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Enhanced thermoelectric performance of highly conductive poly(3,4-ethylenedioxythiophene)/carbon black nanocomposites for energy harvesting

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ABSTRACT

The thermoelectric performance of *para*-methylbenzenesulfonate (*p*-MeBzs) doped highly conductive poly(3,4-ethylenedioxythiophene) (PEDOT) can be improved by the use of carbon black fillers. Thermoelectric nanocomposites were prepared via chemical polymerization. Dodecylbenzenesulfonic acid (DBSA) was introduced before polymerization to act simultaneously as a surfactant for formation of micelles of carbon black and as a doping agent. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Fourier transform infrared spectroscopy (FT-IR) were employed to characterize the morphology of PEDOT coated carbon black and PEDOT. Electrical conductivity of the composites improved with increase in weight percentage of carbon black from 0% to 30%. Extended chain conformations and increase in electron delocalization reduces the carrier hopping barriers. These contribute to the enhancement of charge carrier mobility. Although electrical conductivity is directly proportional to the increase in the filler content, Seebeck coefficient is more or less constant. Relatively small changes of thermal conductivity can be attributed to the phonon scattering effect in both the carbon black and the thermally insulating PEDOT layers. This study reports that the power factor of the composite was estimated to be 0.993 μW/m K^2 for 10 wt% filler content and was more than 1.7 times higher than that for pure PEDOT, and the maximum figure of merit (*ZT*) value was 0.0012 at room temperature.

1. Introduction

Nowadays, as carbon based fossil fuels are gradually disappearing, energy harvesting is considered very significant. Thermoelectric (TE) systems are very effective and promising devices for energy harvesting. Three distinct thermoelectric effects (the Seebeck, Peltier, and Thomson effects) have been identified and are known to be interrelated by the Kelvin relations. Thermoelectric solid state devices have a great potential as energy converters in both power generators and coolers.

Previous research focused on inorganic materials, in order to achieve high thermoelectric efficiency. Recently, studies have focused on inorganic materials, e.g., semiconductors, such as Bi_2Te_3, $CoSb_3$, SiGe, MgSi, conducting oxides, such as $NaCo_2O_4$, $CaMnO_3$, and metal alloys, such as BiSb. One of the most excellent inorganic materials, Bi_2Te_3, and Bi-Te based alloys, are well known for realizing high thermoelectric efficiency [1–3]. However, inorganic thermoelectric materials have various disadvantages. For instance, their cost is prohibitively expensive, they may cause heavy metal pollution and their production process is relatively difficult.

Organic polymer composites are alternatives to the inorganic thermoelectric materials. Although they possess thermoelectric efficiency of almost two to three orders of magnitude less than the inorganic thermoelectric materials, they also exhibit some excellent advantages, such as low thermal conductivity, low cost, plentiful resources, easy processability, and useful flexibility. This indicates that polymer thermoelectric materials are sufficiently competitive, despite their efficiency being less than that of inorganic or semiconductor materials. For polyaniline [4], the values of electrical conductivity $\sigma = 10$ S/cm and Seebeck coefficient $S = 13$ μV/K were obtained, and $S = 5$ μV/K and $\sigma = 21.5$ S/cm were attained in polypyrrole films [5]. Also, $S = 9$ μV/K and $\sigma = 80$ S/cm have been reported for PEDOT:PSS films with dimethyl sulfoxide (DMSO) treated [6]. However, researches have not yet studied enough about conductive PEDOT as a thermoelectric material.

Ferric *para*-methylbenzenesulfonate (Fe(*p*-MeBzs)$_3$) has been used as both an oxidizing agent and dopant for the generation of high electrical conductivity in the EDOT polymerization process [7,8]. The thermoelectric performance can be expressed by a dimensionless figure of merit, $ZT = (S^2\sigma T)/\kappa$, where S is the

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Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. The thermoelectric materials have to exhibit a significant Seebeck voltage, high electrical conductivity, and low thermal conductivity to obtain a high thermoelectric efficiency. Among these factors, high electrical conductivity of thermoelectric material is the most important. Electrical conductivity of the PEDOT has generally ~18.3 S/cm, and therefore does not satisfy the requirements for high thermoelectric performance [9].

To achieve this objective, many researchers focused to improve the electrical conductivity of thermoelectric material by adding small amounts of conductive filler such as carbon black, graphene, and CNT. These conductive fillers can be well dispersed in a polymer matrix and can improve thermoelectric properties by forming a conductive network between the filler and matrix. Du et al. reported that the dimethyl sulfoxide doped poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate) (PEDOT:PSS) filled with carbon black composite film showed power factor of 0.96 μW/m K^2 [10]. The maximum ZT value of 0.02 at 300 K has been reported for conducting polymers such as PANI and PEDOT:PSS filled with carbon nanotubes [11]. In case of the graphene and PEDOT:PSS composite, a maximum ZT value of 0.021 at 300 K has been reported [12]. Single-walled carbon nanotubes and PANI composites have exhibited maximum ZT of 0.004 at 300 K [13]. Carbon black is the carbon based electrically conductive materials which can available at very reasonable cost. Their conductivity is in the range of 0.1–100 S/cm at room temperature [14]. Conductive carbon black has also not yet been reported enough as a thermoelectric material.

In this paper, conductive carbon black filler was dispersed into a *para*-methylbenzenesulfonate (*p*-MeBzs) doped PEDOT matrix in the ratio of 0, 5, 10, 15, 20, and 30%, respectively in order to enhance thermoelectric efficiency. To fabricate homogeneous carbon black and PEDOT composites, the surface of carbon black was coated with a nano-sized PEDOT layer before synthesis. Dodecylbenzenesulfonic acid (DBSA) was used to completely coat the PEDOT layer onto the carbon black particles. Although, monomer EDOT has extremely low solubility in water and carbon black can only just be dispersed in DI water, DBSA acts simultaneously as a surfactant for the formation of micelles and as a doping agent. Therefore, carbon black particles could coat the PEDOT uniformly. Individual carbon black nanoparticles were well dispersed into the PEDOT matrix, as the coated PEDOT nano-layer has an affinity to the PEDOT matrix. It thus enabled the achievement of high electrical conductivity via the electrically connective filler-matrix network.

2. Experimental section

2.1. Materials

Carbon black (Super P) with diameter between 30 and 50 nm was purchased from OCI CO., Ltd. (Seoul, Korea). 3, 4-ethylenedioxythiophene (EDOT, $C_6H_6O_2S$) monomer (Clevios M, Bayer AG) was stored at 3–5 °C prior to use. Dodecylbenzenesulfonic acid (DBSA, $C_{12}H_{25}C_6H_4SO_3H$) and ammonium persulfate (APS, $(NH_4)_2S_2O_8$) were purchased from Daejung Chemicals & Metals Co., Ltd. (Seoul, Korea). Sulfuric acid, ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$), and toluene ($C_6H_5CH_3$) were purchased from Sigma Aldrich.

2.2. Fabrication of nano-sized PEDOT coated carbon black

The overall schematic representation of the fabrication process is illustrated in Fig. 1. 0.2 g of carbon black and 0.326 g of DBSA (MW 326.5) were added to 50 ml of DI water to prepare the aqueous micellar dispersion. These carbon black colloids were stirred at 30 °C for 1 h. Afterwards, 0.472 g of EDOT (MW 142.18) was added to the solution which was stirred at 30 °C for 1 h. After 1 h, 1.824 g of the oxidizer ammonium persulfate (MW 228.2) was dissolved in 10 ml of DI water and then added to the colloidal solution. The reaction mixture was stirred steadily and the temperature was maintained at 30 °C for 24 h. The resulting solution was centrifuged at 8000 rpm for 30 min. The resulting supernatant was poured carefully into a bottle. Then, DI water was added to the sediment and re-dispersed by using an ultrasonic bath for 1 h. This centrifugation, removal of the supernatant, and re-dispersion process was carried out 5 or more times to increase the purity of the resulting powder. Finally, the product was dried in a vacuum oven at 60 °C for 24 h.

2.3. Synthesis of Fe(p-MeBzs)$_3$

The chemical synthesis method of Fe(*p*-MeBzs)$_3$ was as follows. In a round-bottom flask, toluene was reacted with sulfuric acid at 150 °C for 1 h at a mole ratio between toluene and sulfuric acid of 1:1 to synthesize *para*-methylbenzenesulfonic acid. Afterwards, the products underwent recrystallization through the use of a rotary evaporator. The obtained *para*-methylbenzenesulfonic acid was dried in a vacuum oven at 60 °C for 1 h. Subsequently, *para*-methylbenzenesulfonic acid was dispersed in methanol, and ferric chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) was added to the mixture dropwise at 230 °C for 1 h. The mole ratio between ferric chloride hexahydrate and *para*-methylbenzenesulfonic acid was 1:3. The resulting powder was filtered and refluxed 5 or more times in methanol/acetonitrile solvent to obtain the Fe(*p*-MeBzs)$_3$. Finally, the filtered product was dried in a vacuum oven at 60 °C for 24 h.

2.4. Synthesis of PEDOT coated carbon black/PEDOT composites

It was assumed that the presence of carbon black does not affect the kinetics of PEDOT creation from EDOT polymerization. Therefore, the fabrication ratio of the PEDOT coated carbon black and PEDOT composite is presented at different theoretical carbon black loading of wt% with a fixed PEDOT loading. via this chemical polymerization, ferric *para*-methylbenzenesulfonate, acting as both initiator and oxidant, and EDOT monomer were prepared. First of all, the Fe(*p*-MeBzs)$_3$ was dried in a vacuum oven at 80 °C for 48 h to remove residual moisture. 8.196 g of Fe(*p*-MeBzs)$_3$ (MW 513.63) with the different values of the PEDOT coated carbon black filler loading were dispersed in 300 ml of ethanol at 30 °C for 1 h. The weight percentage of the filler contents were 0, 5, 10, 15, 20, and 30%, respectively. 2.832 g of EDOT (MW 142.18) was added to this mixture and stirred at 65 °C for 1 h to create the polymer chains. The mole ratio of the monomer and the oxidant was 1:0.8. In case of EDOT monomer and Fe(*p*-MeBzs)$_3$ polymerization, 1:0.8 ratio is known to achieve the highest electrical conductivity. The reason for this is the increase in concentration of the undoped oxidant in the polymer chain. When greater than 0.8 mol of oxidant is added, the residual unionized Fe(*p*-MeBzs)$_3$ in the polymer act as resistance components [15]. After 1 h, the reaction temperature was increased from 65 to 150 °C and stirred for about 20 min to finish polymerization. The resulting powder was filtered and washed with ethanol solvent two or three times to eliminate the residual EDOT monomers and oxidants. Finally, the filtered product was dried in a vacuum oven at 60 °C for 24 h.

2.5. Characterization of nanocomposites

The morphology and microstructure of the composites were characterized by field-emission scanning electron microscopy (FE-SEM, SIGMA) and field-emission transmission electron