Improved Dispersibility and Thermopower of Single-Walled Carbon Nanotubes in Ionic Polymers

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Abstract

We dispersed single-walled carbon nanotubes (SWNTs) in ammonium-bearing polymers. SWNT/polymer composites showed 3 times larger thermoelectric Seebeck coefficient than those of the SWNT buckypapers. This enhancement was highly related to the dispersibility of SWNTs in ionic polymers.

1. Introduction

Thermoelectric devices are solid-state systems that directly convert electricity into thermal energy or generate electricity from temperature difference. A figure of merit, ZT, expresses the efficiency of the thermoelectric materials, in which the parameter Z is given with the square of the Seebeck voltage per unit of temperature (Seebeck coefficient; S), multiplied by the electrical conductivity (σ) and divided by the thermal conductivity, and T is the absolute temperature.^[1] S of Single-walled carbon nanotubes (SWNTs) has been studied to explore their unique carrier transport properties derived from high aspect ratio and one-dimensional structures. In most case, metallic components SWNTs play a big role in the transport properties.^[2] SWNT samples which consist of both metallic and semiconducting components, exhibit S values in a range between 20 μ V/K and 60 μ V/K at room temperature. Single wire measurements revealed that semiconducting SWNTs possess larger S value which is comparable with conventional inorganic thermoelectric materials.^[3] After the sophisticated metal-semiconductor separation, the SWNT sample, in which semiconducting component is highly enriched, has indicated large S value reaching 170 μ V/K for bulk-scale measurement.^[4] A Different strategy for improving thermoelectric properties has been demonstrated by combining with conducting polymers.

Ionic liquids (ILs) have received considerable interest as environmentally-benign solvents for organic reactions, and self-assemblies. Recent studies have highlighted their use as media for SWNT flakes to exfoliate them into thinner bundles, forming homogeneous pastes, called "bucky gels".^[5] Also this technique has been applied to form their polymer composites using polymerizable ionic liquid (PIL)-bearing monomers, and enhanced their own mechanical toughness.^[6] A computational work has revealed that the van der Waals force, rather than the specific cation- π interaction, plays a dominant role to stabilize SWNTs in the IL matrix.^[7] This soft-chemical dispersion method delivers no significant damage on their structure, while most other dispersion procedures are associated with severe damages such as shortening and unintentional chemical modification.^[8] However, exfoliation of SWNTs with conventional imidazolium-based ILs has been rather limited and complete dispersibility of SWNTs into individual tubes was still challenging. Considering flexibility of molecular design of ILs, there seem to be significant possibility to achieve mono-dispersed SWNTs by means of appropriate dispersant based on ILs and related substances.

We here demonstrated that SWNTs were finely dispersed in PILs, polymethacrylate derivatives bearing cationic units. This polymer composites showed 3 times larger S value than the SWNT buckypapers.

2. Experiments

Preparation of SWNTs/PIL pastes and their polymer composites

PILs were synthesized according to previously reported method.^[7] We used carbon nanotubes made by the supergrowth method (SG-CNT), and purchased from Nanocyl Co., Ltd. (NC-CNT), Southwest Nanotechnologies (Co-Mocat, CM-CNT) and KH-Chemicals Co., Ltd. (KH-CNT). The black pastes made of PIL and SWNTs were solidified using radical polymerization in the presence of 2.2'-azobis(isobutyronitrile) at 333 K for 2 hours. The buckypapers were also prepared as have been reported as were used as reference samples.



Fig. 1 Molecular structures of PILs.

3. Results and Discussion

Thermoelectricity from SWNT composites

First, we studied thermoelectric voltages of the composites made of 1 (poly1) and various SWNTs at 7 wt% of loading level (Fig. 2 (a)). Among the buckypapers and composite films, the composite containing SG-CNTs



Fig. 2 (a) Seebeck coefficient of poly1 filled by SWNTs at 7 wt% loading and 310 K. Open plots indicate the buckypaper, and close ones denote the composites of CM-CNTs (triangles), KH-CNTs (squares), NC-CNTs (circles) and SG-CNTs (diamonds). (b) Seebeck coefficient of SG-CNT composites at 1 wt% loading and 310 K with poly1~6, and the buckypaper. (c) Temperature dependence of Seebeck coefficient of SG-CNT/poly1 at loading level of 0.5 wt% (crosses), 1 wt% (filled squares), 3 wt% (dashes), 7 wt% (orthogonal crosses), and of a buckypaper (filled circles).

showed 2~3 times larger *S* than the SG-CNT buckypapers and others. We then gleaned thermopowers of SG-CNT composites based on various polymers (Fig. 2 (b)), *S* values were enhanced for all the composites. The SG-CNT/poly1 showed the *S* value of 135 μ V/K at 310 K at 1 wt% of loading level.

S value showed significant dependence on the temperature and the loading level of SWNTs (Fig. 2 (c)). At 1 wt% of loading level, we observed the largest temperature-dependence, and the largest *S* value of the 150 μ V/K at 340 K. This value is about 3.8 times larger than that of a SG-CNT film, and almost comparable to those of purified semiconductor-rich SWNTs.^[4]



Fig. 3 Seebeck coefficient of SG-CNT/polymers at 310 K. Polymers were derived from poly1 (circles), 2 (squares), 3 (triangles) and 4 (diamonds). Gray plots represent results of previous reports of CNT/polymer composites. ^{[9]-[14]}

Cross-sectional TEM Characterization

This enhance thermovoltage is specific for ionic polymer composites (Fig. 3), and depends on the loading level, suggesting importance of dispersibility and stability of SWNTs in polymer solids. We investigated the dispersibility of SWNTs by using cross-sectional transmission electron microscopy (TEM). SG-CNTs were dispersed in these ionic polymers and, in particular, they were highly isolated in poly1 at a low loading level (Fig. 4 (a)). This dispersibility was quite different from those of other CNTs such as NC-CNTs (Fig. 4 (d)). We here emphasize that well-dispersed SG-CNTs showed significantly enhanced *S* values. Possible enhancement mechanisms would include large temperature gradients at the CNT junctions in the well-exfoliated and entangled CNT jungle.^[4]



Fig. 4 Cross-sectional TEM micrographs of SG-CNT/poly1 at the CNT loading level of (a) 1 wt% and (b) 5 wt%, SG-CNT/poly3 at (c) 1 wt% and NC-CNT/poly1 at (d) 5 wt%.

4. Conclusions

We demonstrated large Seebeck effect in SWNT/ionic polymer composites, typically SG-CNT/poly1. This work demonstrates a novel route to enhance Seebeck coefficient of SWNT materials.

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