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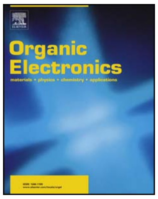

Influence of the incorporation of small conjugated molecules on the thermoelectric properties of carbon nanotubes

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ABSTRACT

Small-bundled single-walled carbon nanotube (SSWCNT) nanocomposite films made with various small molecules were facilely fabricated using the micronizing mill process. Finely dispersed small molecules in the SSWCNT film can effectively reduce the in-plane thermal conductivity of the nanocomposite due to π-π interactions. Furthermore, the micronizing mill process ensures the uniform distribution of the small molecules and the SSWCNTs in the nanocomposite film without any damage or deformation of the SSWCNT structure. Moreover, the influence of the shape of the small molecules on the thermoelectric properties of SSWCNT nanocomposite was systematically investigated. The thermoelectric properties of the pyrene/SSWCNT nanocomposite were found to have been greatly improved by the planar pyrene molecules with a slightly increased electrical conductivity of 978.6 S cm^{-1} and a significantly decreased in-plane thermal conductivity of 13.5 W m^{-1} K^{-2}. The evaluated ZT value of the pyrene/SSWCNT nanocomposite was 4.4×10^{-3} and is about 20 times higher than that of the pristine SSWCNT nanocomposite. A planar-type thermoelectric generator (TEG) consisting of 20 legs was also fabricated using this pyrene/SSWCNT nanocomposite. The TEG showed an open circuit voltage of 20 mV and a short circuit current of 350 μA, resulting in a maximum output power of 1.5 μW at $\Delta T = 20\,^{\circ}\mathrm{C}$.

1. Introduction

Recently, energy harvesting materials such as solar cells, piezoelectrics, and thermoelectrics, which can convert energy from various sources into electric energy to improve energy efficiency, have attracted great attention as auxiliary power systems [1–3]. Thermoelectric (TE) materials can directly convert thermal energy, obtained from sources that generate a small amount of heat like the human body to sources with large quantities of waste heat like that from an industry, into electricity. The efficiency of TE materials is generally evaluated by a dimensionless figure of merit $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the total thermal conductivity, and T is the absolute temperature [4–6]. Ideally, TE materials should possess a large Seebeck coefficient as well as a high electrical conductivity and a low thermal conductivity for practical thermoelectric applications. Such ideal TE materials show an improved performance by generating a large electrical potential, minimizing the Joule heating, and maintaining a large temperature gradient. However, it is difficult to effectively control all TE parameters such as S, σ, and κ in order to achieve high TE performance because they are closely correlated with each other.

Among various materials, organic TE materials are currently drawing much attention due to their advantages in terms of cost effectiveness, mechanical flexibility, and inherently low thermal conductivity. Although the low thermal conductivity of an organic TE material might seem to be beneficial for the enhancement of the TE performance, its corresponding low electrical conductivity is still a major challenge in fabricating efficient TE generators with a high output power. Many researchers have tried to improve the electrical conductivity of organic TE materials using various doping processes; this, however, is rarely achieved due to the huge drop in Seebeck coefficient caused by the increase in carrier concentration by the doping process [7]. As an alternative, nanocomposite systems using organic materials mixed with carbon nanotubes (CNTs), which can facilely improve the electrical conductivity, could be a good candidate for an organic TE material as such physical mixing can minimize the drop in the Seebeck coefficient while simultaneously reducing the thermal conductivity of the CNTs. There are already several reports on the TE properties of CNT nanocomposites fabricated by using various polymers such as polyaniline (PANI), polyvinyl acetate (PVAc), poly(3,4-ethylenedioxythiophene): polystyrene sulfonate (PEDOT:PSS), and poly(3-hexylthiophene) (P3HT). Meng et al. demonstrated PANI/CNT

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composites prepared by wrapping the surface of CNTs with PANI, which exhibited a maximum power factor of 5.04 μW m^{-1} K^{-2} with an enhanced electrical conductivity of 61.47 S cm^{-1}. Yu et al. investigated the TE properties of PVAc/CNT and PVAc/PEDOT:PSS/CNT nanocomposites. PVAc/CNT nanocomposites showed a relatively low electrical conductivity of 48 S cm^{-1}, whereas PVAc/PEDOT:PSS/CNT nanocomposites, using conductive PEDOT:PSS at an optimal composition ratio, presented a maximum power factor of 160 μW m^{-1} K^{-2} with a highly enhanced electrical conductivity of 1350 S cm^{-1}. Although these results successfully described the strategy for improving the electrical conductivity and decreasing the thermal conductivity of CNTs, their improved output power in terms of application in a practical TE generator has never been demonstrated. Furthermore, despite the high electrical conductivity, the observed low Seebeck coefficient, near approximately 30 μV K^{-1}, can be a limitation in their application to enhance the output power of a TE generator [8–17]. Therefore, it is critical to have an appropriate and optimal combination of the organic materials and the CNTs to achieve a synergistic effect in terms of the electrical conductivity, Seebeck coefficient, and thermal conductivity.

From this perspective, we designed a novel approach to enhance the TE properties of the CNT nanocomposite by using conjugated small molecules such as pyrene or fullerene, which are not commonly applied in conventional organic TE nanocomposites. For the preparation of the nanocomposite, small-bundled single-walled CNTs (SSWCNTs) were used because of their very long bundle length as compared to other conventional CNTs. The high carrier mobility due to the structural characteristics of SSWCNTs is suitable for enhancing the electrical conductivity and the Seebeck coefficient of the nanocomposite. At the same time, small molecules with high solubility in organic solvents that can be uniformly distributed in the SSWCNT nanocomposite can efficiently reduce the nanocomposite's thermal conductivity due to their attachment on the SSWCNT surface by a π-π interaction, which can increase the number of phonon scattering sites at the interfaces. Moreover, a small volume of these small molecules can effectively minimize the drop in the electrical conductivity of the SSWCNT nanocomposite by decreasing the distance between adjacent SSWCNT bundles in the matrix, as compared to the conventional bulky polymers. The prepared small molecule/SSWCNT nanocomposites were systematically investigated from the thermoelectric and the nanostructural viewpoint depending on the shape of small molecules. We also demonstrated the fabrication of a TE generator using the pyrene/SSWCNT nanocomposite, showing a high power output of 1.5 μW with a temperature gradient of 20 °C.

2. Experimental

2.1. Preparation of small molecule/SSWCNT nanocomposite films

The small molecules used in this study are the planar pyrene and the spherical fullerene (C_{60}) and phenyl-C61-butyric acid methyl ester (PCBM). Pyrene and C_{60} were purchased from Sigma-Aldrich, and PCBM was obtained from Solenne BV (Germany). SSWCNTs with a flocculated shape of single-walled CNTs were provided by Meijo Nano Carbon Co. (Japan). All materials were utilized without additional purification and chemical treatment. All the small molecule/SSWCNT nanocomposite films, with different types of small molecules, were prepared using the following method: The composition ratio between the small molecules and the SSWCNTs for fabrication of the nanocomposite was determined to be optimal at 4:6 based on our previous study [14]. The small molecules and the SSWCNTs were homogeneously mixed using a micronizing mill (XRD-Mill McCrone, Retsch Inc., USA) for 2 h to uniformly disperse the organic materials in the SSWCNT matrix by applying a planar shearing force. Prior to the micronizing mill process, 72 mg of small molecules and 108 mg of SSWCNTs were dispersed in 20 mL of 1,2-dichlorobenzene (ODCB) to prepare a small molecule/SSWCNT slurry. The milled homogeneously blended small molecule/SSWCNT composites were deposited on polyimide substrates in a silicon mold of the size of 4 cm × 4 cm and baked in a vacuum oven at 60 °C for 4 h. The free-standing nanocomposite films with a thickness of about 30 μm were obtained by removing the polyimide substrates.

2.2. Preparation of pristine SSWCNT film

The pristine SSWCNT film was carefully prepared by the vacuum filtering process after dispersing 108 mg of SSWCNT in 20 mL of ODCB using tip sonication. The free-standing SSWCNT film was obtained by removing the filter paper after drying.

2.3. Fabrication of the thermoelectric generator

A planar-type thermoelectric generator (TEG) consisting of 20 legs connected in series was fabricated using the pyrene/SSWCNT nanocomposite film. The legs of TEG with a size of 2 mm × 15 mm were arranged at intervals of 2 mm and electrically connected to the silver electrode by using the dispenser printing process. An annealing process was carried out at 150 °C on a hot plate for 30 min to improve the electrical conductivity of the silver electrodes and to reduce the contact resistance of the interface between the silver electrodes and the TE legs.

2.4. Characterization of small molecule/SSWCNT nanocomposite films

The surface morphology and nanostructure of the nanocomposite films were investigated using a scanning electron microscope (SEM, SigmaHD, Carl Zeiss, Germany) and a transmission electron microscope (TEM, Tecnai G2, FEI, USA). The interfacial interaction between the small molecule and the SSWCNT was observed using Raman spectroscopy with a 532 nm excitation laser (Senterra, Bruker, Germany). The thermal behavior was investigated using thermogravimetric analysis (TGA, SDT2060, TA Instruments, USA) in the range of 25–800 °C in a N_2 atmosphere.

2.5. Thermoelectric properties of small molecule/SSWCNT nanocomposite films

Electrical conductivity was measured using the four-point probe method with a Keithley 2400 SourceMeter. Thermoelectric properties were evaluated by a home-built setup consisting of a temperature control part, an electrical measurement part, and a measurement stage. The Seebeck coefficient was measured in a vacuum chamber with a relatively low vacuum of 10^{-2} torr to minimize the effect of heat convection and conduction on the measurement. Samples were prepared with silver electrodes separated by a distance of 2 cm for the measurement of the TE characteristics. The temperature difference between both ends of the sample was maintained using Peltier devices that were elaborately controlled by a Keithley 2200 power source and a Keithley 2460 SourceMeter. The Seebeck voltage and the short circuit current were measured using a Keithley 2182A nanovoltmeter and Keithley 6485 picoammeter, respectively. The thermal conductivity was calculated using the equation $\kappa = \alpha\rho C_p$, where α is the thermal diffusivity, ρ is the density, and C_p is the specific heat capacity at constant pressure. The in-plane thermal diffusivity was obtained using a Laser PIT-M2 (Advance Riko, Japan) at 300 K. The density was calculated by measuring the true weight and volume of all samples. The specific heat capacity was acquired using a modulated differential scanning calorimeter (DSC Q1000, TA Instruments, USA).

3. Results and discussion

The interfacial interaction between the various small molecules and the surface of SSWCNTs was investigated by Raman spectroscopy using a laser excitation of 514 nm to verify whether the micronizing mill