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LETTER

Thermal and electrical transport properties of a self-organized carbon nanotube pellet

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Carbon nanotubes (CNTs) have a wide variety of applications because of the unique structure and novel properties. Understanding the physical and chemical behaviors of CNTs is critical for the full utilization of their superior properties. Although the scientific communities make great efforts to investigate the properties of CNTs at a scale of one single nanotube level, the properties of CNT-containing structures (CNT bulks and composites) are also of interest because in many application cases these structures are practically useful. Thermal transport properties of CNTs are fundamental for basic science as well as for technological applications. Theoretical and experimental investigations have demonstrated that the thermal conductivity of individual single-/multi- walled CNTs could exceed that of diamond and graphite which have been well known in nature to have superior thermal performance, reaching several thousands W/m K [1–3]. However, CNT bulks, like mats and arrays, only have thermal conductivities of several W/m K and several tens W/m K [4–6]. The thermal transport properties of CNT composite depend very much on the mass fraction and the properties of the matrix materials [7]. In this study we prepare a self-organized multi-walled CNT pellet which is reversibly water-dispersible and further investigate the thermal transport properties of this pellet.

The preparation process involves concentrated acid treatment of CNTs to add hydrophilic functional groups on nanotube surfaces to enhance CNT dispersibility. The average diameter and length of our pristine CNTs are about 15 nm and 30 μm, respectively. CNT pellet was formed by self-organization when the suspension containing functionalized CNTs was heated to remove water. The detailed preparation processes have been described elsewhere [8]. Figure 1 shows SEM images of the as produced pellet. Nanotubes on the surface of the pellet were self-organized into compact domain structures (Fig. 1). Although these domains are in different orientations and appear to be woven, the nanotubes consisting of one domain are in very good alignment (left upper inset of in Fig. 1). Density measurements of the pellet gave a value of about 0.624 g/cm^3. The packing fraction was about 38% if we use an average density of 1.65 /cm^3 for CNTs.

The thermal diffusivity α of the heat-treated CNT pellet was measured by a laser flash technique. The test pellet was fabricated into a circular plate with a diameter d of 10.3 mm and thickness L of 2.0 mm. When the front surface of a test plate is radiated by a laser pulse, the rear face temperature response $T(t)$ is calculated by Parker et al. [9] as:

$$T(t) = \frac{Q}{\rho C_p L}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(\frac{-n^2\pi^2}{L^2}\alpha t\right)\right] \quad (1)$$

where Q is the absorbed energy per unit area, ρ the density, and C_p the specific heat. $T_{\max}$ represents the largest temperature increase after pulse laser heating and $T_{\max} = (Q/\rho C_p L)$. If time-dependent temperature increase $T(t)$ is recorded from the initial laser pulse, the thermal diffusivity of the test sample can be determined by the following formula.

$$\alpha = \frac{0.139L^2}{t_{1/2}} \quad (2)$$

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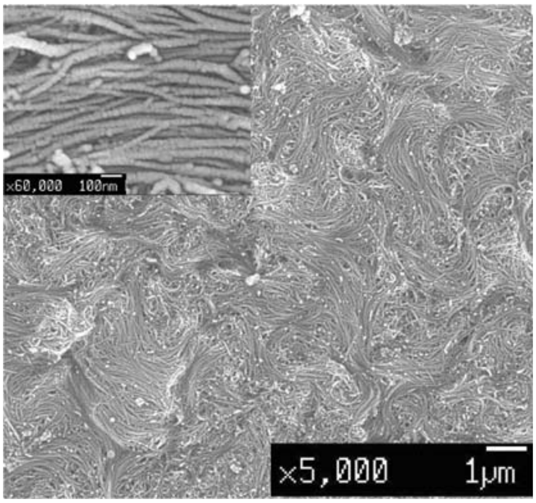

Fig. 1 SEM images of the CNT pellet, upper inset: higher magnification

Where $t_{1/2}$ depicts the time when the temperature increase reaches the half value of $T_{\max}$. In our measurements, a Nb:YAG laser device was used as a radiation source. The laser wavelength is 1064 nm. The test CNT plate was placed in a vacuum furnace and was positioned vertically to the laser beam. The penetration depth of the laser beam into the surface of the CNT plate is estimated to be less than 1 μm. The accuracy is estimated to be within ±5%.

Figure 2 presents the thermal diffusivity of the CNT pellet from room temperature to 700 °C. It is observed that the thermal diffusivity decreases with an increase in the temperature, from 3.63 mm^2/s at 27 °C to 2.59 mm^2/s at 700 °C.

The specific heat of the CNTs from room temperature to 700 °C was measured by Perkin–Elmer DSC-2C. A piece of the CNTs was milled into powder, and then the CNT powder was pressed into a plate with a diameter of 6.0 mm and thickness of 0.8 mm. Sapphire was used as reference material. The differences of the measured data and the recommended values are within ±2% in the tested temperature range. The measured temperature-dependent specific heats are shown in Fig. 3. It is seen that the specific heats increase with temperature. Most of the previous studies on the thermal properties of CNTs, including specific heat, only paid attention to their low temperature behaviors. It has been reported that the specific heats are close to graphite at temperatures lower than room temperature [5, 10]. Our measurements from room temperature to 700 °C show similar results.

We further calculated the thermal conductivity of this CNT pellet by using the correlation of $\lambda = \alpha \rho C_p$. The density of this CNT pellet is decreased to 0.510 g/cm^3 after removing surface oxidation residue by heat treatment at 1100 °C for 1 h. Figure 4 represents the calculated thermal conductivity of this CNT pellet as a function of temperature from room temperature to 700 °C. Two observations can be made from Fig. 4. Firstly, the thermal conductivity increases with temperature and tends to reach a maximal value at about 800 °C. This tendency is very different from previous measurements of a single suspended CNT [2] and CNT bundle [3], in which the thermal conductivity has been measured to have an asymptote near 50 °C. For highly aligned single walled CNTs (SWNTs), it has been reported that the thermal conductivity shows a crossover dependency near 130 °C [11]. Second observation is that the measured thermal conductivity is low compared to the theoretical calculation and previous measurements. Berber et al. [1] theoretically predicted a thermal conductivity of 6600 W/m K for single-walled carbon nanotube at room temperature. Many measurements have given thermal conductivity values from several tens to hundreds W/m K for CNT mats and bundles [4–6]. Experiments conducted by Hone et al. [4] led to a thermal conductivity of 2.3 W/m K for a sintered CNT mat, which is very close to our result. It is worth noting that in our measurement heat flows perpendicularly from the front surface to the rear surface of

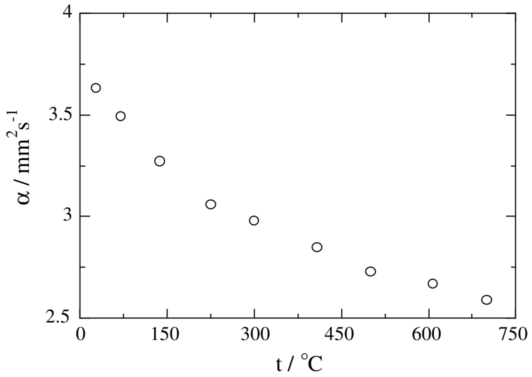

Fig. 2 Thermal diffusivity of the CNT pellet

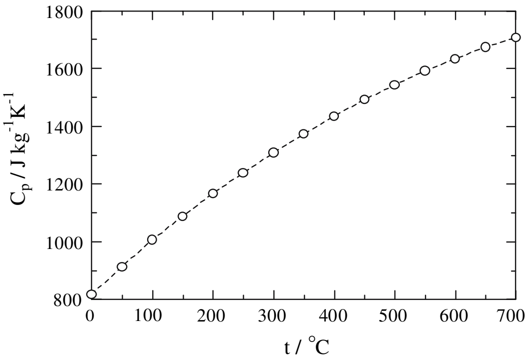

Fig. 3 Specific heat of the CNT pellet

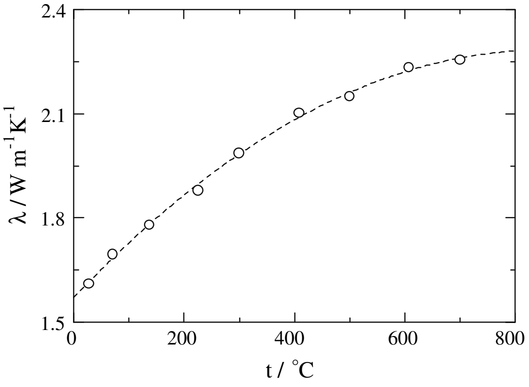

Fig. 4 Thermal conductivity of the CNT pellet

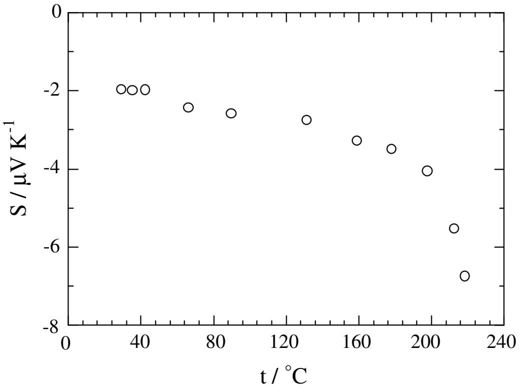

Fig. 6 Thermoelectric power of the CNT pellet

the test pellet. The thermal conductivity is along the direction vertical to CNT alignment direction. CNT walls have similar structures to graphene sheet and the thermal conductivity of CNTs shows greatly anisotropic behavior. Heat transports substantially quicker through axial direction than through radial direction [12]. Furthermore, there exist numerous pores among different domains and surface-surface boundaries even in a well-aligned domain. These pores and boundaries increase the thermal resistance inside the CNT pellet. Therefore the obtained low thermal conductivity is reasonable.

The electrical conductivity σ was determined by four-point measurements. Figure 5 shows the electrical conductivity of the CNT pellet from room temperature to 200 °C. It is seen that in the test temperature range the electrical conductivity increases nearly linearly with the temperature. This positive $d\sigma/dt$ relation is consistent with previous measurements for vacuum-annealed sample in this temperature range [13]. Our experimental data are about two orders of magnitude smaller than the values obtained by Hone et al. [11]. We ascribe this large discrepancy to the dominant tube-tube contact resistance. By comparing the thermal and electrical conductivities of a material, the electronic contribution to the thermal conductivity can be determined. For the CNT pellet, the ratio $\lambda/(\sigma T)$ has a value of 6.5×10^{-6} V^2/K^2 at 300 K, very close to the literature value of 5×10^{-6} V^2/K^2 for CNT mats [11]. This value is more than two orders of magnitude greater than the value expected for electrons, indicating that λ is dominated by phonons.

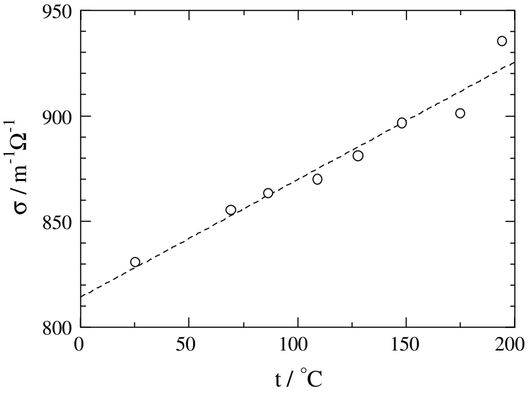

Fig. 5 Electrical conductivity of the CNT pellet

The thermo-electrical power (TEP) was measured by applying a temperature difference at the two surfaces of the CNT pellet. The temperature-dependent TEPs from room temperature to 200 °C are presented in Fig. 6. It is observed that the TEP has a negative sign in the test temperature range and the absolute values increase with an increase in temperature. The absolute value of the slope increases substantially when the temperature is higher than 160 °C. Although this temperature dependence of TEP is similar to that in highly oriented pyrolytic graphite (HOPG) [14], our measurements show very different TEP behaviors from the previous studies, in which the TEPs have positive sign and have values of about 20 μV/K for CNTs [4, 14]. We assume that the majority carriers in the heat-treated CNT pellet are n-type. However, further clarification needs to be done in more detail in future work.

In summary, a reversibly dispersible pellet consisting of self organized and highly aligned CNTs has been produced by heating and dehydrating an aqueous suspension containing hydrophilic CNTs. Due to porous characteristics and boundary resistance, the thermal and electrical conductivities of the heated pellet are much smaller than expected. The experimental results of thermal and electrical transport properties revealed that this self-assembled CNT pellet would possess intriguing features.

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