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Highly oriented carbon nanotube papers made of aligned carbon nanotubes

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Abstract
Paper-like carbon nanotube (CNT) materials have many important applications such as in catalysts, in filtration, actuators, capacitor or battery electrodes, and so on. Up to now, the most popular way of preparing buckypapers has involved the procedures of dispersion and filtration of a suspension of CNTs. In this work, we present a simple and effective macroscopic manipulation of aligned CNT arrays called 'domino pushing' in the preparation of the aligned thick buckypapers with large areas. This simple method can efficiently ensure that most of the CNTs are well aligned tightly in the buckypaper. The initial measurements indicate that these buckypapers have better performance on thermal and electrical conductance. These buckypapers with controllable structure also have many potential applications, including supercapacitor electrodes.

1. Introduction

Carbon nanotubes (CNTs) have attracted significant attention due to their unique combination of thermal, electrical and mechanical properties. Macroscopic forms of CNTs such as arrays, yarns, fibres and films, have been reported and have made the macroscopic manipulation of CNTs feasible for broad applications [1–10]. Carbon nanotube paper, which is a paper-like CNT film, also called buckypaper, is expected to have the same properties as CNTs. Buckypapers and their composites have become a hot topic in CNT research and have been widely reported recently [11–20]. The intrinsic properties of thick buckypapers make them very useful in a broad field including as catalysts and in filtration, actuators, capacitor or battery electrodes, thermal and electrical conductive materials, and so on. In this work, high-quality buckypapers are *in situ* made of aligned CNTs. These buckypapers presented good performance in thermal conductivity, electrical conductivity and capacitance.

Up to now, the most popular way of preparing buckypapers has involved the procedures of dispersion and filtration of suspensions of CNTs [11–20]. Recently, flexible buckypaper composed of a double-walled carbon nanotube (DWNT) has been reported [16, 17]. A property study indicated that the thermal conductivity of a single-walled carbon nanotube (SWNT) film could reach 83 W m^{-1} K^{-1} at room temperature [10]. However, the properties of buckypaper are still not as good as those of individual CNTs. An important reason for this is that the CNTs are not straight in the buckypaper. The crookedness and agglomeration of the CNTs can remarkably reduce the mechanical strength [21] and the thermal conductivity [22] of the buckypapers. The ideal structure of buckypapers should have the following characteristics: the CNTs should be long and straight in the buckypaper and all the CNTs connected with others to form a network structure. Furthermore, alignment of the CNTs in the buckypapers can lead to better thermal and electrical conductive properties. The aligned CNT film which was achieved previously by filtering a suspension in a strong magnetic field showed significant enhancements in thermal and electrical conductivity [9]. However, the effect of the magnetic alignment is limited and cannot solve the crookedness and agglomeration problems of CNTs. The high magnetic field also makes the broad application of this method inconvenient. It will be a great improvement if high-quality buckypapers can be fabricated in a simple and effective way.

In this work, we present a simple and effective macroscopic manipulation of aligned CNT arrays called 'domino pushing'. This is a 'dry' and *in situ* method for the preparation of the aligned thick buckypapers with large areas.

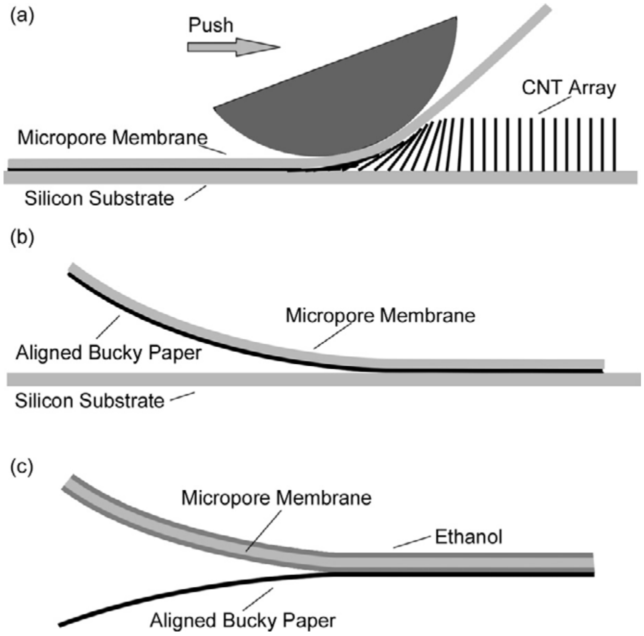

Figure 1. Schematics of the domino pushing method. (a) Forming aligned buckypaper. (b) Peel the buckypaper off from the silicon substrate. (c) Peel the buckypaper off from the microporous membrane.

This simple method can efficiently ensure most of the CNTs are well aligned tightly in the buckypaper.

2. Experimental details

The aligned CNT arrays used in this work were fabricated by a chemical vapour deposition (CVD) method [1] in our lab. Multi-walled carbon nanotube (MWNT) arrays of large area (round diameter 10 cm) and thickness (above 100 μm) can be volume-produced by this method [6]. All CNTs in the aligned CNT arrays are considered to be long and extend from the bottom to the top, forming a thick CNT forest standing on the silicon substrate. Obviously, aligned CNT arrays are good raw materials for preparing the buckypapers with the ideal structure.

The 'domino pushing' method for preparing aligned buckypaper is illustrated in figure 1. The method comprises the following three steps.

(a) Cover the CNT array with a piece of microporous membrane and force all the CNTs of the CNT array down to one direction by pushing a cylinder which is placed upon the CNT array with constant pressure. All CNTs in the CNT array are attracted together due to strong van der Waals forces and form an aligned buckypaper.
(b) The aligned buckypaper can be easily peeled off from the silicon substrate with the membrane.
(c) Ethanol is spread on the microporous membrane and permeates through the membrane, then the aligned buckypaper can be peeled off from the membrane easily.

Measurements of thermal conductivity around room temperature were carried out using an apparatus (figure 2(a)) designed according to a self-heating method.

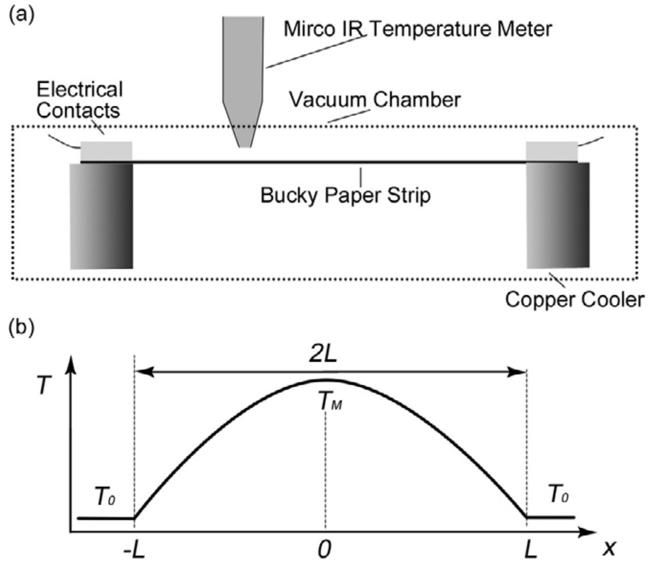

Figure 2. (a) Schematic drawing of the apparatus for thermal conductivity measurements. (b) The temperature distributing on the buckypaper strip while self-heating.

The buckypaper strip sample was $2L$ in length, w in width and t in thickness. The sample was suspended across two copper coolers which can maintain the temperature at T_0. The electrical contacts to the sample were made with silver paste which is also an efficient heat sink and could help to maintain the temperature of the strip edge at T_0. When the temperature rise is not high (below 40 °C in this study), the sample was almost uniformly heated by electricity with total power $P = UI$. The buckypaper strip can be considered as a one-dimensional problem because the length of the strip is much longer than the width and thickness. From the thermal flow theory, we can write the equation as

$$\frac{\partial^2 T}{\partial x^2} + \frac{\phi}{k} = 0 \tag{1}$$

$$\phi = \frac{P}{2Lwt} \tag{2}$$

where ϕ is the thermal flow at one point and k is the thermal conductivity of the buckypaper.

From these equations, the temperature distribution of the strip can be expressed as

$$T_x = T_0 + \frac{P}{4Lwtk}(L^2 - x^2). \tag{3}$$

Its curve is a parabola as shown in figure 2(b) which has a maximum temperature T_M in the middle. If we measure the temperature T_M at the middle of the strip, the thermal conductivity of the buckypaper can be obtained by

$$k = \frac{PL}{4wt(T_M - T_0)}. \tag{4}$$

In this study, the buckypaper strip sample was 5 cm long and 0.5 cm wide. The thermal conductivity measurements were made in a vacuum chamber with a vacuum degree of 10^{-2} Torr. The measurement system was calibrated by measuring the thermal conductivity of the carbon fibre with a known value of ~300 W m^{-1} K^{-1}. The measured value was 321 W m^{-1} K^{-1}. The deviation was less than 10%.

Measurements of electrical conductivity were carried out using a two-point method. The measurements below room temperature were done in a vacuum jacketed flask with liquid nitrogen. The measurements above room temperature were done on a heating station.

The supercapacitors made with buckypaper electrodes were assembled with a structure similar to the literature [23, 24] using an electrolyte of 6 mol l^{-1} KOH. Each electrode was a round buckypaper (diameter 1 cm) and the mass was about 2 mg. Capacitance measurements were carried out using a galvanostatic charge–discharge method with an EG&G potentiostat/galvanostat model 273A.

Scanning electron microscopy (SEM; Sirion 200) and high-resolution transmission electron microscopy (HRTEM; Tecnai G2 F20 S-Twin) were used for the microstructure characterizations. The resolutions of the microscopes were 1.0 nm and 0.24 nm, respectively.

3. Results and discussion

3.1. Structure of buckypapers

Figure 3(a) is a photograph of a typical round (diameter 10 cm) aligned buckypaper as prepared by the 'domino pushing' method. The surface of the buckypaper is very smooth. Figure 3(b) shows a pile of such buckypapers. Figure 3(c) is a swan folded with the buckypaper which is very flexible. The micrographs of the MWNT array and the buckypapers were probed by SEM and are shown in figure 4. Figure 4(a) is a typical side view of a raw CNT array about 500 μm high. The inset of figure 4(a) demonstrates a HRTEM image of an individual MWNT with a diameter of about 15 nm. Figure 4(b) is the typical micrograph of an aligned buckypaper surface, which confirms that the CNTs are well aligned in the buckypaper and the density is much higher than that of a raw CNT array. Figure 4(c) is a higher-magnification image of figure 4(b). We can clearly see that the CNT tips were pushed down one by one, confirming the validity of our domino pushing method. The surface roughness value estimated by SEM was less than 100 nm.

In addition, a floccule-like MWNT suspension can be obtained through an ultrasonic procedure using the MWNT array as source material. Unlike the conventional CNT powders, in which CNTs are usually self-entangled and agglomerated, the CNTs from these aligned arrays tend to maintain their straight morphology in the suspension. Random buckypaper can also be obtained by filtering the suspension using the conventional method. It is noticeable that no surfactant was used in the procedures so that high-purity buckypaper can be obtained. Figures 4(d) shows a micrograph of the random buckypaper surface. Cross linkages of straight CNT bundles can be observed, which ensure a high mechanical strength according to our ideal structure. This indicates that aligned CNT arrays are good raw materials for fabricating both aligned and random buckypapers.

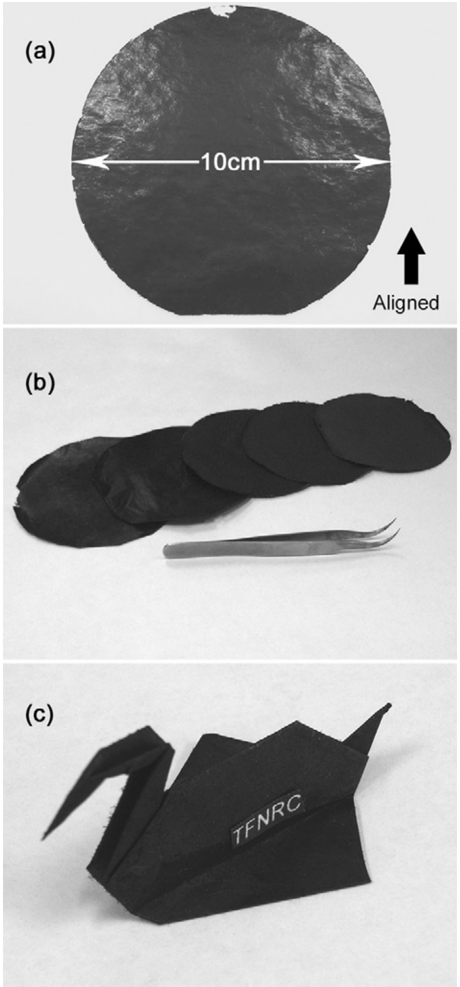

Figure 3. (a) Image of a round (diameter 10 cm) aligned buckypaper. (b) A pile of buckypapers. (c) A swan folded with the flexible buckypaper.

We compared aligned buckypaper and random buckypaper made from the two halves of a round (diameter 10 cm) MWNT array, respectively. The MWNT array was about 500 μm thick and 126.8 mg in weight. The density of the MWNT array was about 0.032 g cm^{-3}. The two buckypapers were made with equal proportions. The thicknesses of the buckypapers measured by screw micrometer were typically 26 μm for aligned buckypaper and 30 μm for random buckypaper. The densities of aligned and random buckypapers can be calculated separately as 0.62 and 0.54 g cm^{-3}. We can see that the density of the random buckypaper is notably less than that of the aligned buckypaper. There is a simple equation shows the relationship between the thickness and the density:

$$\frac{t_{\text{buckypaper}}}{t_{\text{array}}} = \frac{\rho_{\text{array}}}{\rho_{\text{buckypaper}}} \tag{5}$$

where $t_{\text{buckypaper}}$ and t_{array} are the thicknesses of aligned buckypaper and CNT array, respectively; $\rho_{\text{buckypaper}}$ and ρ_{array} are the densities of aligned buckypaper and CNT array, respectively. In this study, the density of aligned buckypaper is about 20 times larger than that of the CNT array. Thus, we can

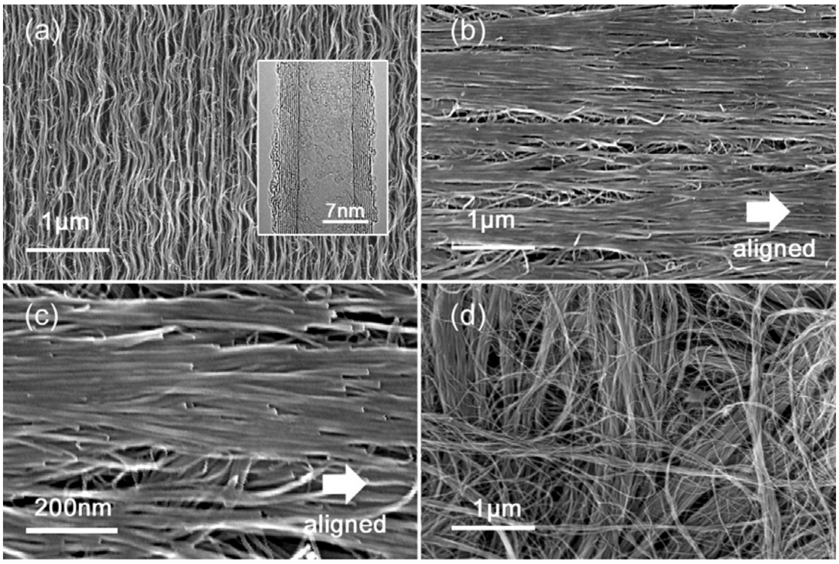

Figure 4. SEM images of a CNT array and buckypaper. (a) Side view of an aligned MWNT array. The inset is a HRTEM image showing the individual CNT structure. (b) Micrograph of an aligned buckypaper surface. (c) Higher magnification image of (b). (d) Micrograph of a random buckypaper surface.

compress the thickness of the CNT array from 500 to 26 μm by using the 'domino pushing' method about 20 times.

3.2. Thermal conductivity measurements

According to the molecular dynamics theory, CNTs have an extremely high thermal conductivity in the axis direction. For a SWNT at room temperature, the value can reach 6600 W m^{-1} K^{-1} [25]. Experimental values for both SWNTs and MWNTs were also as high as 3000 W m^{-1} K^{-1} at room temperature [26, 27]. The high thermal conductivity makes CNTs an ideal candidate for thermal interface material (TIM). Enhancement of thermal conductivity by loading CNTs in composites have been reported in recent works [22, 28, 29]. For pure CNT films the thermal conductivities were in the range of 20–200 W m^{-1} K^{-1} at room temperature [9, 10, 15].

For the aligned buckypaper the measurements were conducted in both directions parallel and perpendicular to the alignment. A higher thermal conductivity 153 W m^{-1} K^{-1} was obtained for the parallel buckypaper sample. A value of 200 W m^{-1} K^{-1} for aligned CNT film had been reported previously [9]. However, that result was a conversion thermal conductivity where the nominal thickness was estimated by the ideal specific density 1.33 g cm^{-3} for SWNTs. As for the MWNTs in this study, the ideal specific density should be slightly larger than that of SWNTs. If we assume the ideal specific density of MWNTs is 1.34 g cm^{-3}, then the effective thermal conductivity of this parallel buckypaper was 331 W m^{-1} K^{-1}, which is much better than the previously reported values. This value is higher than that of the aluminium, and close to that of copper. Although the effective thermal conductivity is only the ideal thermal conductivity of the parallel buckypaper, it denotes the potential value when the buckypaper is pressed thinner with a higher stress. Now, the specific density of these manually pressed buckypapers is about 0.6 g cm^{-3}, only about half of the ideal value 1.34 g cm^{-3}.

Anyway, the thermal conductivity of the buckypaper is still one order of magnitude lower than that of single CNT. On the one hand, the interfacial thermal resistance between CNTs, also called Kapitza resistance, may remarkably reduce the thermal conductivity of the buckypaper [30, 31]; on the other hand, the thermal conductivity of an individual CNT in the buckypapers may become practically lower owing to defects associated with the CVD growth method [32]. The thermal conductivity in the cross direction to the alignment was 72 W m^{-1} K^{-1}. The anisotropy ratio of the parallel thermal conductivity to the cross thermal conductivity for the aligned buckypaper is 2.1, which proves the effect of alignment in the buckypaper. The thermal conductivity of the random sample was 81 W m^{-1} K^{-1}, which is much lower than that of the aligned sample. Lower density and random orientation might be two factors that account for its lower thermal conductivity.

3.3. Electrical conductivity measurements

These pure buckypapers are also good electrical conductors. The measured electrical conductivity of the parallel buckypaper sample was 2.0×10^4 S m^{-1} at room temperature. This electrical conductivity is much better than the reported value for a MWNT array in the parallel direction and as good as the effective value of MWNT array when considering the volume fraction of the CNTs in the MWNT array [32]. The electrical conductivity of the buckypaper is strongly temperature dependent. Figure 5 typically shows the temperature dependence of the normalized resistance R for the parallel buckypaper sample from 200 to 450 K. The result shows a nonmetallic behaviour over the entire range, and the curve is roughly linear in the equation

$$\frac{R}{R_0} = 1.152\text{–}5.587 \times 10^{-4}\ \mathrm{T} \tag{6}$$

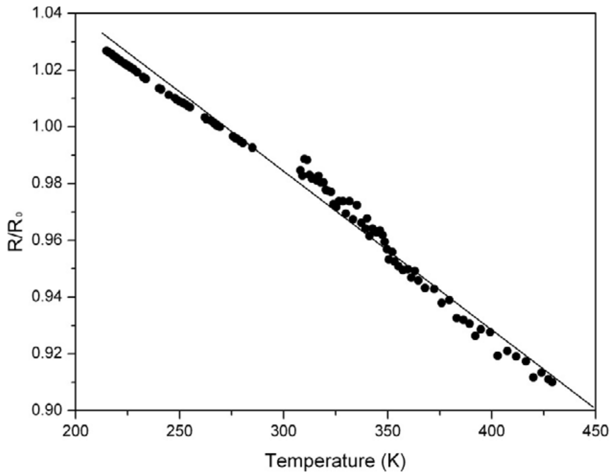

Figure 5. Variation of the resistance of a parallel buckypaper sample versus temperature, R is normalized to R_0 at 273 K.

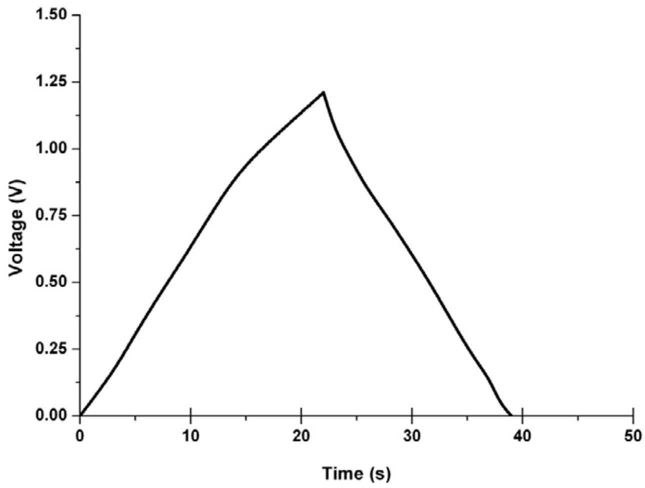

Figure 6. Galvanostatic charge–discharge ($I = 3$ mA) curve of the capacitor built with aligned buckypapers.

where R_0 is the resistance at 273 K. The electrical conductivity in the cross direction to the alignment was 1.1×10^4 S m^{-1}. The anisotropy of electrical conductivity is 1.9 for the aligned buckypaper, which also shows certain electrical enhancement by aligning the CNTs. The electrical conductivity of the random sample was 1.5×10^4 S m^{-1}. This is slightly lower than the value of the parallel sample. The electrical conductivities of these pure buckypapers are usually several orders of magnitude higher than that of these CNT composites [28, 29] which make these pure buckypapers a good candidate for electrode materials.

By measuring the thermal and electrical conductivities of the buckypaper, the contribution to the thermal conductivity can be evaluated. The value of $k_{\parallel}/\sigma_{\parallel}T$ was about 2.6×10^{-5} V^2 K^{-2}, three orders of magnitude greater than the value of the Lorenz number, confirming that the thermal conduction in CNTs is dominated mostly by phonons.

3.4. Capacitance measurements

One important application of CNTs is as supercapacitor electrode materials. Supercapacitors, also called electric double-layer capacitors, attract significant attention for their high power energy storage and long cycle life. Due to the stable structure and huge surface area of CNTs, CNT composites have shown good performance as capacitor electrodes [23, 24, 33–35].

In this study, the supercapacitors were assembled with the buckypaper electrodes and their capacitances were measured by the galvanostatic charge–discharge method. The galvanostatic charge–discharge curve for the supercapacitor made with the aligned buckypaper electrodes is shown in figure 6. The galvanostatic discharge characteristics in the range from 1.2 to 0 V was taken to calculate the capacitance. The specific capacitance for each aligned buckypaper electrode was 81.0 F g^{-1}. By comparison, the specific capacitance for each random buckypaper electrode was 87.5 F g^{-1}. The higher value of the random buckypaper is in accordance with its porous structure and larger surface area. Anyway, all these pure buckypapers have shown better performance and potential application as capacitor electrodes [36].

4. Conclusions

In summary, high-quality flexible thick buckypapers were fabricated by using aligned CNT arrays as source materials. High alignment of CNTs in the buckypaper can be realized by a simple and effective method called 'domino pushing'. Unlike the conventional buckypapers, in which CNT source materials are usually self-entangled and agglomerated, the CNTs in these buckypapers tend to maintain their straight morphology. These buckypapers have shown better performance in thermal and electrical conductance. These buckypapers with controllable structure have also many potential applications including supercapacitor electrodes.

Acknowledgments

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