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Structural transformation of double-walled carbon nanotube bundles into multi-walled carbon nanotubes induced by current treatment

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Abstract

In this paper, double-walled carbon nanotube (DWNT) bundles can be transformed into multi-walled carbon nanotubes (MWNTs) by electric current treatment in vacuum. The morphology of the transformed MWNTs shows an obvious dependence on power density of the current, which changes from partly transformed MWNTs to collapse MWNTs with the increase of power density. The process of this structural transformation follows the tendency of forming more stable structures, and can be ascribed to the sequential coalescence of DWNTs inside the bundles.

Keywords: Carbon nanotubes; Chemical vapor deposition; Morphology

1. Introduction

Investigation of the stability of carbon nanotubes (CNTs) is of primary importance in the context of their potential applications. As well known, CNTs are made up of sp^2 carbon atoms arranged in a graphite honeycomb structure rolled into seamless cylinders. So differing from the stable structure made up of sp^3 carbon atoms, CNTs have the possibility of transforming into more stable structures in some appropriate 'annealing' conditions, which can be provided in various ways.

Electron beam irradiation has been proved to be very effective on inducing the structural transformation of CNTs. Li et al. [1] reported that, extremely large radial dilation of CNTs was observed by focused electron beam irradiation, and the minimum amount of accumulated electron energy required for CNT deformation was estimated to be about 5.61×10^{13} eV. It was also found that two single-walled carbon nanotubes (SWNTs) merged into a single SWNT with larger diameter under illumination of the electron kinetic energy of 1.25 MeV at 800 °C [2]. After fluorating, the SWNT bundles can even transform into multiwall-like structures with electron beam irradiation at dose of 2.1×10^{22} cm^{-2} [3]. This method was also used to form molecular junctions between two individual CNTs [4–6]. Another approach to get structural transformation of CNTs is heat treatment. Coalescence of DWNTs was observed after being heated at the temperature above 2100 °C, which induced the formation of a novel and stable structure consisting of flattened tubules containing two SWNTs [7]. The starting temperature of coalescence could be lowered by 600 °C by doping DWNTs with boron, due to the effect of intercalated boron atoms [8].

No matter how different these 'annealing' processes are, the structural transformation of CNTs occurs in a similar way based on activating and subsequential reconstruction of carbon atoms under energy input. In this study, we report another source of energy input, electric current, to induce the structural transformation of DWNTs. The morphological changes of DWNT bundles were investigated in detail by transmission electron microscopy (TEM) examination and Raman spectroscopy.

2. Experimental

The DWNTs used in this study were synthesized by using a chemical vapor deposition (CVD) method in a quartz tube as described in detail elsewhere [9]. Ferrocene and a small quantity

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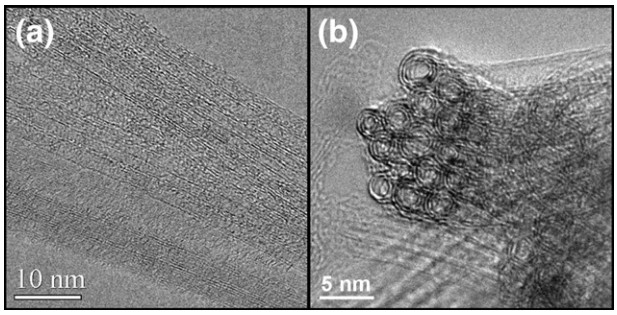

Fig. 1. The HRTEM images of (a) the side view and (b) the cross-section of the DWNT bundle inside the pristine strand. The concentric graphite layers of DWNTs can be clearly seen.

of sulfur (atomic ratio Fe:S = 10:1) was dissolved in the solution as a catalyst precursor, and argon was used as carrier gas. The reaction temperature was 1180 °C. To be treated easily, the as-prepared DWNT films in the initial products were assembled into long strands after immersed in alcohol, as used in the fabrication of DWNT filaments [10]. The diameters of the strands can be approximately controlled in the range of 100–200 μm. Since all the strands used in our experiments were produced from the same film in the initial products, the structure and density of the DWNT bundles inside these strands were almost the same. Fig. 1 shows the typical TEM observation of these DWNT bundles inside the pristine strands.

Current treatment of the DWNT strands was carried out in a vacuum chamber at 10^{-3} Pa. Both ends of the strands were mounted onto two electrodes inside the chamber, and a direct current was passed through the strands by the electrodes. The current was measured by an ammeter. Energy input of the current was estimated by the power density calculated with resistance and diameter of the strands. Currents of three various power densities (10^2 W/cm^2, 10^3 W/cm^2 and 10^4 W/cm^2) were used in this study. All the strands were treated for 60 min.

Structural transformation of DWNT bundles was characterized by a JEM-2010 high-resolution transmission electron microscope, and their Raman spectra were also obtained by using a Renishaw 2000 system (excitation wavelength: 633 nm).

3. Results and discussion

Fig. 2 shows an evolution of morphological changes of the DWNT bundles corresponding to the current treatment of different power densities. When treated at the power density of

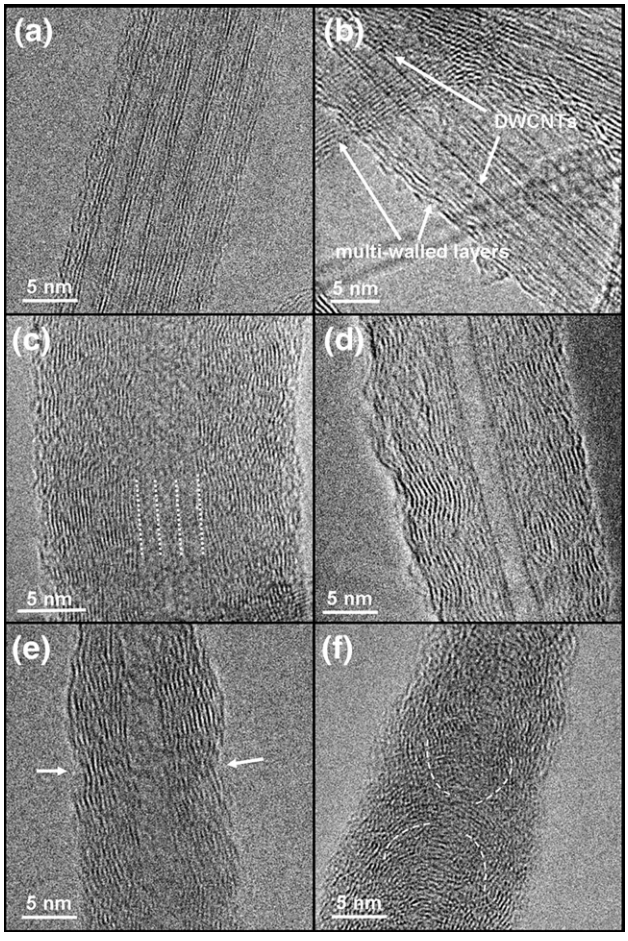

Fig. 2. Evolution of the morphological changes of DWNT bundles corresponding to the current treatment of different power densities: (a)–(b) 10^2 W/cm^2; (c)–(d) 10^3 W/cm^2; (e)–(f) 10^4 W/cm^2.

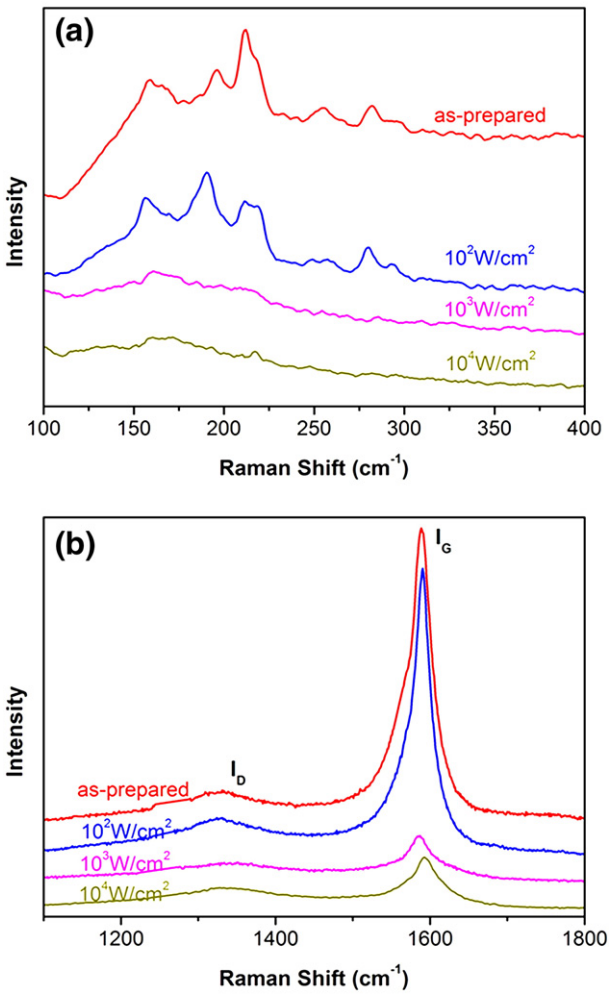

Fig. 3. (a) Low-frequency and (b) high-frequency Raman spectra of as-prepared DWNT bundles and bundles treated at different power densities.

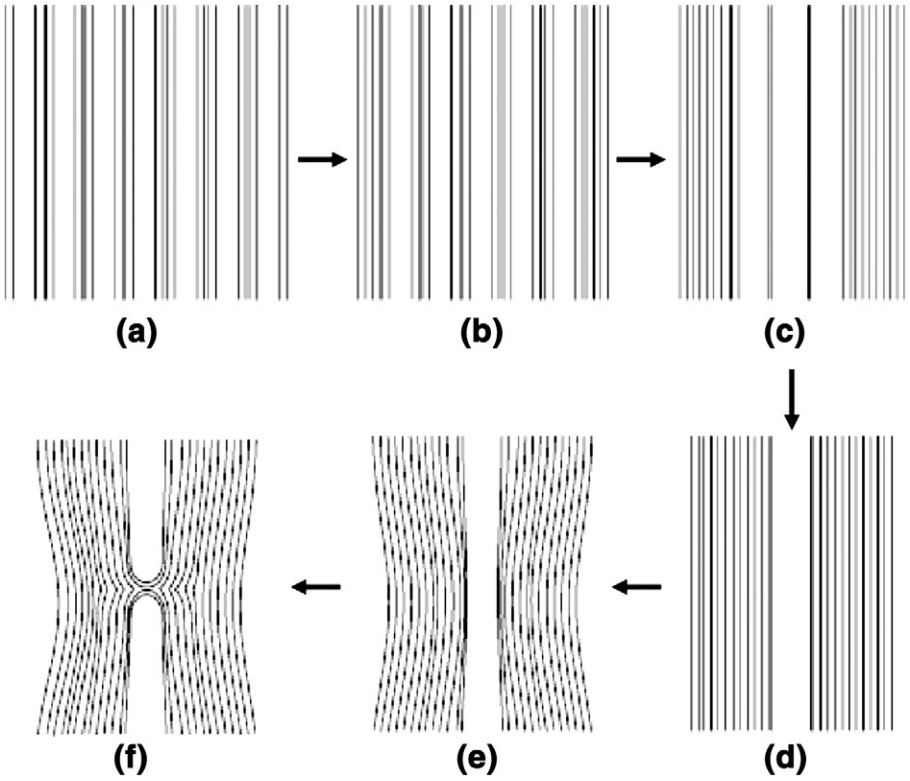

Fig. 4. The process of morphological changes of DWNT bundles as the power density increases.

10^2 W/cm^2, most DWNT bundles didn't exhibit significant structural changes in the TEM observation (Fig. 2a). However, partial transformation could still be found in the rest bundles. As shown in Fig. 2b, the outer parts of these bundles have changed into multiwall-like structures consisting of 4–5 graphite layers, while the main parts of them still retain typical DWNT structures. So, these bundles can be regarded as partly transformed MWNTs.

With the increase of power density to 10^3 W/cm^2, clear morphological changes of DWNT bundles could be observed as illustrated in Fig. 2 c and d. Many initial bundles transformed into multi-walled carbon nanotubes. Moreover, these transformed MWNTs are very different from the as-prepared MWNTs produced by CVD methods. The main difference between them is the sidewall. Unlike the straight and smooth sidewalls of the as-prepared MWNTs, the sidewalls of the transformed MWNTs are distorted and rough, showing an unideal degree of graphitization. According to our measurement, the layer distance of the transformed MWNT is 0.37 nm, which is slightly larger than that of the typical one (0.34 nm). Another difference between the transformed and as-prepared MWNTs is the inner space. The inner space of the transformed MWNT is formed from 1–3 reserved DWNTs at the center of the initial DWNT bundle, showing a trace of the morphological change. Two concentric graphite layers of the reserved DWNT can be clearly seen in Fig. 2d, and the borders between three reserved DWNTs in the inner space can be partly distinguished as marked by white dot lines in Fig. 2c. So, the inner sides of most transformed MWNTs are straight and smooth, despite of their distorted and rough sidewalls.

When the power density further rises to 10^4 W/cm^2, the transformation from DWNT bundles to MWNTs could still be observed. Even so, the morphology of the transformed MWNTs shows great differences in this condition from those treated at 10^3 W/cm^2. As pointed out by arrows in Fig. 2e, necking of their sidewalls happens, which makes them look like peanuts instead of regular tubules. Their inner sides are no longer continuous and clear. It was also found that for some other transformed MWNTs, their sidewalls seemed to curve inside and joined together at the necking parts, inducing the division and even collapse of their inner spaces (Fig. 2f). Both the necking and collapse of these transformed MWNTs are very similar to those that occur during the transformation from MWNTs to carbon onions [11]. This indicates that it may be possible for the initial DWNT bundles to further transform into other structures, such as carbon onions, in this way.

Raman spectra analysis gives consistent results with the above TEM observation. Fig. 3a depicts the radial breathing mode (RBM) of Raman spectra below 400 cm^{-1} for the DWNT bundles treated at various power densities in contrast to the as-prepared sample. It needs to be noted that, since the Renishaw 2000 system we used with excitation wavelength of 633 nm have low sensitivity to the peaks under 150 cm^{-1}, some RBM peaks ($\omega_r <$ 150 cm^{-1}) for outer tubes of large diameter DWNTs are not obviously illustrated in Fig. 3a. However, for some small diameter DWNTs, the RBM peaks for both their outer tubes (156.6 cm^{-1}) and inner tubes (282.1 cm^{-1}, 294.1 cm^{-1}) can be clearly seen. Although the RBM peaks of the sample treated at 10^2 W/cm^2 shows no notable difference from those of the as-prepared DWNT sample, it is noteworthy that some peaks disappear completely

when power density increases to 10^3 W/cm^2 and 10^4 W/cm^2, respectively. This indicates that many DWNT bundles have already changed into other structures. Besides the RBM peaks, the comparison is also made at the G band and D band as shown in Fig. 3b. Compared with the as-prepared sample, the decrease of G band intensities is very obvious for the samples treated at 10^3 W/cm^2 and 10^4 W/cm^2, respectively. And the ratio of G band intensity to D band intensity (I_G/I_D) also changes from 8.4 to 2.5 (the value of as-prepared sample is 10.2), when the power density rises from 10^2 W/cm^2 to 10^4 W/cm^2, showing a decreasing tendency. This could be related to the increase of defects during the formation of MWNTs.

The driving force of transformation between two structures is often attributed to their different stabilities. To be exact, the less stable structures are believed to transform into more stable structures when enough energy is provided. The transformation from DWNT bundles to MWNTs follows the same pathway. By calculating [12,13] and comparing the energy of carbon atoms in SWNTs and fullerenes, the carbon onions are proved to be more stable than the carbon nanotubes. Moreover, the thinner and longer the carbon nanotube is, the lower is its stability [11]. So the evolution of the morphological changes of the DWNT bundles just accords with the tendency of forming more stable structures.

Similar to the structural transformation induced by electron irradiation or heat treatment, the morphological changes induced by current treatment can also be considered as a result of coalescence of the DWNTs inside the bundles. Based on the observation and simulation results in recent research work [7,8,14], the mechanism of the structural transformation in our study is discussed, as illustrated in Fig. 4. It needs to point out that defects are the leading factors promoting coalescence. In other words, coalescence tends to happen easier between the CNTs with more defects, since the carbon atoms near the defects are easier to be activated. So, for the DWNT bundles used in our experiments, their outer parts are easier to merge than the inner parts due to the existence of more defects. At low energy input, the coalescence only happens in the area where less energy is needed to activate the carbon atoms, so that the multiwall-like structures firstly form in the outer parts of the bundles through the merging of DWNTs (Fig. 4a–b). As the energy input increases, besides the outer parts, the coalescence happens in the inner parts as well, but the rate of coalescence in these parts is still much smaller. Therefore, the transformation of a bundle can be regarded as that the concentric graphitic layers are formed layer by layer and from outer part to inner part, until the entire bundle changes into multiwall-like structure except a few DWNTs reserved at the center to form inner space (Fig. 4c–d). Moreover, during this transformation, the smaller diameter DWNTs may coalescence prior to the coarse ones because of their lower stability. Since the reconstruction of carbon atoms during coalescence can hardly be a strict arrangement of hexagon structure due to the lack of enough energy, many defects are introduced into the newly formed graphitic layers, making the sidewalls distorted and rough. When the energy input continues to rise, the sidewalls of the transformed MWNT are no longer stable. Coalescence happens again at the parts where defects aggregate, and induces the necking and collapse of the transformed MWNTs (Fig. 4e–f).

The energy input for the structural transformation in our study is provided by electric current. As we know, the heating effect is the main effect of the current energy input when passing through the bulb filaments. So, the morphological changes of the DWNT strands were supposed to be triggered by this heating effect. However, after measuring the temperature of the strands during treatment with an infrared thermometer (Raytek MR1S), it was surprising to find that the maximum value was only 1500 °C. This temperature was much lower than the starting temperature of coalescence reported by other researcher [7]. This indicates that there might be other effects of current energy input besides heating effect in the treatment, which still needs to be studied in our future research work.

4. Conclusion

The structural transformation from DWNT bundles into MWNTs was realized by current treatment. With the increase of current power density, the morphology of initial DWNT bundles changes in the sequence of partly transformed MWNTs, completely transformed MWNTs, necking MWNTs and collapse MWNTs. These morphological changes are driven by the tendency of forming more stable structures, and are related to the sequential coalescence of DWNTs inside the bundles. Our work may propose a possible way for the structural modification of CNTs.

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