Characterization and Thermoelectric Behavior of Super-growth Carbon Nanotube Films Co-loaded with ZnO and Ag Colloids

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ABSTRACT

The fabrication of low-temperature waste heat power conversion modules will require the development of thermoelectric materials based on mass-produced nanotubes such as super-growth carbon nanotubes (SGCNTs), rather than high-quality nanotubes generated on the laboratory scale. In this work, SGCNT films co-loaded with colloidal ZnO (which has a high Seebeck coefficient) and Ag (which enhances electrical conductivity) were prepared to optimize both carrier concentration and mobility. The resulting carbon-based hybrid films were found to have a p-type power factor of 100.4 µW m⁻¹ K⁻² at 383 K, which represented one of the highest values yet reported for a SGCNT system.

1. Introduction

Thermoelectric technology capable of converting heat directly to electrical energy and vice versa has attracted much interest as a potential clean energy source that may help to address issues related to fossil fuel consumption and attendant environmental problems. In particular, low noise thermoelectric power generation devices contain no moving parts and have the added benefit of being able to recycle unused waste heat. The requirement for high conversion efficiency has resulted in numerous efforts to develop inorganic thermoelectric materials incorporating heavy transition metals or rare earth elements, such as Sb and Te. At present, because of the increasing interest in green chemistry and the development of an information-based society, there is also a demand for versatile thermoelectric materials for sensor devices related to the internet-of-things, based on earth-abundant and eco-friendly constituent elements. Conductive polymers (such as polyaniline and poly(3,4-ethylenedioxythiophene)) and nanocarbon materials (including graphene and carbon nanotubes (CNTs)) are lightweight, flexible and low cost, and so have extremely high potential for applications in wearable devices.

Because it is often difficult to accurately determine the thermal conductivity of organic thermoelectric films, the performance of such films is evaluated based on their power factor (PF), as determined using the equation

\[ PF = S^2 \sigma, \]

where \( S \) and \( \sigma \) are the Seebeck coefficient and electrical conductivity, respectively. \( S \) becomes smaller with increasing the charge carrier concentration in the material, whereas \( \sigma \) is directly proportional to the carrier concentration. Therefore, the PF value can be increased by adjusting the carrier concentration in such a way that the trade-off relationship between the \( S \) and \( \sigma \) values is optimized. CNTs can be doped with organic molecules to precisely control the carrier concentration, producing high PF values. Examples include CNTs doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane, a p-type material with a PF of 2250 µW m⁻¹ K⁻², and CNTs doped with benzyl viologen, an n-type material with a PF of 3103 µW m⁻¹ K⁻². In fact, it has been predicted that the performance of these organic substances will soon equal that of inorganic thermoelectric materials. Even so, the PF value is almost always determined primarily by the quality of the CNTs, including factors such as the semiconductor content, structural defects and electronic states. Consequently, there has been a research focus on the fabrication of high-quality CNTs using proprietary preparation methods on the laboratory scale. The investigation of various means of modifying industrial CNTs could allow this material to be used in a wide range of applications, including thermoelectric power generation. Additionally, hybrid materials based on commercial
demonstrated a polymer-CNT composite on its surface. However, analysis of the ZnO particles on the material were highly dispersed colloidal Ag species. This report the importance of industrial nanotube-based hybrid films co-loaded with metallic and semiconducting colloids for the purpose of producing organic thermoelectric materials.

2. Experimental

A ZnO-loaded CNT film (ZnO/SGCNT) and a Ag-loaded ZnO/SGCNT film (Ag+ZnO/SGCNT) were fabricated by the procedure described in the Supporting Information (SI). The details of the structural analyses of these materials are also described in the SI.

3. Results and Discussion

Scanning electron microscopy (SEM) was used to confirm the surface morphology of the series of samples (Figs. S1(a), (b) and (c)). The formation of CNT bundles as a result of van der Waals forces as well as π–π interactions between the nanotubes was observed. The pure SGCNT, ZnO/SGCNT and Ag+ZnO/SGCNT specimens all had similar diameters, with values of 22.1 ± 6.2 nm, 22.1 ± 6.6 nm and 22.0 ± 6.6 nm, respectively. That is, each specimen comprised a microscopic thermoelectric film. Interestingly, only the Ag+ZnO/SGCNT specimen exhibited colloidal particles on its surface. However, analysis of the ZnO/SGCNT product by scanning transmission electron microscopy with energy dispersive X-ray spectroscopy (STEM-EDS; Fig. S2) showed the presence of particles on the CNT bundles along with co-deposited Zn and O species, which indicated the presence of numerous ZnO colloids (31.0 ± 10.2 nm) on the CNT bundles. These results confirm that the ZnO/SGCNT film comprised a true hybrid of ZnO and CNTs rather than a simple physical mixture. SEM-EDS analysis of the Ag+ZnO/SGCNT film (Fig. 1) showed that the particles on the material were highly dispersed colloidal Ag species with particle sizes in the range of 66.7 ± 20.9 nm. The above results establish that CNT films with well dispersed colloidal particles of ZnO and Ag were successfully prepared. Although a recent study demonstrated a polymer-CNT composite film incorporating the toxic tellurium alloy,16 our study is the first report of a SGCNT film co-loaded with metal and metal oxide particles as a useful strategy for accessing structurally novel polymorphic thermoelectric materials.

Related studies are currently underway in our laboratory to determine the elemental ratios in these film, and the results will be reported in a forthcoming paper.

Figure 2 summarizes the S, σ and PF values determined at 345 K for the pure SGCNT,7(434,770),(606,900) ZnO/SGCNT and Ag+ZnO/SGCNT samples. Each membrane showed p-type conductivity derived from the CNTs. The S value for the pure SGCNTs was increased from 40.3 to 43.5 µV K⁻¹ with ZnO loading, although the σ value was somewhat degraded. Conversely, the application of the Ag colloids dramatically increased the electrical conductivity (from 354.7 to 532.5 S cm⁻¹) without causing a significant decrease in the S value. As a result, a PF of 91.5 µW m⁻² K⁻¹ was obtained, which represents an increase of 22% relative to the pure SGCNTs. Interestingly, enhanced thermoelectric power values of SGCNT were achieved with both the ZnO and Ag particles, despite the minimal changes in the CNT bundle diameter and surface morphology, which typically determine electrical conductivity.

The variations in the stability and thermoelectric properties of the Ag+ZnO/SGCNT material with changes in temperature were investigated (Fig. S3). Both the S and σ values of the sample were found to gradually increase with increases in temperature up to approximately 390 K, with no significant degradation of the specimen. The PF also gradually increased in proportion to the
temperature, which resulted in a value of 100.4 µW m⁻¹ K⁻¹ at 383 K. The highest PF value previously reported for a SGCNT-based film was 44.3 µW m⁻¹ K⁻¹, and the present Ag+ZnO/SGCNT films exhibits a PF value approximately 2.3 times higher than this. To obtain insights into the effects of ZnO and Ag colloid loading on carrier transport mechanisms, logarithmic plots of the electrical conductivity values of the SGCNT, ZnO/SGCNT and Ag+ZnO/SGCNT specimens as functions of temperature were plotted (Fig. S4). These data were analyzed based on the one-dimensional range variable hopping model using the equation

$$\sigma(T) = \sigma_0 \exp \left( -\frac{T_0}{T} \right)^{1/2},$$

where \( \sigma_0 \) is a constant (determined by the density of states of the material, the length of the average transition and the frequency of molecular vibrations), \( T_0 \) is the characteristic Mott temperature (which is typically determined by the carrier hopping barriers), and \( T \) is the sample temperature. The data for this series of samples exhibits a good linear relationship between \( \ln \sigma \) and \( T^{-1/2} \) within the measured temperature range, and the \( T_0 \) values for the SGCNT, ZnO/SGCNT and Ag+ZnO/SGCNT specimens estimated from the fitting were 94.7, 75.6 and 32.3 K, respectively. The ZnO loading of the SGCNTs evidently increased \( T_0 \), which in turn increased the carrier hopping barrier such that there was a high potential barrier to inter-nanotube hopping. According to the Boltzmann equation, the \( S \) value and the \( \sigma \) value will have an inverse relationship, such that an improvement in one will result in a degradation of the other. In the present case, the ZnO also modulated the carrier concentration and increased the \( S \) value of the CNTs while there was a slight decrease in the \( \sigma \) value. Conversely, Ag loading reduced the \( T_0 \) of the ZnO/SGCNT material and lowered the carrier hopping barrier to facilitate one-dimensional carrier transfer between nanotubes. Compared with ZnO, Ag likely had less of an effect on the carrier concentration, because the \( S \) value was lowered by only 2.0 µV K⁻¹.

Based on these results, ZnO colloids immobilized on nanotube walls appear to directly affect the carrier concentrations in the SGCNTs and reduce the conductivity of the films, and are also effective in increasing the Seebeck coefficient. Additionally, highly conductive Ag particles dispersed throughout the film surface may form localized conductive channels, which results in the promotion of one-dimensional carrier flow throughout. This, in turn, produces high PF values. Further investigation will be necessary to determine the effects of varying these parameters and the resulting impacts on the macroscopic thermoelectric properties of the hybrid films.

4. Conclusions

This study demonstrated improvements in the p-type thermoelectric properties of SGCNTs using a process based on loading colloidal additives that would be amenable to mass production. The PF value of SGCNTs co-loaded with colloidal ZnO and Ag was found to be 91.5 µW m⁻¹ K⁻¹, which was 22% higher than that of the pure SGCNTs. Preliminary analyses of the thermoelectric behavior and charge transport mechanism indicate that loading with ZnO enhanced the Seebeck coefficient while Ag loading improved conductivity in the SGCNT films. Furthermore, the PF value of this hybrid material reached 100.4 µW m⁻¹ K⁻¹ at 383 K in trials evaluating heat resistance and chemical stability. Precise control of the metal species and the colloid size in these carbon-based hybrid materials provides a new route to developing organic thermoelectric films that are free of toxic and expensive elements. The results of this study are expected to play an important role in allowing the industrial use and commercialization of SGCNTs as part of the realization of a sustainable society.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-64067.

Author Contributions

All authors contributed equally.

Notes

The authors declare no competing financial interest.

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