotube [18], the products comprised of some unreacted Te or Bi and longer reaction duration is needed for the synthesis of Bi_2Te_3 obtained by using PVP and SDS as surfactants. All these methods are very useful and of widespread importance, but some limitations hinder their utility. For example, negative impact on TE performance of organic residue from the nanoparticle capping ligands, the use of expensive organometallic precursors and toxic agents such as H_2Te, relatively high temperature, high pressure or rigid anaerobic atmosphere etc. It is therefore essential to develop a new Te source to obtain Bi_2Te_3 materials for high performance TE applications.

The TE properties of Bi_2Te_3 can be controlled as both p-type and n-type characteristics depending on the chemical composition [21]. Even though they have been actively investigated with p-type semiconductors, research into the n-type bismuth tellurium (Bi_2Te_3) is relatively rare, likely because of its low ZT value. In terms of both fundamental understanding and practical applications, it is desirable to develop a general, one-step, less hazardous route to the synthesis of n-type Bi_2Te_3 nanostructures. Unlike hot TOPO-based Bi_2Te_3 synthesis approaches, where rather severe experimental conditions (e.g., toxic chemicals and high temperatures) are generally required, electrochemical methods could provide much "greener" environment. As demonstrated in our recent work [22,23], the green synthesis of tellurides can be achieved by cathodic polarization of Te electrode in an electrolyte solution containing a sulfhydryl capping agent and Bi^{3+} ions. Herein, we report the new development of electrogenerated Te precursor as Te source for facile preparation of n-type Bi_2Te_3 NRs in presence of mercaptopropionic acid (MPA) as a capping agent. The crystalline structure of NRs was closely analyzed with high-resolution transmission electron microscopy (HRTEM) and powder X-ray diffraction (XRD) spectroscopy. In addition, after the NRs were welded, the thermal conductivity and transport properties were evaluated to verify the phonon scattering effect caused by the nanostructured grains in the temperature range of 250–350 K. The obtained ZT in the vicinity of 0.4 was obtained due to the synergetic effect of the basically low thermal conductivity and increased power factor of our NRs, which will potentially be applied in TE device.

2. Material and methods

2.1. Chemical and materials

Mercaptopropionic acid (MPA) (>98%), and $Bi(NO_3)_3$ were purchased from Sigma–Aldrich Co. and used without further purification. The Te disc electrode (4.0 mm in diameter) was prepared by sealing a Te rod (donated by Leshan Kaiyada Photoelectricity Co., China) in a glass tube with epoxy glue. All other chemicals were of analytical grade and used as received. Millipore water (sterilized in Milli-Q plus) with a resistivity value of 18 MΩ cm was used throughout experiments. All solutions and electrolytes were thoroughly deaerated by purging with high purity nitrogen before each electrochemical experiment. Unless otherwise stated, all experiments were conducted at room temperature of 25 °C.

2.2. Apparatus

Near-infrared absorption and photo-luminescent spectra were recorded with a UV-3600 spectrophotometer (Shimadzu Co.) and a RF-5301 fluorescence spectrometer (Shimadzu Co.), respectively. The phase composition and structure of the as-prepared Bi_2Te_3 NRs were characterized by XRD analysis with Co Kα radiation (λ = 1.5418 Å) and accelerating voltage of 45 kV (D8 Advanced, Bruker). The XRD patterns were analyzed with the X'pert HighScore plus version 2.0 (PANalytical B.V., Netherlands). The morphology and nanostructure of the obtained Bi_2Te_3 were further characterized with field emission HRTEM (Tecnai G2 F20 S-Twin, operated at 200 kV) coupled with electron diffraction and energy-dispersive X-ray spectroscopy (EDS) (GENESIS 2000 XMS, EDAX Co. USA). The analysis for HRTEM was performed with the software Gatan Digital Micrograph™ version for GMS 1.8.0. Samples of Bi_2Te_3 for HRTEM were obtained by dispersing in ethanol with ultrasonic and dripping a droplet of suspension on a carbon-coated holey film on a Cu grid, followed by drying the copper grid at room temperature.

The electrochemical measurements and electrogenerated precursor for Bi_2Te_3 nanocrystals were performed with a CHI 660C workstation (CH Instrument Co., Austin, TX, USA) using a conventional three-electrode system composed of a glass carbon electrode (GCE, 3.0 mm diameter) or a Te electrode as the working electrode, a Pt wire as the counter electrode, and a saturated calomel electrode (SCE) (+0.242 V vs NHE) as the reference electrode. The working electrode was polished and ultrasonically cleaned before each voltammogram in order to ensure a clean uniform surface for each scan.

2.3. Synthesis of Bi_2Te_3 NRs

The procedure for the synthesis of Bi_2Te_3 NRs was modified on the basis of our previous report of cathodic stripping of Te electrode [22]. Firstly, the electrolyte solution for cathodic stripping was prepared by dissolving $Bi(NO_3)_3{\cdot}5H_2O$ with distilled water at the concentration of 2 mmol L^{-1} in presence of 5 mmol L^{-1} MPA as capping agent, followed by adjusting the pH to 11.0 with 0.50 M of NaOH. Secondly, the Te_2^{2-} ion was electrochemically generated with cathodic stripping Te electrode at potential of −1.05 V in above electrolyte solution. The Bi_2Te_3 precursor was formed via the solution-phase chemical reaction between the Te_2^{2-} and $Bi(MPA)_3$ complex. The reaction progress was accompanied by the color change of the electrolyte solution from faint yellow to yellow and finally to light brown. The amount of Te_2^{2-} ions produced can be