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The influence of nitrogen doping on thermal conductivity of carbon nanotubes

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ABSTRACT

In this study, we investigated the influence of nitrogen doping on thermal conductivity of carbon nanotubes (CNTs) experimentally and theoretically. The nitrogen-doped CNTs were synthesized by using thermal chemical vapor deposition method and were used to prepare silicone composites. The thermal conductivity of silicone composites with these CNTs improves greatly. A negative influence of nitrogen doping on thermal conductivity of CNT/silicone composites is observed. The calculated thermal conductivity of CNTs indicates that the thermal conductivity of nitrogen-doped CNTs decreases rapidly with the nitrogen content in CNTs. This is attributed to defects in nitrogen-doped CNTs, which act as phonon scattering centers.

1. Introduction

Carbon nanotubes (CNTs) have been extensively studied due to their outstanding physical and chemical properties which show promise for possible technological applications [1,2]. Among numerous properties, the single-walled or multi-walled CNTs exhibit thermal conductivities as high as 2000–6000 W/mK [3], which is much higher than that of copper and silver [4]. Using CNTs as thermal conductive materials for thermal management is of great interest [3,5–7]. However, perfect CNTs are virtually impossible to obtain. The defects and impurities produced during the growth of CNTs will influence the physical and chemical properties of CNTs. The thermal conductivity of CNTs will be fundamentally reduced because the defects and impurities will result in phonon scattering [8,9].

Many studies have shown that doping or surface chemical modification of pristine CNTs could influence their electrical conductivity and electrochemical properties [10–14]. Meanwhile, such treatments for tailoring CNT thermal conductivity hold great potential for realizing thermally-anisotropic/graded nanocomposites [15]. Nitrogen is considered to be an excellent dopant, since it has roughly the same atomic size as that of carbon. And nitrogen-doped CNTs have attracted considerable attention due to the possibility to tailor and improve the physical and chemical properties of pure CNTs [16]. Several methods have been devoted to synthesize and study the nitrogen-doped CNTs focusing on their electrical, electronic and catalytic properties [10,11,17,18]. Currently, only a few studies investigate the influence of nitrogen doping on thermal conductivity of CNTs. Chien et al. [8] used non-equilibrium molecular dynamics simulation to calculate the thermal conductivity of nitrogen-doped CNTs. It was found that the thermal conductivity depends on geometric variations of doped nitrogen and temperature. Li et al. [15] systematically investigated the effects of different surface chemical modification on thermal conductivity of nitrogen-doped CNTs film, un-doped CNTs film and their nanocomposites. Their results showed that the gradient in thermal conductivity within the nanocomposite allowed for controlled heat transport and temperature distribution. Even though some theoretical models have been developed to predict the effective thermal conductivity of the CNT composites [19], there is still a lack of experimental study with regard to thermal conductivity of nitrogen-doped CNTs. Therefore, developing a straightforward and effective method to analyze the influence of nitrogen doping on thermal conductivity of CNTs is desirable.

In this work, we report a thermal chemical vapor deposition method to synthesize nitrogen-doped CNTs with different nitrogen content. The Fe-supported Y zeolite was used as catalyst and nitrogenous organic compounds were used as carbon source and nitrogen source. Silicone composites containing different CNTs were prepared in order to extract the thermal conductivity of nitrogen-doped CNTs. The thermal conductivities of different nitrogen-doped CNTs were further calculated by comparing our experimental results with theoretical prediction model.

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Additionally, the influence of nitrogen doping on thermal conductivity of CNTs was investigated, the influence mechanism is discussed as well.

2. Experimental

2.1. Preparation of Fe-supported Y zeolite catalyst

Zhang et al. [20] have reported the synthesis of Fe-supported Y zeolite catalyst for synthesis of N-doped CNTs. Some modification has been done in this work. The dealumination treatment of the zeolite was omitted. The Fe-supported Y zeolite catalyst was prepared by direct impregnation with an $Fe(NO_3)_3$ aqueous through ion exchange reaction as follows. 1 g NaY zeolite was added to 56 ml deionized water, and then 100 ml $Fe(NO_3)_3$ aqueous (1 g/ml) was added by dripping slowly under magnetic stirring. The reaction lasted for 5 h under continuous stirring. The resultant mixture was dried in an oven at 80 °C (6 h), and subsequently, the dry sample was calcinated in a muffle furnace at 500 °C for 3 h. The obtained solid was mashed and ground into fine powder, which was the Fe-supported Y zeolite catalyst.

2.2. Synthesis of N-doped CNTs

The above catalyst (2 g) was heated to 800 °C in flowing nitrogen (60 ml/min) and maintained for 30 min, followed by a reaction at the same temperature in flowing stream of different organic matter for 2 h. The obtained black powder was a mixture of as-synthesized CNTs and catalyst. The mixture was reacted with hydrofluoric acid at room temperature for 48 h under magnetic stirring to remove the catalyst. Then it was washed with deionized water until the pH of the wash became neutral and dried at 80 °C for 12 h. The reactants were cyclohexane, triethylamine, diethylamine and ethylene diamine, and the corresponding CNTs were marked as C-CNT, T-CNT, D-CNT and E-CNT, respectively.

2.3. Preparation of different silicone composites

The silicone composites with different CNTs were prepared as follows: the C-CNTs with different volume fraction were mixed with the silicone base by using a planetary mixer/dearator (Mazerustar KK-250S, Kurabo, Japan) for 30 min at room temperature, the silicone composites with different loading C-CNTs were obtained. The silicone composites with different loading of T-CNTs, D-CNTs and E-CNTs were prepared by the same procedure.

2.4. Characterization

The morphology and nitrogen content of different CNTs were analyzed by a field-emission scanning electron microscope (SEM) (S4800, Hitachi, Japan) with an energy dispersion X-ray (EDX) analyzer. The crystal structure of the samples was characterized by X-ray diffractometer (XRD) (D8 Advance, Bruker, Germany) equipped with a copper target and nickel filter. X-ray wavelength used in the analysis was 0.154 nm of CuKa. The Raman spectra of different CNTs were obtained using a laser light with wavelength of 532 nm with a Renishaw inVia Raman microscope. The thermal conductivities of the composites were measured by a thermal conductivity analyzer (C-Therm TCi, C-Therm Technologies Ltd., Canada), which is based upon the modified transient plane source principle. For this measurement, the samples were filled into the mould with a thickness of 2 mm. The uncertainty of this test method is estimated to be within ±1.0%, which is decided by the test instrument. The thermal conductivity of each sample is tested 5 times to obtained average value. The experimental error was obtained through mathematical calculation, that is, the maximum *D*-value between arithmetic mean value and measured value. The temperature of test system was controlled by constant temperature box (Shanghai Boxun Industry & Commerce Co., Ltd.).

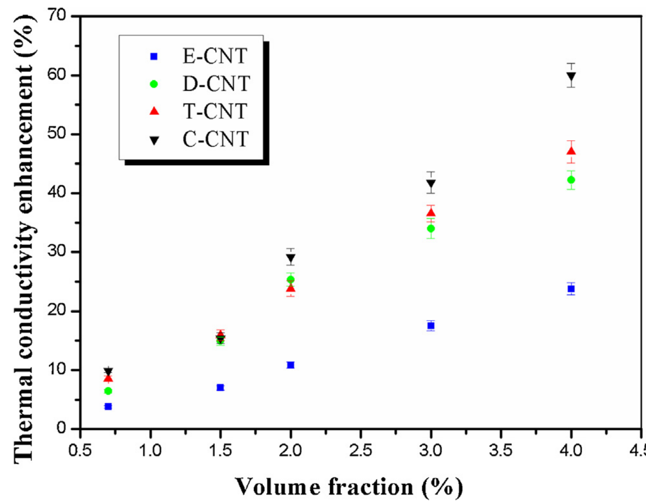

Fig. 1. Thermal conductivity enhancements of silicone composites with different CNTs as a function of volume fraction.

3. Results and discussion

3.1. Thermal conductive property of different silicone composites

Different CNTs were synthesized by using a thermal chemical vapor deposition method. Fe-supported Y zeolite was used as catalyst; organic compounds with different N/C molar ratio were used as reactants. The structural formulas of cyclohexane, triethylamine, diethylamine and ethylene diamine are shown in Table 1. Because of good compatibility of silicone base, the silicone composites containing different CNTs were prepared to deduce the thermal conductivity of nitrogen-doped CNTs. The loading and the inherent thermal conductivity of CNTs have a significant influence on thermal conductivity enhancement of the composites, which is shown in Fig. 1. Compared with the silicone matrix, for all the different nitrogen-doped CNTs, their composites' thermal conductivities improve greatly. When the volume fraction is below 2.0%, the thermal conductivity enhancements of all the composites are not very large. This is because the CNTs surrounded by matrix cannot touch each other at low filler loading, hence, the thermal conductivity increases very slowly resulting from high thermal contact resistance inside the composites [21,22]. As such, the effect of the big difference in thermal conductivity of different CNTs does not appear. Beyond the volume fraction of 2.0%, the CNTs could contact with each other and create thermal conductive pathways resulting in a great improvement in thermal conductivity. The significant influence of inherent thermal conductivity of different CNTs begins to highlight. Compared with the matrix, the thermal conductivity enhancements of its composites with 4.0 vol.% C-CNTs, T-CNTs, D-CNTs and E-CNTs are 60 ± 2.1%, 47 ± 1.9%, 42 ± 1.6% and 23 ± 1.0%, respectively. This indicates that the nitrogen doping has a negative influence on thermal conductivity of CNTs and CNT/silicone composites.

3.2. Calculated thermal conductivities of different nitrogen-doped CNTs

Nan et al. [19] developed a simple theoretical model for predicting the effective thermal conductivity of the CNT composites in terms of an effective medium approach incorporated with the