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Percolation of two-dimensional multiwall carbon nanotube networks

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We highlight the significance of multiwall carbon nanotube (MWCNT) shape on the electrical percolation. For rodlike MWCNTs, percolation threshold depends on aspect ratio (L/d). For random coil-like MWCNTs, the percolation threshold does not depend on L/d but depends on the shape factor of MWCNTs represented by the ratio between static bending persistence length and diameter. Surface resistivities of various MWCNTs converge into single curve when we plot their dimensionless surface concentration versus surface resistivity. The surface resistivity of MWCNT films decrease with increasing temperature, particularly at low concentrations, indicating the films can be used as a negative temperature coefficient thermistor. © *2009 American Institute of Physics*. [doi:10.1063/1.3238326]

Two[1–3] or three[4–19] dimensional carbon nanotube (CNT) networks are attracting attention both in academic and industrial fields due to their good electrical conductivity with high light transmittance, which are strong candidate materials in applications such as conductive composites,[4–19] transparent electrode for display,[1] and touch panel.[2,3] Electrical conductive networks constructed by single wall CNTs (SWCNTs) generally show better transparency than those made of multiwall CNTs (MWCNTs) by virtue of their smaller diameter.[1–3] In commercial applications, however, MWCNTs have a certain merit due to easy mass production through a chemical vapor deposition method. If the mesoscopic shape of MWCNTs is controlled during synthesis, regular pattern may be applied along the tube axis such as a needlelike shape or springlike coiled shape. In many cases, however, the shape of MWCNTs is tortuous when grown randomly by chemical vapor deposition method.[20,21]

Electrical conductivity of a polymer-CNT hybrid material is achieved by dispersing CNTs into a polymer with higher concentration than percolation threshold in the percolation scaling law.[4–19] The high aspect ratio of CNTs makes electrical conductive hybrid material at lower concentrations compared to conventional carbon black.[19] One would assume that electrical conductivity of CNT hybrid materials or networks strongly depends on the degree of tortuousness as well as the aspect ratio. In order to verify this assumption, we need a quantitative factor which can characterize various CNT shapes. The bending ratio (D_b) is defined as the ratio of the mean square end-to-end distance ($\langle R^2 \rangle$) and the square contour length (L^2).[20]

$$D_b \equiv \frac{\langle R^2 \rangle}{L^2}. \tag{1}$$

Equation (2) gives the relationship between the mesoscopic shape and the overall size.[20–23]

$$\langle R^2 \rangle = 2l_{sp}L + 2l_{sp}^2(e^{-L/l_{sp}} - 1), \tag{2}$$

where l_{sp} is the static bending persistence length (maximum straight length that is not bent by a permanent structural deformation) and L is contour length along the tube axis. When $L \gg l_{sp}$, the rigid random-coil limit, $\langle R^2 \rangle = 2l_{sp}L$. When $L < l_{sp}$, the rigid rod limit, $\langle R^2 \rangle = L^2$.

The purpose of this work is to discover the relationship between shape and surface resistivity in two-dimensional MWCNTs networks. We obtained four groups of MWCNTs from various sources[24] which are designated as MWCNT1, MWCNT2, MWCNT3, and MWCNT4. In order to fabricate the MWCNT networks, following procedure was applied to each group. 200 mg of MWCNTs and 20 ml of ethanol were placed into a zirconia pot (150 ml) and ball milled using 28 zirconia balls with diameter of 5 mm at 500 rpm for 2 h. The ball-milled MWCNTs solution from the zirconia pot was poured into a 50 ml conical centrifuge tube and centrifuged to isolate the MWCNTs. The MWCNTs were then freeze dried for 24 h. The MWCNTs were then baked at 300 °C for 30 min in air to remove impurities and then ground by mortar and pestle. 10 mg of the MWCNTs were dissolved in 50 ml of dimethyl formamide (DMF) and then the solution was sonicated for 2 h at 50 °C using a bath-type sonicator operating at 45 KHz. The solution was then centrifuged for 20 min at 5000 rpm. 10 ml of supernant was extracted and then diluted with an additional 40 ml of DMF. Diluted solution in volumes of 1, 3, 5, 7, 10, 15, 20, 25, 30, and 35 ml was dropped onto the substrate (Anodisc 20 nm, diameter of 47 mm) and then filtered. MWCNT1, treated by the above procedure is designated as M1, MWCNT2 as M2, MWCNT3 as M3, and MWCNT4 as M4, respectively. The buckypaper obtained was dried at 160 °C for 4 h in the dry oven in order

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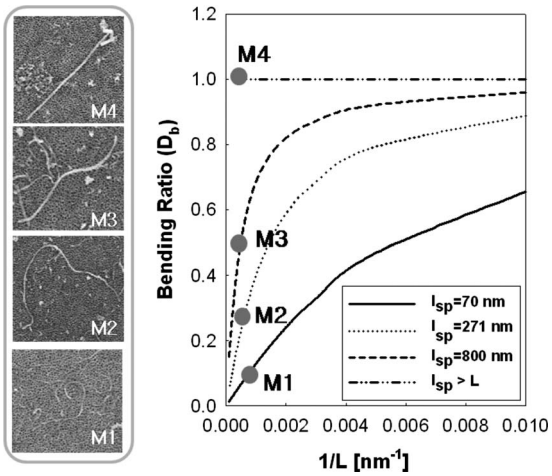

FIG. 1. Mesoscopic shape of MWCNTs. SEM image shows the representative shape of M1, M2, M3, and M4. M1 and M2 meet the rigid random-coil limit. M4 meets the rigid rod limit. M3 is in the intermediate range. Lines are obtained by Eqs. (1) and (2).

to evaporate DMF which was used for CNT dispersion. Then, the surface resistance of the CNT film was measured by the "Van der Pauw" method using an electrical analysis system (Model 2400, Keithly). To observe the dependency of electrical conductivity on the thermal energy, the CNT film surface resistance was measured on a hot plate (MSH-20D, Wisestir Inc.). The characteristics of M1, M2, M3, and M4 have been evaluated as follows:[20] static bending persistence length (l_{sp}) of M1, M2, M3, and M4 was 70, 271, 800, and >3000, respectively. Outer diameter of M1, M2, M3, and M4 was 9.5, 21, 35, and 50 nm, respectively. Weight averaged contour length (L) of M1, M2, M3, and M4 was 1416, 1718, 2045, and 2035 nm, respectively.

M1 and M2 meet the rigid random coil limit $L \gg l_{sp}$, showing tortuous shape as seen in Fig. 1. M3 is in intermediate range between rigid random-coil limit and rigid rod limit and M4 meets rigid rod limit, $l_{sp} \gg L$, showing needle-like shape in Fig. 1.

Figure 2 shows scanning electron microscopy (SEM) images and schematic illustrations for MWCNT two-dimensional networks. The area inside the circle depicted in Fig. 2 is designated as a cell in this work. For a rigid random coil M1, the area of cell scales with R^2 as depicted in Fig. 2. For a rigid rod M4, the area of cell scales with L^2 as depicted in Fig. 2. For both cases, the area of cell depends on $D_b L^2$ according to Eq. (1). The mass of single MWCNT in the cell depends on $d^2 \rho L$, where d is the average outer diameter of

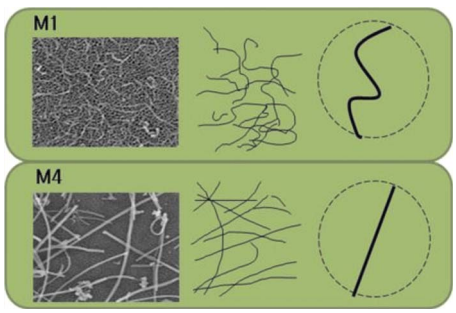

FIG. 2. (Color online) MWCNTs networks on the porous substrate. Network made of rigid random coil (M1) and rigid rod (M4). Area inside the drawn circle is defined as the cell area where single MWCNT is located.

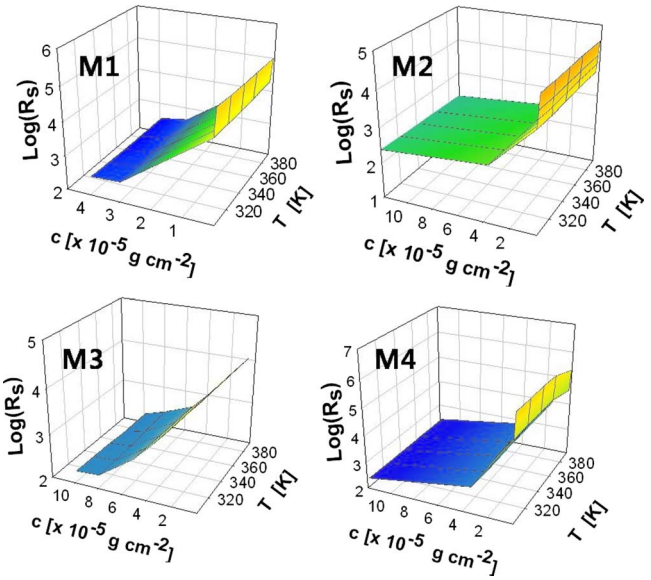

FIG. 3. (Color online) Effect of surface concentration and temperature on the surface resistivities of various MWCNT networks.

MWCNTs and ρ is the density of MWCNT. Assuming the substrate surface on which MWCNTs lay consisted of N cells and each cell had been occupied by a single MWCNT, a fully occupied concentration (c_m) could be defined as $(d^2\rho)/(D_b L)$ with unit of (g/cm^2).

We have measured surface resistance of two-dimensional networks in various surface concentration range and temperatures from 303 to 393 K. Figure 3 shows surface resistivity with respect to concentration and temperature. The percolation scaling behavior is observed for four groups of MWCNTs which are designated as M1, M2, M3, and M4 in Fig. 3. An interesting result is that surface resistivity decreases with increasing temperature for all groups of MWCNTs, particularly at low concentrations. For M3 network at 1.23×10^{-6} g/cm^2, surface resistivity reduces from 1.2×10^7 to 3.1×10^6 Ω/square in Fig. 3. This result indicates that a transparent MWCNT film can be used as a negative temperature coefficient (NTC) thermistor sensor.

Figure 4(a) shows the change in surface resistivity with increasing dimensionless concentration for M1, M2, M3, and M4 measured at 303 K. Dimensionless concentration (c^*) is obtained by the surface concentration (c) divided by the fully occupied concentration (c_m) such as $c^* = (cD_bL)/(\rho d^2)$,

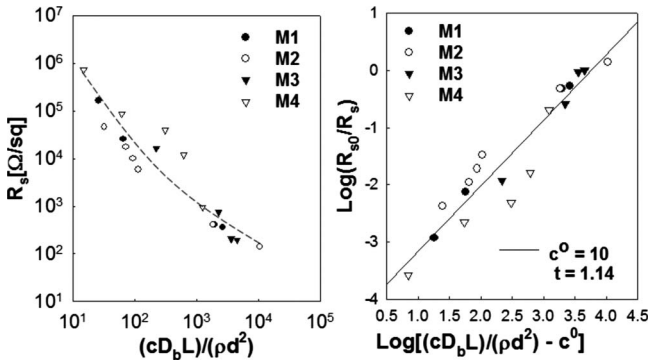

FIG. 4. Surface resistivity of MWCNTs networks with respect to the dimensionless surface concentration. (a) Surface resistivities of networks made from groups M1, M2, M3, and M4. (b) Percolation scaling law fitting.

where c is mass of MWCNT on unit surface area of substrate. The percolation scaling law[25] can be expressed as $\log(R_{s0}/R_s)=\log(c^*-c^0)^t$. Figures 4(a) and 4(b) show that all data measured from all groups of MWCNTs converge into a single curve when we fit the data using c^* instead of c. The exponent was found to be 1.14, indicating all MWCNT networks exhibit two-dimensional behavior. By fitting all data using c^* as shown in Fig. 4(b), we obtain the following expression for the concentration of percolation threshold (c^p) for any group of MWCNTs.

$$c^p = \frac{10\rho d^2}{D_b L}. \tag{3}$$

Equation (3) has universality for the percolation threshold of any group of MWCNTs. Because M1 and M2 are in the rigid random-coil limit, D_b in Eq. (3) can be replaced by $2l_{sp}/L$. Then, Eq. (3) reduces to $c^p=(5\rho d^2)/l_{sp}$, indicating that c^p depends on l_{sp}/d and d, not depending on L. For a rigid rod M4, bending ratio (D_b) has unit value, thus Eq. (3) reduces to $c^p=(10\rho d^2)/L$, indicating that c^p depends on L/d and d.

In conclusion, various MWCNTs stayed on the same line when we plotted the dimensionless surface concentration versus surface resistivity of MWCNTs networks. The percolation threshold of MWCNTs in rigid random coil conformation does not depend on their contour length, instead, depending on their diameter and mesoscopic shape factor (which is the static bending persistence length). On the contrary, percolation threshold of MWCNTs in rigid rod conformation depends on their contour length as well as diameter. Two-dimensional MWCNT networks exhibit NTC thermister behavior for all groups of MWCNTs studied.

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