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Chemical synthesis and enhanced electrical properties of bulk poly(3,4-ethylenedioxythiophene)/reduced graphene oxide nanocomposites

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ABSTRACT

PEDOT, poly(3,4-ethylenedioxythiophene), is an important conjugated conducting polymer, and a complex salt PEDOT:PSS has been widely researched on account of its advantages of favorable workability, excellent film-forming ability and decent electrical conductivity. Although PEDOT films with excellent thermoelectric properties have already been intensively described in the literature, few reports focused on thermoelectric properties of bulk forms of PEDOT. Here, we report on bulk PEDOT and its composites with reduced graphene oxide (PEDOT/rGO) synthesized by a chemical method combined with cold pressing and thermal treatment. The impact of the rGO doping and the thermal treatment on the electrical transport properties of PEDOT and PEDOT/rGO is discussed. The results show that 0.44 wt% of rGO doping improves the electrical conductivity of PEDOT by a factor of about 2. The electrical conductivity of PEDOT/0.44 wt% rGO is further increased by about 3 times after the thermal treatment. Moreover, the power factor of bulk PEDOT is enhanced by a factor of 16 following the thermal treatment. The π–π interaction between rGO and PEDOT, the closer packing within the polymer matrix, as well as the more ordered structure within the polymer matrix induced by the thermal treatment and the addition of rGO are of crucial importance for the remarkable improvement of the electrical conductivity and the power factor.

1. Introduction

Recently, investigations concerning sustainable clean energy have attracted worldwide attention as attempts to mitigate the environmental pollution and address the energy crisis. As a form of energy conversion technology, thermoelectricity can directly convert heat into electricity by utilizing the Seebeck effect and, *vice versa*, provide cooling by making use of the Peltier effect [1]. Thermoelectric energy conversion offers distinct advantages of no moving parts, no abrasion, no noise, no harmful exhaust species, no pollution and, above all, an unprecedented reliability. The performance of a thermoelectric material depends mainly on the material's dimensionless figure of merit ZT, defined as $ZT = \alpha^2\sigma T/\kappa$, where σ, α, κ and T are the electrical conductivity, the Seebeck coefficient, the thermal conductivity and the absolute temperature, respectively [2]. Compared to traditional inorganic thermoelectric materials, conjugated conducting polymers are notable for their light weight [3], solution processing ability, and flexibility [4–6], which make them attractive for thermoelectric applications. As a representative conducting polymer, PEDOT is particularly promising because of its ability to be doped by water-soluble organic salts, such as polystyrolsulfon acid (PSS) and *p*-toluenesulfonic acid [3,7,8]. Extensive studies have focused on solution processed PEDOT/organic salt compounds, as well as on thin film forms of these compounds prepared by spin-coating [3,9]. Thin films of the commercially available PEDOT:PSS compound, known as Clevios™ PH1000, are widely used in the field of electronics and possess an excellent electrical conductivity and favorable transparency [10]. The non-negligible drawbacks of Clevios™ PH1000 are its high cost and an inevitable waste of the material during the spin-coating process, both impeding its widespread applications. Yoo et al. [11] have reported that the electrical conductivity of PEDOT:PSS could be improved to an excellent value of 689 S cm^{-1} upon doping by both carbon nanotubes and graphene. In addition, Bae et al. [9] proposed that the electrical conductivity of PEDOT:PSS films could exceed 4800 S cm^{-1} after a sulfuric acid solution treatment. Chen et al. [12] achieved uniform dispersion of surfactant functionalized graphene in PEDOT:PSS by means of ultrasonic substrate vibration-assisted spray coating, and electrical conductivity up to 720 S cm^{-1} was observed. Wang et al.

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[13] reported that phase separation can be observed in PEDOT:PSS film by adding amphiphilic tertiary amine (PEGO) to the pristine PEDOT:PSS aqueous solution, and the electrical conductivity of the sample with 5 wt% PEGO showed an ten-fold increase in the film conductivity compared to the pristine PEDOT:PSS film. Such significantly improved electrical conductivity is clearly beneficial for the *ZT* value of PEDOT-based films, which motivates the investigation of PEDOT as a thermoelectric material. However, to the best of our knowledge, there have been few reports concerning thermoelectric properties of bulk forms of PEDOT [14,15]. Wang et al. [16] prepared PEDOT and PbTe-modified PEDOT nanotubes. The powders were cold pressed and the thermoelectric properties were measured at room temperature, and extremely large absolute Seebeck coefficient as 4088 μV/K was obtained for the sample cold-pressed from PEDOT nanotubes with low electrical conductivity as $0.064\ \mathrm{S\ m^{-1}}$. Jiang et al. [17] prepared PEDOT:PSS powder with different organic additives, and the powder was then cold pressed for the characterization of thermoelectric properties. The thermal conductivity is low and the highest figure of merit ($ZT = 1.75 \times 10^{-3}$) was observed at 270 K. To sum up, PEDOT:PSS films have more extensive investigations compared to PEDOT in the bulk form, due to their potential applications as flexible electronics [18,19]. However, the investigation of PEDOT in the bulk form in this research would be an important supplement to current researches, since the mainstream applications of thermoelectric materials are based on bulk thermoelectric materials.

Numerous investigations have shown that the incorporation of a metallic secondary nano-phase into the matrix of thermoelectric materials could improve the electrical conductivity quite effectively [20–22]. Graphene is a well-known two-dimensional semimetal material with sp^2-hybridized and covalently bonded carbon atoms [23]. Relying on its high carrier mobility ($\sim 2 \times 10^5\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$) [24] and large specific surface area ($\sim 2630\ \mathrm{m^2/g}$) [25], graphene has been used to improve the electrical performance of polymers [22]. The π–π conjugated system within the graphene structure provides pathways for the charge carriers when graphene is introduced into PEDOT to form composite materials. Xu et al. [15] developed a novel strategy for the construction of PEDOT-rGO with pie-like structure. The power factor of the nanocomposite at room temperature was $5.2 \pm 0.9 \times 10^{-6}\ \mathrm{Wm^{-1}\ K^{-2}}$. However, there was no discussion about the effect of the rGO content and the temperature dependent properties in Xu's work.

In this work, the reduced graphene oxide (rGO) is chemically dispersed into PEDOT in order to obtain PEDOT/rGO nanocomposites through an *in-situ* micro-emulsion polymerization method. Bulk PEDOT/rGO nanocomposites are obtained by cold pressing the product powder followed by the thermal treatment. The influence of the rGO content and the thermal treatment on the microstructure and electrical properties of bulk PEDOT/rGO nanocomposites is then explored and discussed. The results indicate that the rGO doping and the thermal treatment lead to a significant enhancement in the electrical conductivity and only a minor deterioration in the Seebeck coefficient and, thus, the power factor of bulk PEDOT/rGO composites is much improved.

2. Experimental procedure

2.1. Preparation of the reduced graphene oxide

Graphene oxide (GO) was prepared by the modified Hummers method [26] with graphite/$KMnO_4$ mass ratio of 1:1. 20 mL of the resulting GO supernate was added into a round-bottom flask, which was followed by the addition of ammonium hydroxide, hydrazine hydrate and *N*-methyl pyrrolidone. The mixture was stirred with the oil-bath at 90 °C for 24 h. The resulting solution was centrifuged and the sediment was washed by de-ionized water and then freeze-dried in order to obtain the reduced GO (rGO).

2.2. Preparation of PEDOT

4.03 g of dioctyl sodium sulfosuccinate and 0.5 g of EDOT monomer was dispersed uniformly in 70 mL of *n*-hexane under sufficient stirring. 1.6 g of anhydrous ferric chloride was dissolved in 2 mL of deionized water and the resulting solution was added drop-wise into the reacting system. The reaction was carried out at room temperature for 24 h, and dark blue precipitates were obtained after the reaction. The product was then washed, in turn, with acetonitrile and methyl alcohol, and was vacuum dried at 50 °C in order to obtain a powder of PEDOT [27].

2.3. Preparation of PEDOT/rGO

For the preparation of polymer/carbon nanomaterials composite, the interfacial polymerization method and the *in situ* polymerization method are often the choices [28,29]. Here, the PEDOT/rGO composite was prepared by the *in situ* micro-emulsion polymerization method. The procedure for preparing PEDOT/rGO composite powder was analogous to the preparation of PEDOT, except that the rGO powder was adequately dispersed in 70 mL of *n*-hexane in advance by sonication [30] before the addition of dioctyl sodium sulfosuccinate and the EDOT monomer.

2.4. Fabrication of bulk samples

Bulk PEDOT and PEDOT/rGO samples were obtained by cold pressing the corresponding PEDOT and PEDOT/rGO powder at room temperature under pressure of 25 MPa. The cold-pressed products were round pellets of 12.5 mm in diameter and about 3 mm in thickness. Pellets were then cut into rectangular bars with size of ~2.5 mm × 3 mm × 8 mm for the subsequent characterization of electrical properties. Bulk PEDOT and PEDOT/rGO samples were also vacuum sealed in a quartz tube for thermally annealing in a furnace under 200 °C for 2 h. Samples that experienced a thermal treatment at 200 °C are marked as HT, while samples prepared at room temperature are marked as RT. 0.44 wt% designates a PEDOT/rGO composite containing rGO in the weight ratio of 0.44%. Similarly, 0.88 wt% implies the content of rGO in the weight ratio of 0.88%. The optical pictures of the fabrication process for bulk samples can be seen in Fig. S1 of the supplemental material. We have explored PEDOT/rGO composites with a wide range of the rGO addition. The formability of the bulk ingot during the cold pressing decreased dramatically when the addition of rGO exceeds a certain value of 0.88 wt%. Therefore, the rGO content of 0.44 wt% was selected as the example for investigating the influence from the rGO content and the annealing process.

2.5. Structure characterization and electrical property measurement

The functional groups and compositions were characterized by a Fourier Transform Infrared (IR) Spectrometer (Nicolet 6700) and a RENISHAW Raman Microscope (INVIA). The phase structure was determined by XRD utilizing a PANalytical X'Pert diffractometer. The morphology was characterized by a Scanning Electron Microscope (Hitachi SU8020). The chemical composition of PEDOT/rGO was measured by the Energy Dispersive Spectrometer (Bruker). The thermal stability was studied by the Thermogravimetric Mass Spectrometry (TG-MS, Nestal STA449F3). The electrical conductivity and the Seebeck coefficient were measured simultaneously by a four probe method under He atmosphere utilizing a commercial system of ULVAC-RIKO ZEM-3 apparatus. For the Seebeck coefficient measurement, a temperature difference was created at the two ends of sample by resistance heating at one end, which generates the thermoelectric voltage (ΔV) between two probes with temperature gradient of ΔT. The Seebeck coefficient is then calculated by $\alpha = \Delta V/\Delta T$.