

Recent progresses on the new condensed forms of single-walled carbon nanotubes and energy-harvesting devices

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We demonstrate an effective method to prepare a new condensed form of single-walled carbon nanotubes (crystal of SWNTs) using a series of diamond wire drawing dies. X-ray diffraction indicates that the SWNTs form a two-dimensional triangular lattice with a lattice constant of 19.62 Å. An intertube spacing of 3.39 Å of between adjacent SWNTs results in a sharp (002) reflection in the X-ray diffraction pattern. Meanwhile, we developed an approach based on the Coulomb explosion to separate SWNTs from their bundle. The separated SWNTs have a typical length of several microns and form a nanotree at one end of the original bundle. The separation is convenient and involves no surfactant. In studying devices comprising SWNTs, we find that a four-probe technique can be employed to study the filling of and flow within the inner channel of an individual SWNT. Current/voltage can drive water molecules to have directional flow along an SWNT, and the flowing of water inside an SWNT can induce a voltage gradient force (an induced electromotive force) along the SWNT. This energy conversion is realized by the mutual coupling of water dipoles and charge carriers present in SWNTs. The results suggest that SWNTs can be exploited as molecular channels for water and may find potential application in nanoscale energy conversion. Moreover, a surface-energy generator comprising SWNTs was demonstrated to harvest the surface energy of ethanol. The performance (the induction rate for V_{oc} , the value of V_{oc} and the output power) can be significantly enhanced by the Marangoni effect.

single-walled carbon nanotube (SWNT), crystal of SWNT, SWNT tree, energy conversion, surface-energy generator

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Since its discovery by Iijima in 1991, the carbon nanotube has attracted much attention because of its remarkable phenomena related to the nanoscale confinement, which lead to the possibility of developing a wide range of applications of new materials and advanced devices. Many interesting phenomena of single-walled carbon nanotubes (SWNTs), which have smaller diameters than multiwalled nanotubes, have been demonstrated; e.g., the Aharonov-Bohm effect [1], Coulomb blocking effect [2–4], and Josephson effect [5,6]. It is well known that fullerenes have their most interesting properties when in their condensed form [7,8]; e.g., superconductivity in alkali-doped C_{60} . Theoretical works predict that this may also be true for carbon nanotubes

[9,10]. However, in experiments, it is still a great challenge to grow SWNTs with identical diameters and chirality; hence, it is not possible to obtain a crystalline form of SWNTs. A highly densely packed SWNT array (SWNT solid) [11] has been achieved by exploiting the liquid-induced collapse of SWNT forests [12], while high-performance fibers [13] have been obtained by the direct spinning of carbon nanotube fibers [14]. For these two materials, although a peak of (002) was observed in the X-ray diffraction (XRD) pattern, there is diffuse intensity at angles below the (002) peak. This indicates that some of the interlayer spacings are greater than those typical of graphene stacks. Recently, we found that SWNTs form a crystalline structure via the van der Waals force when they are perfectly aligned and ideally densely packed after treating with a series of

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diamond wire drawing dies [15]. This work opens a new research field of the condensed form of SWNTs and possible superconductivity in crystals of SWNT after proper doping.

In this review, we also present another interesting form of SWNTs: a nanotree of SWNTs obtained by Coulomb explosion of their bundle [16]. Furthermore, we also introduce energy-related devices of individual SWNTs and a rope of SWNTs: individual water-filled SWNTs as hydroelectric power converters [17] and a surface-energy generator comprising SWNTs [18], respectively.

1 New condensed form of SWNTs

1.1 Crystal of SWNTs

SWNTs are usually grown using one of three techniques: arc discharge [19], laser ablation [20], or chemical vapor deposition [21]. The SWNTs grown using these methods are a mixture of individual SWNTs with different diameters and chirality. Meanwhile, the SWNTs are usually entangled and poorly ordered. We established an inexpensive and effective method to align SWNTs using a series of diamond wire drawing dies [15]. As shown in Figure 1, during each drawing, the SWNTs form a bundle with the same diameter as that of the die used. The SWNTs produced are gray with a metallic luster.

From scanning electron microscopy (SEM) images of the SWNT bundles, it is seen that the SWNTs fabricated in this way are perfectly aligned and highly densely packed (HDPAs-SWNTs) as shown in Figure 2(a). High-resolution transmission electron microscopy (HRTEM) also reveals the as-fabricated SWNTs have a perfectly aligned microstructure as shown in Figure 2(b). It should be noted that these bundles are composed of dense SWNTs, and the number of SWNTs in each bundle is estimated to be as high as 10^6 . These SWNT materials are clean and free of amorphous carbon.

The XRD pattern of these HDPAs-SWNTs differs from that of untreated SWNTs, as shown in Figure 3(a). At a low angle in the XRD pattern, a strong and discrete peak appears at $2\theta = 5.20^\circ$. This Bragg peak can be indexed to (10) diffraction ($d_{(10)}$ -spacing of 16.97 \AA) for a two-dimensional triangular lattice of SWNTs. Therefore, the lattice

constant, $a = 19.62 \text{ \AA}$, is obtained by the equation $a \times \sqrt{3}/2 = d_{(10)}$ -spacing. The following four relatively broad peaks can be indexed as (11), (20), (30) and (40). Another interesting and important feature of the XRD pattern is that there is a very sharp and strong peak at $2\theta = 26.3^\circ$ corresponding to a d -spacing of 3.39 \AA and lattice constant $a = 19.62 \text{ \AA}$, which is believed to arise from the nearly ideal graphitic packing of SWNTs due to van der Waals interaction. The sharp (002) reflection arises from an intertube spacing of 3.39 \AA for adjacent SWNTs, and it is not observed for individual SWNTs or small crystalline ropes of SWNTs. Therefore, these highly dense and perfectly aligned SWNTs (HDPAs-SWNTs) are a condensed and crystalline form of SWNTs.

The crystal of SWNTs and the as-grown SWNTs film were characterized by micro-Raman spectroscopy with 632 nm laser excitation, as shown in Figure 3(b). In comparison with the as-grown SWNTs, the radial breathing mode of the SWNT crystal changes significantly: the radial breathing mode signals for larger-diameter SWNTs HDPAs-SWNTs are suppressed. This suppression may result from the stronger coupling between the neighboring SWNTs in the crystal of SWNTs, which results from smaller intertube spacing of 3.39 \AA compared with 9 \AA in the SWNT solid [17].

1.2 Nanotree of SWNTs

SWNTs are often entangled with each other and readily form bundles with a large van der Waals binding energy ($\sim 500 \text{ eV}/\mu\text{m}$ of tube-tube contact) [22,23]. This has been a major obstacle for potential applications of SWNTs in nanodevices and nanoelectronic circuits. To overcome this limitation, many researchers have explored selective chemistry to obtain monodispersed SWNTs [24–27]. These chemical approaches have doping effects on SWNTs [28,29], and the obtained individual SWNTs are usually very short. We developed a novel effect of Coulomb charging to separate nanotubes from their bundles, and this simple physical technique should be performed directly on the substrates to avoid chemical modification [16].

Figure 4 is a typical SEM image of an SWNT rope, SWNT bundles, and an SWNT nanotree. The SWNTs mainly separated at one end of an SWNT bundle, and radiated

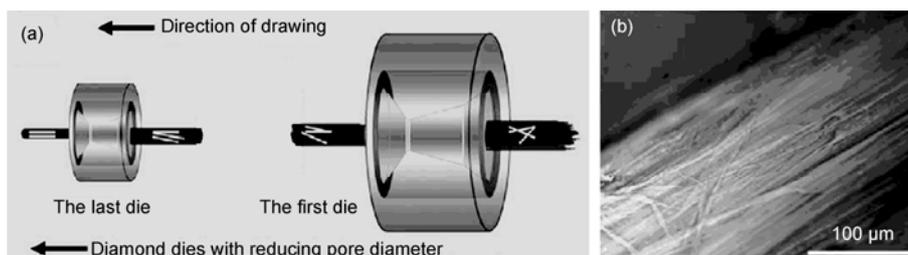


Figure 1 Alignment of SWNTs. (a) Schematic diagram of the diamond wire drawing dies used to align SWNTs. (b) Optical image of SWNTs after treating.

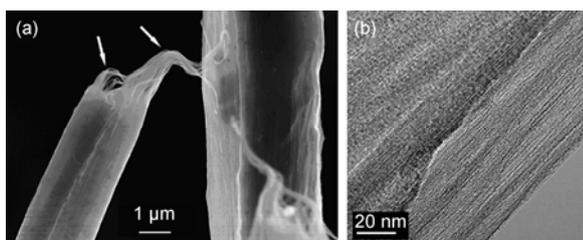


Figure 2 (a) SEM image of two bundles of SWNTs. The good flexibility of SWNTs is shown by the white arrows. (b) HRTEM image of a crystal of SWNTs.

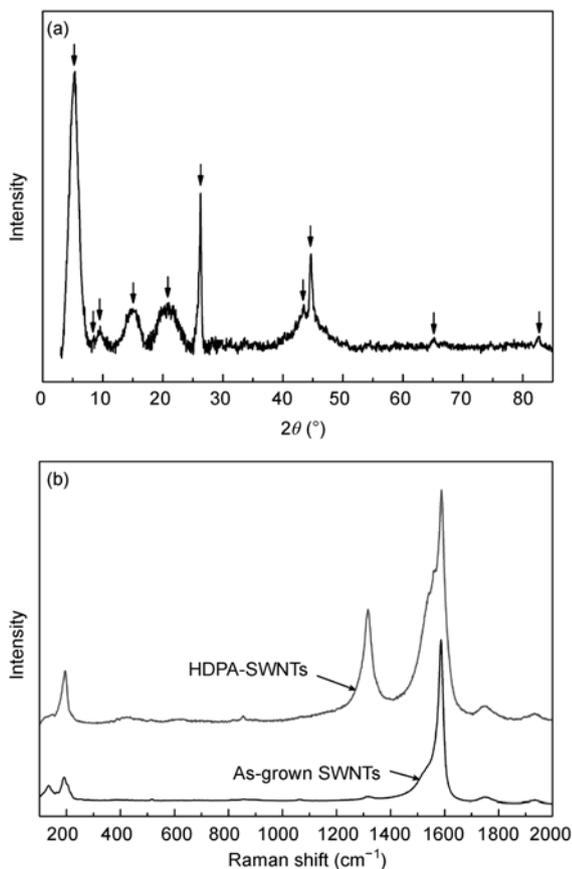


Figure 3 (a) XRD patterns of HDPA-SWNTs after subtraction of the background. (b) Raman spectra of the as-grown SWNTs and the HDPA-SWNTs.

from one center. These isolated SWNTs are relatively straight and separated from each other as far as possible. The mechanism of the formation of these nanotrees is as follows. Before the individual SWNTs are charged, they are linked to each other with van der Waals binding energy. When the SWNTs are positively charged, a Coulomb repulsion and van der Waals force exist simultaneously. As the electrostatic potential increases, the increasing charge induces Coulomb explosion and the separation of SWNTs.

Interestingly, we also observed similar morphologies of SWNTs at breaking points resulting from electrical heating in a vacuum, as shown in Figure 5. After heating with a DC

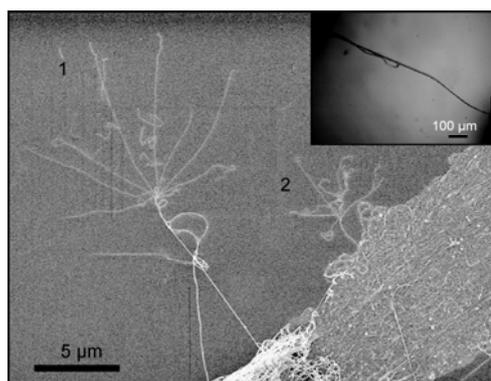


Figure 4 SEM image of two typical nanotrees of SWNTs formed at the ends of two SWNT bundles via Coulomb explosion. The inset is an optical image.

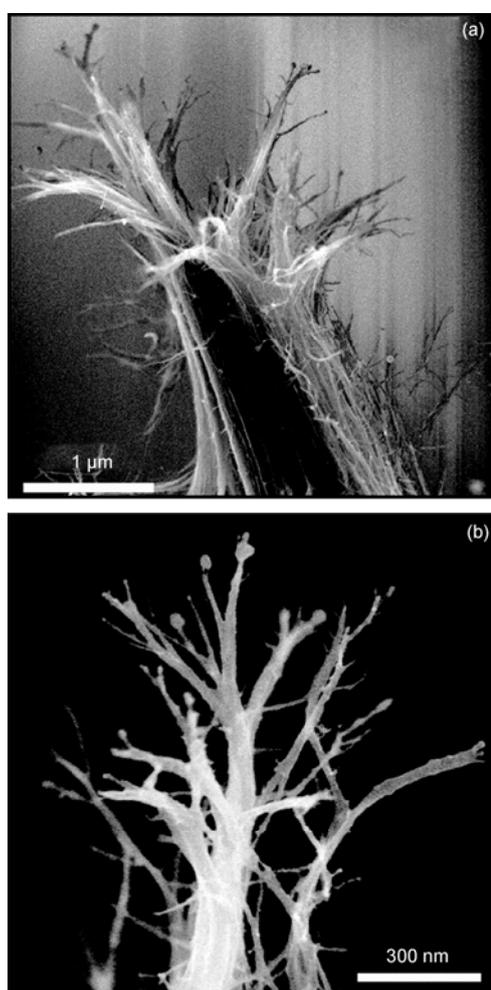


Figure 5 SEM images of typical nanotrees of SWNTs formed at the breaking points of an SWNT bundle.

bias for about 10 min, the SWNT bundle radiated light and finally broke down because of Joule heating. At the tips of the SWNTs tree, there are spheres that are believed to be due to the surface tension produced by the melted carbon and/or catalyst at the breakdown instant [30].

2 Energy transformation devices comprising SWNTs

2.1 Individual water-filled SWNTs as hydroelectric power converters

Water flowing inside/outside SWNTs is a unique nanofluidic system in which the water molecules and the walls of the SWNTs form an intimate interface at the atomic level. It is possible that the coupling between water dipoles and free charge carriers in the nanotubes is mutual [31–34], and a constant current can induce a directional water flow inside the nanotube. We find that a significant voltage difference can be detected at one part of an individual SWNT device when a current is applied at another part of the same SWNT after the device is exposed to water vapor [17], as shown in Figure 6.

The current-voltage characteristics of the device were measured, as shown in Figure 7. In a vacuum, V_1 and V_2 are nonzero and equal to each other. When the device is exposed to water vapor, V_1 and V_2 are no longer equal to each other, and a voltage difference ($\delta V = V_1 - V_2$) is thus measured in the “generator” part of the device. δV has a linear dependence on the current applied to the “motor” part.

2.2 Surface-energy generator comprising SWNTs

Surface energy plays an important role in surface physics, biophysics, surface chemistry, and catalysis [35,36]. A gradient of surface energy between a solid and liquid interface can induce the transport of liquids [37–39]. For low power consumption of nanodevices and high specific surface area of nanomaterials, it is attractive to use the surface energy as an energy source at the nanoscale. We demonstrate an effective design of SWNTs to harvest surface energy of ethanol and convert it into electricity. A rope of SWNTs can be used to study the coupling between liquid outside SWNTs with carriers of SWNTs [18].

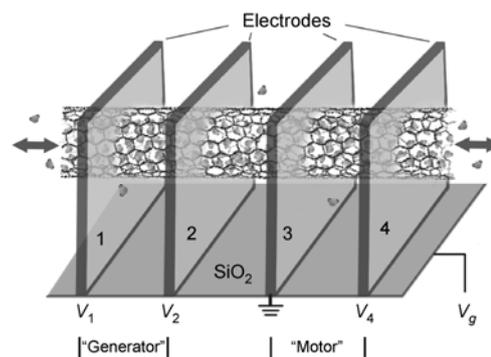


Figure 6 Schematic diagram of the hydroelectric power converter. Current/voltage is applied between electrodes 3 and 4 (the “motor” part) and the induced voltage difference is measured between electrodes 1 and 2 (the “generator” part) when the device is exposed to water vapor.

In an open beaker, V_{oc} is initially zero (Figure 8(a)). When the ethanol level reaches the SWNT rope, V_{oc} begins to increase linearly from zero to 200 μV for the first 240 s, and then saturates at 219 μV , where it remains constant for over 6 h. The mechanism relating to these observation is that ethanol molecules are pulled up along the channels formed among individual SWNTs by the capillary force; thus, V_{oc} is induced by the coupling between the charge carriers of the SWNTs and the ethanol molecules flowing at the interface [33,40]. When the beaker is covered, V_{oc} gradually decreases to its original value (Figure 8(b)). This process can be repeated and the characteristics of varying V_{oc} can be well reproduced.

If an SWNT rope is pretreated with deionized water, a very sharp increase in V_{oc} is observed when the ethanol level reaches the SWNT rope, as shown in Figure 9. V_{oc} jumps to 853 μV in less than 1 s. V_{oc} changes much more quickly and by a much larger magnitude compared with V_{oc} of an untreated device. Ethanol has lower surface tension than water, and the difference provides an additional driving force for ethanol to climb up along the channels among the SWNTs, which is called the Marangoni effect [41–43].

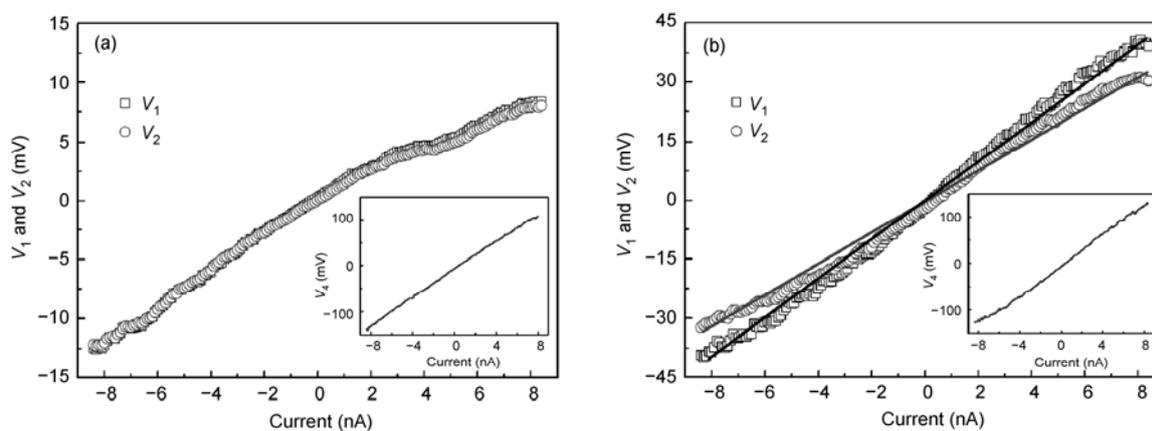


Figure 7 (a) In a vacuum, V_1 and V_2 are almost equal and have linear dependence on the current applied. (b) If water vapor is present in the chamber, there is a significant difference between V_1 and V_2 .

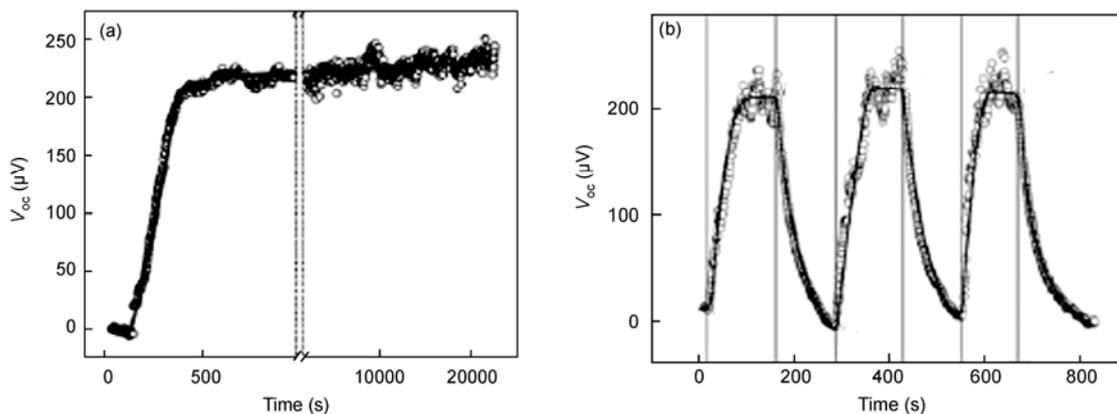


Figure 8 Dynamic characteristics of V_{oc} . (a) Zero V_{oc} is observed until the ethanol level reaches the SWNT rope. V_{oc} increases to a saturated value of 219 μV in about 300 s. (b) V_{oc} decreases gradually back to its original value when the beaker is covered as indicated by region 2.

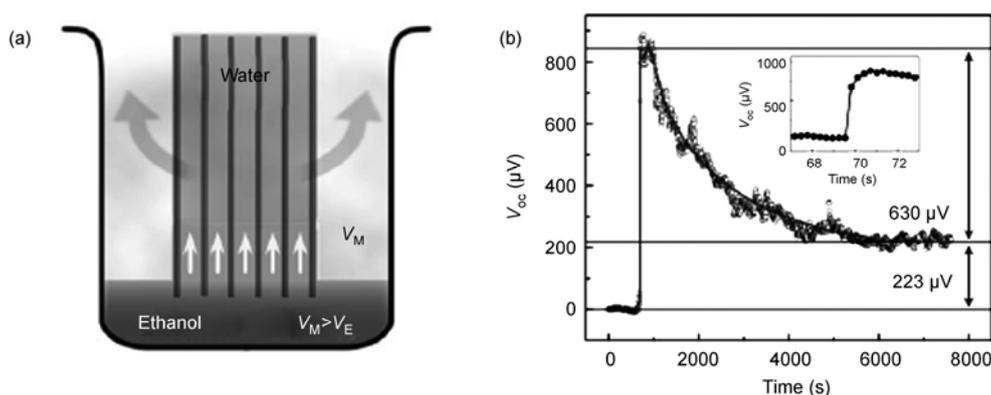


Figure 9 (a) If the SWNT is pretreated with water, the flowing velocity of ethanol is increased by the Marangoni effect. (b) Once the SWNT is pretreated with water, V_{oc} jumps to 630 μV in less than 1 s, indicating much faster induction and a larger value of V_{oc} for the surface energy generator owing to the Marangoni effect.

3 Conclusion

In summary, an inexpensive and effective method to prepare a crystal of SWNTs is demonstrated using a series of diamond wire drawing dies. XRD indicates that the SWNTs form a two-dimensional triangular lattice. Additionally, a sharp (002) reflection is seen in the XRD pattern. Meanwhile, we developed an approach based on the Coulomb explosion to separate SWNTs from their bundle. This technique is convenient and involves no surfactant. In studies of devices comprising SWNTs, we find that current/voltage can drive water molecules to have directional flow along SWNTs, and the flowing of water inside an SWNT can induce a voltage gradient force (an induced electromotive force) the SWNT. The results suggest that SWNTs can be exploited as molecular channels for water and may find potential application in nanoscale energy conversion. Moreover, a surface-energy generator (SEG) comprising SWNTs was demonstrated to harvest the surface energy of ethanol. The performance (the induction rate for V_{oc} , the value of V_{oc} and the output power) can be significantly enhanced by the Marangoni effect.

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