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Thermal and electronic transport of semiconducting nanoparticle-functionalized carbon nanotubes

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ABSTRACT

Semiconducting nanoparticle-functionalized carbon nanotubes are very promising for many electronic systems and devices. In this paper, the synthesis of carbon nanotube/semiconducting nanoparticle hybrids was firstly demonstrated by a facile solution method and the effect of nanoparticle functionalization on electronic/thermal transport was investigated. Both experimental tests and theoretical analysis indicated that the thermal conductivity of nanoparticle/carbon nanotube network at room temperature was reduced by ~37% in comparison with non-functionalized carbon nanotube networks, and this could be ascribed to the nanoparticle decoration-induced phonon scattering. In addition, the thermoelectric power factor was increased by 24-fold while the figure of merit was enhanced by 30-fold. The theoretical analysis suggested these significant improvements should originate from the carrier scattering at the carbon nanotube-nanoparticle interfaces and the decoration-augmented mismatch of the Fermi level and the mean transport energy level.

1. Introduction

Modulating electronic transport characteristics of carbon nanotubes (CNTs) through nanocrystal decoration is very interesting to make CNTs as competitive thermoelectric materials. Since CNTs demonstrate electronic density of states (DOS) with spike-like Van Hove singularities [1], it would be convenient to adjust the Fermi level by nanocrystal- or molecule-doping. Yu et al. [2] reported that the thermoelectric properties could be enhanced by modifying the relative position of Fermi level of CNTs to the transport energy level *via* metal nanocrystal decoration. However, metals usually have very small Seebeck coefficient and it may not lead to high thermoelectric (TE) figure of merit $ZT = S^2\sigma T/\kappa$, where S, σ, κ, T denotes the Seebeck coefficient (uV/K), electrical conductivity (S/cm), thermal conductivity (W/mK), and absolute temperature (K), respectively [3]. On the other hand, semiconducting nanocrystals, such as bismuth telluride (Bi_2Te_3), show with large Seebeck coefficient (>150 uV/K) [4] and have been extensively explored for thermoelectric applications. The decoration of CNTs with such semiconducting nanocrystals could more effectively enhance thermoelectric properties. The thermoelectric nanocrystal decoration would involve with: (1) possible carrier energy scattering in CNT-nanocrystal interfaces *via* engineered potential barrier [5]; (2) manipulating electronic transport properties by altering Fermi level of CNTs [2]. Moreover, the direct growth of nanocrystals on CNT surfaces would effectively disrupt thermal transport by phonon scattering [6].

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Many efforts have been made to synthesize inorganic nanocrystal-decorated CNTs [7–11]. The strategies include *ex situ* approaches by attaching the synthesized nanocrystals onto the CNT surface, and *in situ* approaches by directly forming nanocrystals on the CNT surface. There have been numerous reports related to CNT supported nanocrystals, such as CNT/metals (CNT/Au [12], CNT/Pt [13]), CNT/metal oxides (CNT/TiO_2 [14], CNT/MnO_2 [15], CNT/SnO_2 [16]), and other CNT/semiconductors (CNT/CdSe [17], CNT/CdTe [18]). For *in situ* synthesis of nanocrystals onto CNT surfaces, many methods have been developed. Unitary inorganic nanoparticles were deposited on CNTs *via* sputtering, evaporation or thermal deposition [19–21]. Chemical vapor deposition (CVD) was also attempted under the oxygen-free environment at very high temperature [22]. However, those methods are limited to the binary oxygen-free nanoparticle decoration. CdTe quantum dots have been attached to the CNT surface by Banerjee and wong [18] at high temperature (250 °C). Zhou et al. [23] attached Bi_2Te_3 nanocrystals onto CNT surface by microwave-polyol method at 170 °C. The procedure is complicated and high energy-consumption. The resultant Bi_2Te_3 nanocrystals on CNT surface were irregular and showed wide size distribution. To the best of our knowledge, no effort has been made for *in situ* growth of Bi_2Te_3 nanocrystals onto CNT surface at a lower temperature and there is also a lack of fundamental understanding of how semiconducting nanocrytals could modulate electronic and thermal transport of the decorated CNTs.

Herein, we report *in situ* synthesis of Bi_2Te_3 nanocrystals on the surface of multi-walled carbon nanotubes (MWCNTs) by a facile solution chemical method at a low temperature for the first time. The morphology of nanocrystals decorated on MWCNT surface was investigated, and the organic/inorganic interfacial contribution to the thermoelectric properties was revealed.

2. Experimental section

2.1. Acid treatment of MWCNTs

95% purity MWCNTs (C150-P) with outer mean diameter ~13 nm were purchased from Bayer Material Science AG. 50 mg MWCNTs were added into 150 ml 6 M nitric acid in a two-necked, round-bottomed glass flask, and refluxed at 120 °C for 5.5 h After refluxing, the mixture was cooled down to room temperature, washed with copious amount of deionized water, and filtrated using 0.2-micron Nylon filter paper (Millipore Inc.). Finally, acid-treated MWCNTs were dried in a vacuum oven at 80 °C overnight.

2.2. Synthesis of Bi_2Te_3-decorated MWCNT nanostructures

All chemicals were purchased from Sigma–Aldrich and used without any further purification. In a typical synthesis, 6.06 g bis(2-ethylhexyl) sulfosuccinate (AOT) was dissolved in 40 ml isooctane. Then, 37 mg telluric acid ($Te(OH)_6$) was dissolved in 0.6 ml deionized water. Another solution was also prepared by addition of 33.5 mg bismuth chloride ($BiCl_3$) into the 0.4 ml nitric acid. Subsequently, 20 ml AOT/isooctane was added into each solution. Next, 0.06 ml thioglycolic acid (TGA) was introduced into the $BiCl_3$/AOT/isooctane mixture. Both solutions were then sonicated for 15 min to form uniform solutions. Afterwards, 50 mg acid-treated MWCNTs were added into $BiCl_3$/AOT/isooctane solution followed with subsequent bath sonication for 1.5 h Then two solutions were mixed and subjected to ultrasonic processing for 1 h. Subsequently, 1.5 g hydrazine monohydrate (64–65 wt.%) was added into the mixture with vigorous stirring at room temperature overnight. The resultant precipitates were collected by filtration through the 0.2-micron Nylon filter membrane, and the solid samples were extensively washed with isooctane, ethanol and copious amounts of deionized water in sequence to remove any impurity residuals, including thioglycolic acid on Bi_2Te_3 nanocrystals, and AOT *etc.* Other samples were also prepared at the same procedure with different AOT concentrations (0.341 M and 0.085 M).

2.3. Structure characterization of Bi_2Te_3-decorated MWCNT nanostructures

Bi_2Te_3-decorated MWCNTs nanostructures were characterized by transmission electron microscopy (TEM, Hitachi H-8100) and high-resolution TEM (HRTEM, JEM 2100). The Bi_2Te_3-decorated MWCNT nanostructures dispersed and sonicated in toluene were drop-casted onto an ultrathin holey carbon-coated copper grid, and dried prior to electron microscopy. Energy-dispersive spectroscopy (EDS) was used to quantify atomic ratios. As-received MWCNTs and acid-treated MWCNTs were also characterized by Raman spectroscopy (Senterra Raman microscopy, Bruker Inc.) using a 532 nm laser. The samples were also characterized by Powder X-ray Diffraction (PXRD) with a Rigaku Ultima III diffractometer using Cu Kα. To prepare the samples for powder X-ray diffraction, the sample was finely grounded. The measurements were taken at a 2θ range of 20–60° at a step-width of 0.03 sec^{-1}. Powder XRD patterns were analyzed by referring to the International center: for Diffraction Data (ICDD) powder diffraction file (PDF) database. Size distributions for Bi_2Te_3 nanocrystals on MWCNTs were analyzed in commercial software, ImageJ.

2.4. Thermal/electrical characterization

Thermal conductivities were measured by Nanoflash thermal analysis equipment (LFA 447, NETZSCH Instruments). For the Seebeck coefficient measurement, the Seebeck voltage was collected by connecting Keithley 2182A Nanvoltmeter with two identical bare copper wires, which were bonded onto pellets at 10 mm spacing by silver paste. The temperature gradient was obtained using two K-type thermocouples (Omega Inc.), controlled by SM325 thermometer data logger). The Seebeck coefficient measurement was calibrated before measurement, and the Seebeck coefficient was calculated with $S = -\Delta V/\Delta T + S_{Cu}$, where S_{Cu} is 6.5 uV/K at room temperature [24]. Electrical conductivity was measured using a SRM probe (Bridge Technology Inc.) by a standard four-point probe method with a Keitley 2400 current source meter and a Keitley 2182A nanovolt meter at the room temperature. Acid-treated