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A simple strategy to fabricate polyaniline/expanded graphite composites with improved power factor

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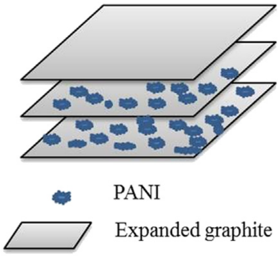
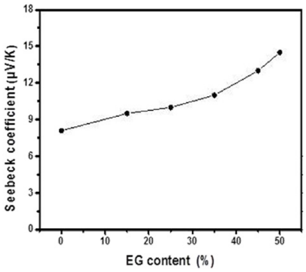
HIGHLIGHTS

- PANI intercalates into the EG sheets and forms a sandwich structure.
- Ultrasonic mixing PANI with EG method is simple and effective.
- Power factor of PANI/EG is higher than some PANI based composites.

GRAPHICAL ABSTRACT





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ABSTRACT

Polyaniline/expanded graphite (PANI/EG) composites with enhanced thermoelectric properties have been successfully synthesized by a simple ultrasonic mixing method with different EG contents. Their structure and morphology were investigated by XRD, SEM, and FTIR. Besides, thermal stability was investigated by TG analysis, which indicated that the PANI/EG composites exhibit better thermal stability than pure PANI. The PANI/EG composites show an interesting structure: PANI intercalates into the EG sheets and forms a sandwich structure. The thermoelectric properties of the samples were measured at room temperature. With the EG content increasing, the electrical conductivity and Seebeck coefficient were improved. As a result, a remarkably improved thermoelectric power factor was achieved. This work demonstrates a simple and effective method for improving the thermoelectric properties of conducting polymers.

1. Introduction

Thermoelectric (TE) materials, widely used in Peltier coolers and thermoelectric power generators, have drawn a lot of attention in recent years [1]. TE materials have been promising candidates to replace traditional fossil energy due to their great advantage in the conversion between thermal energy and electrical energy [2]. The energy conversion efficiency of TE materials is evaluated by a dimensionless figure of merit ZT $= S^2\sigma T/\kappa$, where S (in V K^{-1}), σ (in S m^{-1}), T (in K), and κ (in W m^{-1} K^{-1}) are Seebeck coefficient, electrical conductivity, absolute temperature, and thermal conductivity, respectively. Obviously, for a high-performance TE

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material, excellent Seebeck coefficient, high electrical conductivity and low thermal conductivity are required [3]. However, S, σ and κ are interdependent-changing one alters the others, making optimization extremely difficult [4]. Fortunately, when variation of thermal conductivity is secondary to modulation in electrical conductivity, power factor (PF), PF $= S^2\sigma$ in W m^{-1} K^{-2}, is employed to evaluate TE property of a material [5]. Especially for polymer TE materials, due to the low value of κ, TE properties are often assessed with PF [6].

Inorganic semiconductors and metal alloys are the mostly reported TE materials mainly due to their high ZT and PF values, such as Bi_2Te_3 [7–10], BiCuSeO [11], Bi–Sb–Te bulk alloy [12]. However, they also have shortcomings: firstly, inorganic TE materials usually contain toxic and rare elements such as Bi, Te, Sb [13]. Secondly, processes to fabricate inorganic materials like melt-spinning, ball milling and hot pressing are high cost and need a long payback time. Thirdly, most inorganic materials are expensive, heavy and brittle. However, organic materials are abundant, light-weight, flexible and low-cost [5,14]. Therefore, they are regarded as promising candidates for TE materials and are attracting more and more attention. The majority of organic TE materials are based on conductive polymers like polyaniline (PANI), polypyrrole (PPY), and poly(3-hexylthiophene) (P3HT) [15–18]. Among these conductive polymers, PANI has attracted special attention because of its unique electronic, easy synthesis, and good environment stability [4]. Different methods have been employed to improve the TE properties of PANI, including doping it or blending it with different kinds of filling materials to prepare functional PANI composites [19]. Zhang et al. showed that the multi-walled carbon nanotube (MWCNT)/PANI composite fabricated by cryogenic grinding is an effective way of improving the TE properties of PANI [1]. PANI/graphite composites synthesized by mechanical ball milling exhibited higher electrical conductivity and Seebeck coefficient than pure PANI, and the TE power factor was remarkably improved [20]. The improvement in the properties of TE materials follows the known percolation law: once a critical volume fraction of filling materials is reached, dramatic enhancement of TE properties can be achieved [14].

Expanded graphite (EG), an excellent conductive material, is composed of stacks of nanosheets that may vary from 100 to 400 nm and has good affinity for polymer [21], so it can be good filling materials to fabricate functional polymer composites. The PANI/EG composites synthesized by emulsion polymerization show good electrical property [22]. In the present paper, we use a simple and effective method to fabricate PAN/EG composites and then investigate their TE properties.

2. Experiential

2.1. Materials

Expandable graphite was obtained from Huadong Graphite Co. Aniline, hydrochloric acid (HCl), ethyl alcohol, ammonium persulfate ($(NH_4)_2S_2O_8$) were all from Tianjin Chemical Reagent Co. All Chemicals were used as received without any further purification.

2.2. Synthesis of PANI

Aniline (0.466 g) was mixed with 20 mL of 1 M HCl solution in a vessel with stirring at 0 °C for 20 min to form a solution. Weighed $(NH_4)_2S_2O_8$ (1.141 g) was dissolved in 20 mL deionized water to form a solution which was then transferred to the dropping funnel and slowly added to the aniline solution. The mixture reacted for 10 h at 0 °C, and then the product was filtered, washed with distilled water and ethyl alcohol for several times, and dried at 60 °C in a vacuum to obtain the dark-green PANI.

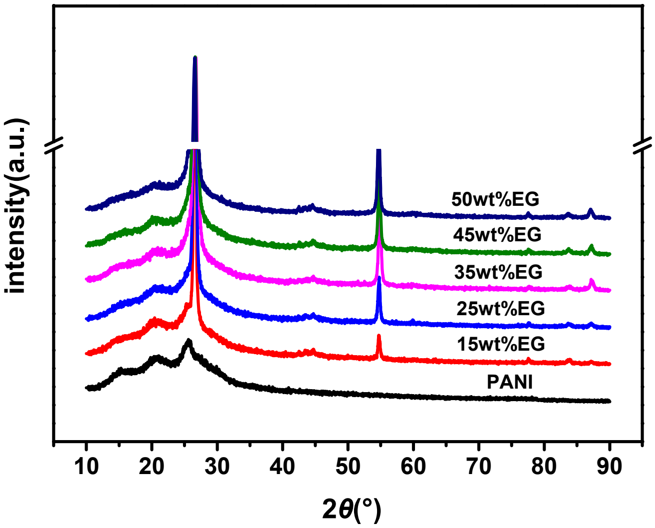

Fig. 1. X-ray diffraction patterns of the PANI and PANI/EG composites with different contents of EG.

2.3. Preparation of expanded graphite

EG was obtained by thermal treatment of expendable graphite at 800 °C for 1 min in the muffle furnace. A mixture of 0.5 g EG and 30 mL ethanol was treated using an ultrasonic cleaner for 7 h in a beaker, and the final EG was collected by filtration and then dried at 60 °C for 12 h.

2.4. Preparation of PANI/EG composites

EG and dark-green PANI were weighed and added to 20 mL ethyl alcohol in a beaker, then the mixture was treated using an ultrasonic cleaner for 2 h. Once the PANI/EG composite was homogeneously mixed, the blend was filtrated and then dried under vacuum at 60 °C overnight. The dry composite was put in a glass mortar and mechanically ground. In order to measure the TE properties of the PANI/EG composite, the powdered composite was molded into pellets using a steel die of 13 mm diameter in a hydraulic press under a pressure of 12 MPa for 3 min.

2.5. Characterization

The X-ray diffraction (XRD) patterns of the samples were measured using an X-ray diffractometer (BDX3300) with a reference target, Cu Kα radiation (λ = 0.154 nm) voltage, 30 kV, and current, 30 mA. And the samples were measured from 10° to 90° with steps of 4°/min. Fourier transform infrared spectroscopy (FTIR) of the samples was measured with a PerkinElmer Paragon-1000 FTIR spectrometer in the range of 500–4000 cm^{-1}. The structure of the PANI/EG composites was observed by scanning electron microscope (SEM, JEOL-6700F ESEM, Japan). Their thermogravimetric diagrams (TG) were measured with an analyzer

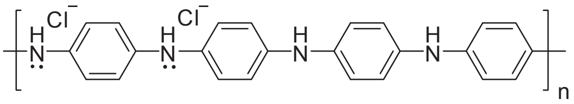

Fig. 2. Chemical structure of PANI emeraldine hydrochloride salt.