Independent Control of Phonon and Carrier Transports in Carbon Nanotube Solids with Biomolecular Junctions for Improving Thermoelectric Performance

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Abstract

Carbon nanotube (CNT) composites have been gathering more attention for the application to flexible thermoelectric generators. However, their thermoelectric performance is restricted by the large thermal conductivity. Recently, a novel material design to improve performance by inserting bio molecules at CNT/CNT junctions has been proposed. In this work, we demonstrate that thermal conductivity is dramatically suppressed, but PF is not decreased much by the insertion of cage-shaped proteins with semiconducting cores. As a result, the ZT value increases over 800-fold.

1. Introduction

Thermoelectric devices directly convert heat flow into electrical energy without any moving parts and complicated structures, which realize their high reliability compared with other power generation devices. Recently, in economic terms, thermoelectric technology for energy harvesting from low temperature have been attracting increasing attention. Therefore, wide-area, low-cost, and mechanically flexible thermoelectric devices are strongly desired to collect low-density heat flux effectively.

Carbon Nanotubes (CNTs) are promising material for this purpose because of not only their mechanical strength, lightness, and richness in element resources, but also high electrical conductivity^{1,2)}. They are, however, not ideal for thermoelectric applications in nature because of its high κ . The performance of thermoelectric conversion is generally evaluated by $PF=\alpha^2\sigma$ or the dimensionless figure of merit, $ZT = PF \times T/\kappa$ (α, σ, κ , and T are Seebeck coefficient, electrical conductivity, thermal conductivity, and absolute temperature, respectively). Accordingly, low thermal conductivity is required to obtain high ZT. Furthermore, actual efficiency in the various scenes of energy harvesting strongly requires a low-thermal-conductance design of the devices because temperature gradient in the active area is determined by the device thickness and the thermal conductivities of the device components. Sufficiently low thermal conductivity, < 0.1 W/Km, is required to achieve desired temperature gradient by considering a bottlenecking heat resistance between the device and ambient air. Thermal transport of the CNT composite material must therefore be further suppressed without decreasing its PF.

Recently, we have applied a bio-nano technology to improve thermoelectric performance of CNT composites³. The method employed caged-shaped proteins called Listeria innocua Dps (DNA-binding protein from starved cells)⁴ that can accommodate semiconductor cores (Fig. 1). Dps is 9.5 nm in outer diameter and 4.5 nm in inner diameter and is composed of 12 protain subunits. To provide an ability to adsorb on CNTs, we genetically added the subunit with a peptide aptamer with an affinity with carbonaceous materials (NHBP-1)⁵. The mutant Dps subunits self-assemble into a cage-shaped protein shell with 12 aptamer peptides on the outer surface, herein referred to as C-Dps. For their affinity to CNTs, CNT-protein-CNT junctions are automatically formed when the films are made from the mixed dispersion. Applying a heat flow to the composite, a steep temperature gradient at the junction is caused by phonon scattering at the CNT/protein interface but carriers flow through the semiconductor core by tunneling the thin protein shell. As a result, the "phonon-blocking and electron transporting" struc-



Fig. 1 Schematic illustration of a cage-shaped protein with modified peptides and an inorganic core.



Fig. 2 "Phonon-blocking and electron transporting" structure realized by the CNT/protein/CNT junction.



Fig. 3 *PF* and thermal conductivity of pristine CNT and Dps(Co) composites.

ture, which is an ideal structure for thermoelectric materials, is realized in a self-assemble manner (Fig. 2).

2. Experimental

Two types of CNTs were used in this work, one is synthesized with arc discharge method (CNT A) and another is with the enhanced direct injection pyrolytic synthesis (eDIPS) method ^{6.7} (CNT B). CNT dispersion in water (0.2 mg/ml) was mixed with C-Dps aqueous solution (0.3 mg/ml) by sonication. CNTs not attached to C-Dps molecules were precipitated and removed by centrifugation at 8,500 rpm. CNT/C-Dps were obtained as a precipitation by further centrifugation at 80,000 rpm. Thus separated, C-Dps/CNT was dispersed in pure water by sonication. The dispersion was then dropped on a UV/O₃-treated glass substrate and dried for *ca.* 24 h under an ambient condition. Typical thickness of the drop-casted composite films was 50–100 nm. For thermal conductivity measurement, thicker films (*ca.* 30 µm) were prepared by pressure filtration.

Seebeck coefficient and electrical conductivity were measured using lab-made instrument⁸ in vacuum. Thermal diffusivity toward the thickness direction was measured using *ai-Phase Mobile (ai-Phase)* in air, which employs the temperature wave analysis method.

2. Results and discussion

Figure 3 graphically shows the variation of *PF* and thermal conductivity by the insertion of C-Dps molecules with Co cores into the junctions. Values are also shown in Table 1. In this experiment, the C-Dps molecule with a Co_3O_4 core, which generally work as a p-type semiconductor, was used. All sample exhibited p-type Seebeck coefficient. As shown is Fig. 3, thermal conductivity of pristine CNT is dramatically suppressed in both types of CNTs by forming compo-

Table 1 Thermoelectric properties of CNT and C-Dps(Co) composites

	σ	α	ĸ	PF	ZT ^(*)
	(S/cm)	$(\mu V/K)$	(W/mK)	$(\mu W/K^2m)$	
CNT A	0.30	56.0	17.2	0.19	5.7×10-7
CNT A/C-Dps(Co)	0.89	73.7	0.098	0.51	1.5×10-3
CNT B	91.3	23.5	65	5.0	2.3×10 ⁻⁵
CNT B/C-Dps(Co)	28.6	37.2	0.063	4.0	0.019

* Note that the absolute value is not reliable because thermal conductivity was not measured by the same sample and direction as other properties.

sites. *PF* increases when the conductivity of pristine material is low (CNT A) but slightly decreases when it is high (CNT B). These results imply that the C-Dps molecule inserted at CNT/CNT junction effectively suppress the phonon transport, but carrier transport is not significantly disturbed. In addition, Seebeck coefficient is increased by the addition of p-type Seebeck effect at the junction, resulting the small decrease of *PF*. As a result, *ZT* of CNT B/C-Dps(Co) is expected to be enhanced by over 800 fold against pristine CNT.

3. Conclusions

We succeed to suppress thermal conduction and improve *ZT* value by phonon scattering at the biomolecular junction. Thermal conductivity of CNT/C-Dps composites was less than 0.1 W/mK, which is comparable to those of typical heat insulators. Such extreme suppression of heat conduction without using porous structure is hard to obtain by conventional design of thermoelectric materials.

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