



Fabrication of freestanding tellurium nanofilm and its thermoelectric performance



Wenfang Wang^a, Changcun Li^a, Xia Li^a, Yanhua Jia^a, Fengxing Jiang^{a,b,*}, Congcong Liu^a, Rongri Tan^{a,b}, Jingkun Xu^{a,**}

^a Jiangxi Engineering Laboratory of Waterborne Coatings, Jiangxi Science and Technology Normal University, Nanchang 330013, China

^b Department of Physics, Jiangxi Science and Technology Normal University, Nanchang 330013, China

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ABSTRACT

Low-dimensional tellurium-based nanowires (NWs) have gained much attention as ideal thermoelectric materials. The preparation of high quality NWs remains a challenge in the field of nanotechnology. Owing to the superior performance, tellurium (Te) NWs are attractive materials for many applications. In this work, the Te NWs were synthesized by a hydrothermal route. We acquired the ultra-fine Te NWs through optimization, and the diameter is 10–35 nm. The optimized Te nanofilm was freestanding and the Te/polyvinylidene fluoride film can be rolled up by a pencil which showed the flexibility of the membrane. The as-prepared Te NWs films have been investigated by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and Raman spectroscopy. Although the ultra-fine Te NWs film shows the acceptable electrical conductivity, its Seebeck coefficient is as high as $551 \mu\text{V K}^{-1}$ and the thermal conductivity is as low as $0.16 \text{ W m}^{-1} \text{ K}^{-1}$. To achieve a higher thermoelectric performance, the effort will be devoted into the improvement of electrical conductivity in next work.

1. Introduction

Thermoelectric (TE) material gains great attention due to its ability that can achieve the direct conversion between electrical and heat energy [1,2]. Therefore, they have been widely applied in environment-friendly refrigeration and waste heat recycling [3–5]. Among TE materials, semiconducting nanowire materials have garnered significant concern because of their superior TE performance [6,7].

Tellurium (Te), a narrow bandgap *p*-type semiconducting TE material, has earned great attention due to its thermoelectric, catalytic, photoconductive, piezoresistive, and nonlinear optical properties [8]. Low-dimensional Te-based nanomaterials show the unique pattern and internal features and attractive inherent properties such as phase-change memory, photoelectricity, and thermoelectricity [9,10]. Kevin et al. [11] and Yee et al. [12] reported that Te had a high Seebeck coefficient of $\sim 408 \mu\text{V K}^{-1}$ and $400 \mu\text{V K}^{-1}$, respectively. Also, it is known that Te-based materials unusually possess high TE properties [13–15], such as Ag_2Te [16], Bi_2Te_3 [17], Sb_2Te_3 [18], ZnTe [19], CdTe [20], and PbTe [21]. Te-based composites also exhibit high TE properties. $\text{Te-Bi}_2\text{Te}_3/\text{PEDOT:PSS}$ hybrids have demonstrated a power factor of $60.05 \mu\text{W m}^{-1} \text{ K}^{-2}$ [22]. The low-dimensional nanomaterials

show enhanced TE figure of merit (*ZT*) owing to the low thermal conductivity from the increased phonon scattering and surface quantum confinement [23].

One-dimensional (1D) Te nanowires (NWs) have been widely investigated in TE materials. Various methods have been employed to prepare the Te and Te-based NWs with a good TE performance. Lin et al. prepared bulk Te nanofilm with a Seebeck coefficient of $\sim 320 \mu\text{V K}^{-1}$ by melting the stoichiometric amount of high purity elements, quenching in cold water, which showed a more superior TE performance than the bulk materials of Te [24]. Generally, the preparation of Te-based NWs has been explored through common synthesis methods such as hydrothermal, solvothermal, electrodeposition, and so on. Feng et al. prepared Te-based NWs with the diameter of 10–20 nm by a hydrothermal method [25]. Gang and co-workers fabricated ultra-long single crystal $\beta\text{-Ag}_2\text{Te}$ NWs through a solvothermal route [26]. Stavila et al. used a low-temperature wet-chemical approach to synthesize Te nanoparticles [27]. Zhang et al. developed a facile visible-light-assisted solution-phase approach to synthesize trigonal Te nanostructures [28]. The formation mechanism of Te NWs have been widely explored from synthesis methods and conditions. Mayers et al. demonstrated the effect of different solvents on Te growth and

* Correspondence to: F.X. Jiang, Department of Physics, Jiangxi Science and Technology Normal University, Nanchang 330013, China.

** Corresponding author.

E-mail addresses: f.x.jiang@live.cn (F. Jiang), xujingkun@tsinghua.org.cn (J. Xu).

nucleation mechanisms [29]. However, few work report the preparation of freestanding Te nanofilms based on ultra-fine Te NWs for wearable TE device. It is desired the TE nanofilms can be developed for wearable electron devices with a higher electrical conductivity and thermopower [30–32].

In this work, we fabricated ultra-fine Te NWs by simple hydrothermal method. A freestanding film of Te NWs was prepared by simple vacuum filtration. The preparation condition of Te NWs were investigated at different reaction temperature and time. We found that the as-prepared pure Te nanofilms showed high Seebeck coefficient and acceptable electrical conductivity. In order to improve the flexibility of the nanofilm, polyvinylidene fluoride (PVDF) was added into the Te nanofilm. Though the introduction of PVDF decreased the electrical conductivity, a high Seebeck coefficient still could be observed and a better flexibility was achieved, which providing a promising route to develop wearable TE films.

2. Experimental

2.1. Materials

Sodium tellurite (Na_2TeO_3), Polyvinylpyrrolidone (PVP, $M_w \sim 40,000$) and hydrazine hydride ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$, 80%) were purchased from Shanghai J&K Scientific Ltd. Aqueous ammonia solution (25–28%) was purchased from Aladdin.

2.2. The fabrication of Te NWs and Te/PVDF films

The ultra-fine Te NWs were synthesized according to the previous reports [24,29]. In a typical synthesis, 184.4 mg Na_2TeO_3 (0.8 mmol) and 1.0 g PVP were dissolved in 66 mL of deionized water with vigorous stirring. Then 6.7 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and 3.3 mL of $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ were added into the solution. The mixture was again stirred vigorously and poured into a 100 mL Teflon container. Then the container was closed and coated by stainless steel autoclave. The reaction was maintained at 180 °C for 5 h by heating in the oven. After that, the autoclave was allowed to cool to room temperature by immersing it into cool water. The freestanding Te nanofilms were acquired by vacuum filtration using a Hirsch funnel and washed several times with deionized water and ethanol. Then an appropriate amount polyvinylidene fluoride (PVDF) solution was dropped on the as-prepared Te NWs TE films with under vacuum filtration. The as-obtained films were transferred onto the plastic substrate. Finally, the Te/PVDF films were dried at 60 °C for 12 h in vacuum. All processes were performed under the condition of low temperature and low light. The detailed schematic was illustrated in Fig. 1a. The thickness was measured about $\sim 25 \mu\text{m}$ with a certain quality of $\sim 100 \text{ mg}$ using the thickness gauge.

2.3. Characterization and measurements

The as-obtained Te NWs were characterized by X-ray diffraction (XRD, $\text{CuK}\alpha$ radiation ($\lambda = 0.154056 \text{ nm}$) over the 2θ range of 10° – 90°). X-ray photoelectron spectroscopy studies were carried out using Multifunctional imaging electron spectrometer (Thermo ESCALAB 250XI) using an Al $\text{K}\alpha$ excitation source with a photon energy of 1486.6 eV. Binding energy can be calibrated with C1s 284.8. Raman spectra of the thin composite films were measured by a micro-Raman spectrometer (Renishaw inVia Microscope) with a 532 nm laser as the excitation source. Energy-dispersive X-ray analysis (EDX) were carried out in GENESIS energy spectrometer instrument equipped with a UHR pole piece. Scanning electron microscope (SEM) images were obtained using an S-4800 electron microscopy (Hitachi, Japan) with an accelerating voltage of 5.0 kV. Transmission electron microscopy (TEM) images were obtained using a JEM-2010F electron microscopy (Hitachi, Japan) with an accelerating voltage of 100 kV. The in-plane thermal conductivity of Te/PVDF was obtained from the thermal diffusivity

measured using a Thermo-Reflectance system (TC3000, NanoTR/PicoTR), which was based on the transient hot-wire method. Carrier concentrations were performed with an HMS-3000 (Ecopia) Hall Measurement system at 0.55 T and 1 mA.

The electrical conductivity of the fabricated thin films were measured by a standard four-point probe technique with a Keithley 2700 using four metal lines that were patterned on the sample with silver paint. The Seebeck coefficient of Te NWs were obtained by measuring the induced TE voltage in response to an applied temperature difference (ΔT) between the two inner 4-point probe contacts. The 4-point measurements of both contact lines, and the measured resistance (R) versus temperature (T) calibration curves were used to calculate the ΔT between them. The Seebeck coefficient was calculated by $S = -\Delta V/\Delta T$, where ΔV and ΔT were the induced TE voltage across the material and the through-plane temperature difference of the films, respectively. ΔT between two ends of samples was maintained at $\sim 5.0 \pm 0.5 \text{ K}$.

3. Results and discussion

The freestanding Te NWs were synthesized using the procedure described in the experimental section and illustrated in Fig. 1a. However, the acquired Te nanofilm displayed low flexibility after vacuum filtration. It is well known that the removal of residual PVP (capping agent) is difficult because of its adhesion property. Sodium borohydride solution has been reported by Zhang and co-workers [33] to disperse in the original Te NWs solution and thereby remove the residual PVP. However, Luo et al. showed that the displaced capping agents can be re-adsorbed quickly onto the Au-NPs with the depletion of the sodium borohydride [34]. In our present work, to avoid the reabsorption of PVP, vacuum filtration was used immediately with a hydrazine hydride aqueous solution (10%).

In order to enhance the flexibility of the nanofilms, PVDF solution was applied to the surface of the Te NW films as the flexible matrix, and the resulting Te/PVDF TE thin films showed better flexibility. The Te nanofilms can be folded into cylinders after vacuum filtration, which demonstrates that the pure Te NWs also form a good freestanding film without PVDF and can be completely transferred to a plastic substrate in Fig. 1b. Noted that the freestanding nanofilm with PVDF could be rolled up on a pencil in Fig. 1c indicating the good flexibility.

As we know, the preparation of Te NWs strongly depends on the growth conditions [6,28]. It has been demonstrated that the nucleation of Te NWs mainly origin from the one-dimensional direction of trigonal tellurium (*t*-Te) where it has a lower free energy and a linear structure [35]. To obtain the optimum condition of ultra-fine Te NWs, the synthesis condition was investigated systematically. We investigated the effects of different temperatures and time on the morphology of Te. Fig. 2 shows the SEM images of the freestanding Te NWs prepared under different reaction conditions. According to previous report, Chen et al. [36] found that the Te NWs would become longer as the increasing reaction time. Xia et al. [28] pointed out that the Te NWs would get longer as the temperature was raised without the change of NWs structure. In contrast, the results of Fig. 2 show that the good Te NWs cannot be synthesized simply by delaying the reaction time and changing temperature. One can find that the increased reaction temperature until 180 °C have a positive effect on the formation of Te NWs. However, the Te nanoplatelets were formed by combining Te NWs at 180 °C with the reaction time is which longer than 10 h. Generally, the formation of Te NWs do not only depends on the reaction temperature and time, but also refers to the concentration of capping agent PVP as well as the pH value.

As shown in Fig. 3a and b, the Te NWs were obtained at 180 °C for 5 h with 1.0 g and 0.2 g PVP. One can clearly see the smart morphology of overlapped NWs, which are more apparent than those obtained in Fig. 2. With the 1.0 g PVP at 180 °C, the reaction time of 5 h resulted in the much clearer and uniform NWs morphology. It is worth noting in Fig. 3c and d that the diameters of Te NWs were in the range of

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