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A simple thermoelectric device based on inorganic/organic composite thin film for energy harvesting

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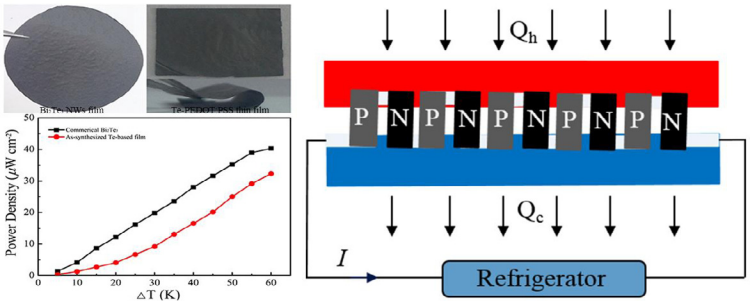
HIGHLIGHTS

- Te nanowires-PEDOT:PSS film shows good thermoelectric performance and stability.
- A simple thermoelectric film device consists of Te-PEDOT:PSS and Bi_2Te_3 nanowires.
- The film device exhibits a stable output voltage with a 60 K temperature difference.
- The power density of film device is closed to that of commercial Bi_2Te_3.

GRAPHICAL ABSTRACT

A simple thermoelectric film device is designed by consisting of Bi_2Te_3 NWs film as *n*-type legs and Te-PEDOT:PSS as *p*-type legs, and exhibits a high output power density of 32 μW cm^{-2} at temperature difference of 60 K closed to that of commercial Bi_2Te_3.



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ABSTRACT

Thermoelectric materials have been widely used in the power generation and cooling. Tellurium (Te) nanomaterial has gained great attention due to its enhanced thermoelectric performance, however, the researches are lacking of practical applications for energy harvesting. Here, a simple thermoelectric device was built with *n*-type and *p*-type Te-based (Bi_2Te_3 and Te-PEDOT:PSS composite) nanowires (NWs) thin film as legs for the first time. Firstly, a facile solution method was used to synthesize Te and Bi_2Te_3 NWs. A composite thin film was composed of Te NWs and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) to achieve a higher thermoelectric performance and a better environmental stability. The thermoelectric thin film device, consisting of Bi_2Te_3 NWs as *n*-type leg and Te-PEDOT:PSS as *p*-type leg, exhibits a stable output voltage of 56 mV and high output power density value of 32 μW cm^{-2} at temperature difference of 60 K, which is only 20% lower than that composed of commercial Bi_2Te_3. However, Te-based thin film device can effectively decrease its costs and be further improved to achieve a larger output voltage in the future.

1. Introduction

Thermoelectric (TE) materials offer a promising solution to harvest the waste heat or natural heat into the useful electrical power, which attracts the widely attraction [1–3]. Thermoelectric devices [1,4] present attractive advantages, such as long life, no loose parts, no emission of toxic gases and high reliability. They play an important role in the sustainable development. Thermoelectric performance of a material is assessed in terms of the dimensionless figure of merit, *ZT*, defined as $ZT = S^2\sigma T/\kappa$, where *S* is Seebeck coefficient, σ is accounted for electrical conductivity, κ is total thermal conductivity, and *T* is absolute temperature. Good thermoelectric

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materials need high electrical conductivity, large Seebeck coefficient and low thermal conductivity [5].

Tellurium nanomaterials [6] are widely researched because of their intriguing properties such as unique photoconductivity [7], nonlinear optical response [8] and high thermoelectric conversion along with piezoelectric responses [9,10]. One-dimensional (1D) Te-based nanomaterials such as nanowires (NWs) [11], nanorods [12] and nanotubes [13] exhibit higher migration rate and improved electrical properties than two-dimensional (2D) or three-dimensional (3D) block materials, depending on the limited carrier mobility in the axial direction [14,15]. 1D structure of Te nanomaterials in thermoelectric material also could exhibit great efficient heat engines capable of converting a temperature difference directly into electrical voltage via Seebeck effect [16,17] and low thermal conductivity due to the quantum size effect and enhanced interface scattering of phonons [18,19]. Nevertheless, the synthesized Te NWs suffered from a low electrical conductivity and high oxidation, which hampered its preparation for practical application in device. In order to optimize the thermoelectric performance, there were two different methods to choose: (i) template-directed synthesis corresponding tellurides (Bi_2Te_3, Sb_2Te_3, PbTe and so forth) [20–22]; (ii) composite with an optimum material through an adequate method [23,24].

Bi_2Te_3, one of the best candidates as TE materials, shows a high *ZT* value around room temperature and has been widely acknowledged and researched [25,26]. 1D Bi_2Te_3 nanostructures were widely fabricated by solution-based approaches during the past two decades, because the figure of merit *ZT* for 1D nanostructure could be improved noticeably by reducing the thermal conductivity [27]. Template-directed synthesis, as an important solution-based approach, is one of the most straightforward routes for 1D nanostructure depending on its simple high-throughput procedure and variability in controlling structure and chemical composition of products [28,29]. The thermoelectric performance of the NWs displayed great increase, when Bi atoms were introduced into Te NWs. Wang et al. [30] synthesized the uniform Bi_2Te_3 NWs with Te NWs as the template, which yielded the increased electrical conductivity and power factor significantly as Bi atoms attached on the surface of Te NWs. Zhang et al. [31] also reported a kind of 1D Bi_2Te_3 nanomaterials with the template-directed synthesis method, which achieved an enhanced *ZT* value of 0.96 due to the significantly reduction of thermal conductivity derived from phonon scattering at interfaces of 1D nanomaterials. Both better thermoelectric properties of *n*-type materials and high quality of *p*-type materials are required for the fabrication of thermoelectric devices. Conducing polymers would play an important role in improving electrical conductivity and reducing thermal conductivity for inorganic-organic thermoelectric composites. According to the previous reports, it has been confirmed that the complex of Te and conducting polymer provide a promising way to achieve high quality of *p*-type Te-inorganic composite materials [23,32,33].

Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as one of the promising candidates for organic thermoelectric materials [34] exhibited an important role in enhancing the thermoelectric properties of Te NWs owing to its high electrical conductivity through direct dilution-filtration [35] or second treatment [36,37] and low thermal conductivity. See et al. [17] reported a water-soluble composite nanocrystal composed of Te core and the conducting polymer PEDOT:PSS, and it achieved a high *ZT* value about 0.1 at room temperature. Coates et al. [38] demonstrated an unusual electrical transport behavior in Te-PEDOT:PSS thermoelectric composite, where electrical transport occurred predominantly through a highly conductive volume of polymer that existed at the Te-PEDOT:PSS interface. Bae et al. [37] fabricated a wearable flexible thermoelectric device with optimized Te-PEDOT:PSS thermoelectric materials by simple chemical treatment and then generated an output voltage of 2 mV using human body heat. Te-PEDOT:PSS composite film was regarded as a great potential candidate for thermoelectric devices, but the researches of Te-PEDOT:PSS composite materials for thermoelectric devices are lacking of practical application.

Herein, we fabricate a thermoelectric film device with the as-synthesized *p*-type Te-PEDOT:PSS thin films and *n*-type Bi_2Te_3 NWs films. The *n*-type Bi_2Te_3 NWs are synthesized by the reported template-directed method with Te NWs as template [39], and the power factor is one order of magnitude higher than original Te NWs. Another self-standing *p*-type Te-PEDOT:PSS thin films with an increased power factor were successfully achieved using the direct composite dilution-filtration method [40]. The as-fabricated thermoelectric film device exhibits an acceptable output voltage and a high output power density. A novel strategy to fabricate thermoelectric device with Te-PEDOT:PSS composite films will promote the application of composite materials in thermoelectric devices.

2. Experimental section

2.1. Material

Tellurium dioxide (TeO_2, 99%), bismuth nitrate ($Bi(NO_3)_3{\cdot}5H_2O$, 98%), polyvinylpyrrolidone (PVP, MW ~ 40,000), potassium hydroxide (KOH, ≥85%), Ethylene glycol (EG, ≥99%) and L-ascorbic acid (AA, 99%) were purchased from J&K Scientific Ltd. PEDOS:PSS aqueous solution (Clevios PH1000) was purchased from HC Stark. Commercial *n*-type (σ: 500 ~ 1000 S m^{-1}, *S*: −180 ~ −200 μV K^{-1}) and *p*-type (σ: 500 ~ 1000 S m^{-1}, *S*: 190 ~ 230 μV K^{-1}) Bi_2Te_3 were provided by Thermonamic Electronics (Jiangxi) Corp., Ltd.

2.2. Synthesis of Te and Bi_2Te_3 NWs

For synthesis of Te NWs, 0.16 g TeO_2 (1 mmol), 0.5 g PVP, 1.5 g KOH, and 15 mL EG were added to a 50 mL two-neck round bottom flask and heated to 120 °C with nitrogen condition. Meanwhile, 1.89 M L-ascorbic acid aqueous solution was made in a separate glass container via heating to 80 °C. When the Te solution reached to 120 °C, 3 mL of L-ascorbic acid solution was rapidly injected into the mixture solution. The Te NWs were obtained when the mixture kept at 120 °C for 24 h. The products were separated by centrifugation at 10,000 rpm for 30 min. Then the as-synthesized Te NWs were re-dispersed in 1 M potassium hydroxide aqueous to remove the residual PVP. Finally, the products were re-separated by centrifugation, and washed with deionized water and ethanol for three times, respectively.

For the preparation of Bi_2Te_3, 0.323 g (0.67 mmol) $Bi(NO_3)_3{\cdot}5H_2O$ and 0.1 g PVP were dissolved in 4 mL ethylene glycol at 80 °C in a separate container and rapidly injected into the fresh Te NWs reaction solution, following by the addition of 3 mL of 1.89 M L-ascorbic acid aqueous solution. The mixture was kept at 120 °C for another 24 h to allow the conversion to Bi_2Te_3 NWs. The suspension of Bi_2Te_3 NWs were vacuum-filtered through a porous PVDF filter membrane with 0.22 μm pores, and repeatedly washed with ethanol and deionized water to move the redundant raw materials and by-products. The Bi_2Te_3 film was peeled from the membrane, and dried under vacuum at 60 °C for 10 h.

2.3. Fabrication of flexible Te-PEDOT:PSS film

A 200 μL PEDOT:PSS aqueous solution was added into the Te NWs ethanol solution with a designed ratios, and the resulting mixture was sonicated for 15 min. Then, the vacuum filtration of