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Power factor enhancement via simultaneous improvement of electrical conductivity and Seebeck coefficient in tellurium nanowires/reduced graphene oxide flexible thermoelectric films

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ABSTRACT

The simultaneous improvement of electrical conductivity (σ) and Seebeck coefficient (S) is essential to realize the thermoelectric materials with high power factor value. Here, we report the discovery that the redox reaction happened between the reduced graphene oxide (RGO) sheets and tellurium (Te) nanowires can lead to a simultaneous improvement of σ and S in the RGO/Te nanowires hybrid films. With optimization, the electrical conductivity and Seebeck coefficient can reach 633 S/m and 382 μV/K, respectively, pushing the power factor value up to 68.4 μW/(mK^2), approximately 25 times larger than the reported pure Te nanowires film. Based on all of the characterizations, the redox reaction between the RGO sheets and Te nanowires have been confirmed and the transportation characteristics of the hybrid films are predicted. We demonstrate the new approach that via turning the redox reaction, the interfacial interaction can be optimized, enabling a novel flexible thermoelectric films with superior performance. To our knowledge, this is the first time that the TE properties of RGO/inorganic hybrid films are reported.

1. Introduction

Thermoelectric (TE) materials have great potential in applications on power generation and solid state heating/cooling systems, realizing direct conversion between thermal energy and electrical energy without involving moving mechanical components or hazardous working fluids etc [1]. The energy conversion efficiency of TE materials is usually evaluated by the materials' dimensionless figure-of-merit $ZT = (S^2\sigma T)/\kappa$, where σ is the electrical conductivity, S is the Seebeck coefficient (named as thermopower as well), κ is the thermal conductivity and T is the absolute temperature. The intrinsic power factor (PF) value is calculated from the measured electrical conductivity and Seebeck coefficient where $PF = S^2\sigma$. A material with favorable TE property is desired for an excellent σ, a high S and a low κ [2]. However, the κ,σ, and S of materials are determined by the electronic structure and scattering of charge carriers, thus they are closely interrelated, making optimization extremely difficult [3].

In 1993, Hicks and Dresselhaus [4,5] predicted that the reduced physical dimensionality of TE materials (quantum confinement) may lead to greatly enhanced TE performance. In consequence, various special nanostructures, such as superlattices [6], nano-inclusions [7] and composites [8] have been introduced into inorganic TE materials later. Significant improvement on ZT has been achieved in these novel nanoscale materials, especially via preferentially phonon scattering to reduce the κ without the loss of PF [9], and via energy filtering to independently promote the S without losing carrier mobility [10]. However, the costly raw materials and production facilities, potential risks for heavy metal pollution [11] as well as the poor processability limit their applications in many novel TE systems [12]. Consequently, developing cost competitive TE materials with high performance and good processability is of key importance for the potential benefit of their properties to be realized.

Due to the advantage of being flexible, cost-effective and facile to synthesize and process, the conductive polymers have been gradually applied in thermoelectric materials in the recent decade.

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To build efficient energy filtering interface, intimate contacts between polymer and nanoparticles as well as the similar work function of polymer and nanoparticles are necessary [13,14]. Recently, several articles have reported that the strategy of introducing nanostructured interfaces to filter low-energy carriers also work well in TE films based on conductive polymers. Enhanced S and PF were obtained in polyaniline/carbon nanotube (CNT) composites and this behavior was probably attributed to the size-dependent energy-filtering effect caused by the nanostructured polyaniline coating layer wrapped around the CNT [13]. Besides, by rationally engineering the organic–inorganic semiconductor interfaces of polymer composites, the improvement of the S and PF in the poly (3-hexylthiophene)/Bi_2Te_3 nanowires was realized [15].

These previous works reveal that optimizing the nanostructured interfaces is an effective approach to enhance the performance of thermoelectric materials based on conductive polymers. However, due to the excessive carrier concentration and low carrier mobility that result in poor Seebeck coefficient value, the PF values of these composites are still less than 20 μW/(mK^2). To solve this problem, reduced graphene oxide (RGO) sheets become an appealing option due to its high electrical conductivity [16] and good dispersibility [17], provided that graphene oxide (GO) sheets are reduced under proper condition. Meanwhile, the bandgap and work function of RGO can be easily tuned by changing the reduction degree of RGO [18]. Thus, it possibly also works well to maintain the high Seebeck coefficient without reducing the electrical conductivity by adjusting the interface of RGO/inorganic composite. Our group concentrated our attention on RGO/tellurium (Te) composite. Te possesses a high Seebeck coefficient [19] and is easily synthesized in nanocrystalline form in water solutions in the presence of a structure directing surfactant [20]. In this context, we demonstrate that high TE performance can be realized in the water-processable RGO/Te nanowires hybrid films. These hybrid films have combined the dispersible RGO sheet with Te nanowires and achieved a much higher PF of 68.4 μW/(mK^2) than the previous polymer/inorganic films. We later verify that it is the redox reaction on the interface between the RGO sheets and Te nanowires that leads to the increased carrier mobility of the hybrid films and thereby the simultaneous improvement of σ and S, which accounts for the significant enhancement of PF. The present approach to optimize the interfacial interaction by adjusting the redox reaction between the RGO sheets and inorganic nanowires provides a novel effective route to achieve flexible TE films with high performance.

2. Experimental

2.1. Materials

Graphene oxide (GO) was prepared by the modified Hummers' method [21]. The sodium tellurite (Na_2TeO_3, 98%), poly(sodium-*p*-styrenesulfonate) (NaPSS, M.W. 500k, analytical grade), hydrazine hydrate ($N_2H_4{\cdot}H_2O$, 98%), aqueous ammonia ($NH_3{\cdot}H_2O$, 25%), hydrobromic acid (HBr) solution (48%), and polyvinylpyrrolidone (PVP, M.W. 30k, analytical grade) were purchased from Aladdin Chemical Co., Ltd. All of these agents were used without further purification.

2.2. Preparation of RGO dispersion

20 mg of GO and a certain amount of NaPSS were dispersed in 15 mL of deionized water and the dispersion was ultra-sonicated for 10 min to form a homogeneous solution. Then 30 mL HBr solution was added into the brown dispersion and the mixture was violently stirred at 120 °C for 36 h to get a black dispersion. After being cooled to room temperature, the product was centrifuged and washed by deionized and ethanol for several times to remove the HBr solution, then the resulted product was dried in a vacuum oven at 50 °C overnight to obtain black RGO sheets. Finally the RGO sheets were dispersed in deionized water to form a homogeneous black dispersion (1 mg/mL).

2.3. Preparation of Te nanowires dispersion

Te nanowires were synthesized according to a similar procedure reported by Liang et al. [22]. Generally, 2 g of PVP and 0.18 g of Na_2TeO_3 were dissolved in 70 mL of deionized water to form a homogeneous solution under vigorous magnetic stirring at room temperature. Next, 2.86 mL of $N_2H_4{\cdot}H_2O$ and 6.7 mL of $NH_3{\cdot}H_2O$ were added into the mixture. The obtained solution was stirred for 10 min then transferred into a Teflon-lined stainless steel autoclave (100 mL in total volume), which was closed and maintained at 180 °C for 3 h. After the system cooled to room temperature naturally, 250 mL of acetone was added into the Te nanowires

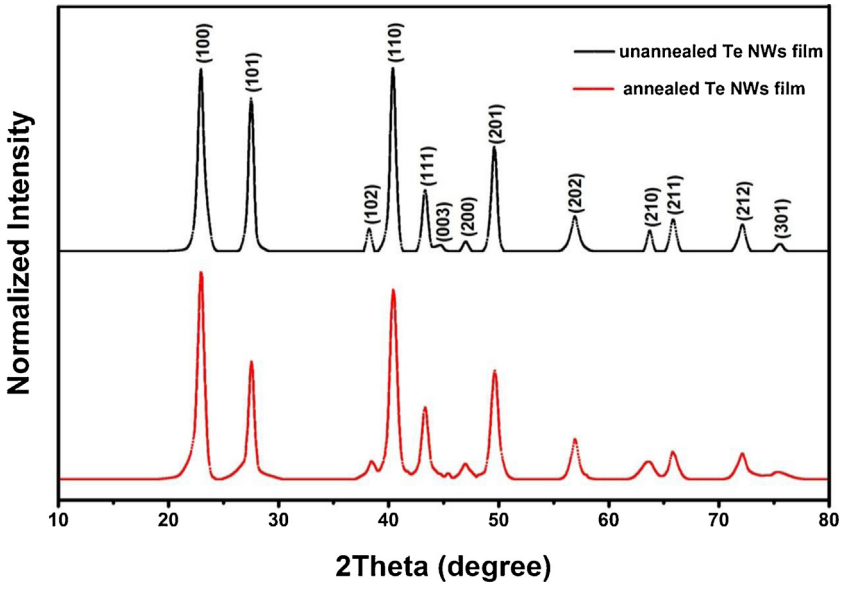

Fig. 1. The XRD patterns of the unannealed and annealed Te nanowires film.