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Multiwall Carbon Nanotubes Made of Monochirality Graphite Shells

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Multiwall carbon nanotubes (MWCNTs)[1] promise many applications with great technological importance because of their robust structure and flexible atomic conformation; MWCNTs especially have excellent behaviors as carriers of functionalized molecules,[2,3] field electron emitters,[4] conductive wires,[5] and bearers of rotational motors,[6] etc. Both theoretical predictions[7−12] and experimental results[13−15] suggest that MWCNTs have exotic electronic structures and intriguing transport properties, which are highly dependent on tube chirality. However, the structural defects and the random distribution of chirality of each concentric graphitic shell make the MWCNTs difficult for basic research and technological applications. Although various methods have thus far been developed to prepare carbon nanotubes, it is still a challenge to get the high crystalline MWCNTs with limited atomic conformation, aiming at receiving MWCNTs with identical chiralities.

In this communication, we report the synthesis of high crystalline MWCNTs with nearly identical chiralities by a low-temperature chemical vapor deposition (CVD) process in surrounding plasma. Structural analysis, carried out by transmission electron microscopy (TEM) image and electron diffraction methods, reveals that the MWCNTs are well-crystallized and that most of them are made of monochirality graphite shells, i.e., monochiral MWCNTs.

The preparation of the monochiral MWCNTs is performed by using a microwave plasma-assisted CVD apparatus, in which tubular graphite cones with identical chirality of zigzag type have been successfully synthesized previously.[16] Silicon wafers with ferric oxide coatings prepared by a sol−gel process are applied as substrates. In this study, two steps are taken. The first step is for low-temperature plasma CVD (LTP−CVD) growth of monochiral MWCNTs. The growth chamber is evaluated below 0.1 Pa, the substrate is heated to 600 °C, and then the precursor gases N_2 and H_2, with respective flow rates of 150 and 20 sccm, are introduced into the chamber, where a total pressure of 2.7 kPa is maintained. A $N_2 + H_2$ plasma ball is produced by a 700 W microwave excitation. After etching the substrate surface for 5 min, the H_2 source is turned off, and CH_4 with a flow rate of 20 sccm is injected into the growth chamber. The samples are grown inside plasma. The growth time is 15 min, and then CH_4 is turned off. Usually, the product by the first step is a mixture of a large quantity of carbon nanotubes and polymerized nanobells. In the second step, purification is carried out in an in situ chamber. We continued using N_2 plasma to etch the grown film for 5 min. Due to the van der Waals interactions between the nanobells, the polymeric nanobells are easily broken[17] under plasma etching and become a mass of separated single nanobells (see Supporting Information). At last, a large quantity of high crystalline MWCNTs is retained.

TEM images show that the prepared MWCNTs have outer diameters in the range of 20−80 nm, and their walls consist of several tens of graphite layers. We probe the chiralities in different areas along each nanotube. Figure 1a is a TEM image of a MWCNT, along which the same chiral angle was detected in different local areas. In Figure 1, b_1−b_3 show the recorded electron diffraction patterns corresponding with the areas marked by circles 1−3 in Figure 1a. The patterns are an overlap of two simple hexagonal patterns, indicating that all of the layers in the MWCNT have nearly identical chirality. The intensities of the two sets of $(10\bar{1}0)$ spots are slightly different, as indicated by arrowheads 1 and 2 in Figure $1b_2$; where the diffraction spots closely display a center symmetry, it suggests the presence of well-defined stacking in these nanotubes. The observation of $(10\bar{1}l)$ ($l = 1, 3, 5$) reflections shows that the positional correlation between the internal structures of the walls has a tendency of AB stacking.

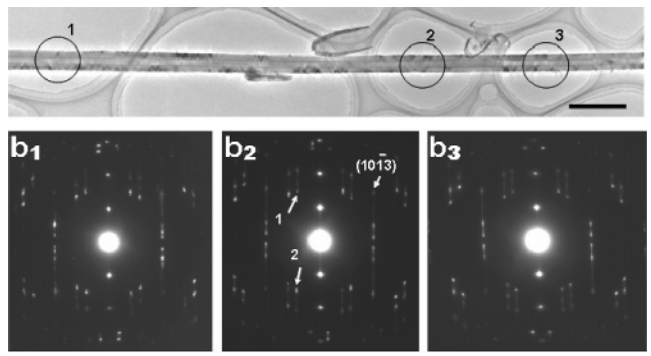

Figure 1. Typical high crystalline MWCNTs with nearly identical chirality. (a) TEM image, scale bar: 100 nm. (b_1−b_3) Electron diffraction patterns recorded from the areas marked by circles 1−3 in (a). In (b_2) the arrowheads 1 and 2 indicate that the two sets of {10 $\bar{1}$ 0} have different intensities. The diffraction pattern displays the center symmetry. The (10 $\bar{1}$ 3) spot is indicated by the arrowhead, presenting in certain parts of AB stacking sequence among the graphite layers of the nanotube.

Figure 2 shows detailed structural analysis of a MWCNT. The electron diffraction pattern (Figure 2b) indicates that the tube has nearly identical chirality for all of the concentric graphitic layers, as a zigzag-type MWCNT. Besides the sharp (0002) and $(10\bar{1}0)$ reflections, $(10\bar{1}1)$ lattice fringes appear, which result from the curved graphite sheets of the side wall closely parallel to the incidence of the electron beam. In Figure 2, c and d are high-resolution TEM images corresponding to the area of wall and hollow center of the nanotube, marked by area 1 and 2 in Figure 2a, respectively. A fast Fourier transformation (FFT) from the wall of the nanotube (inset in Figure 2c) obviously shows $(10\bar{1}1)$ lattice fringes. The FFT for the hollow area of the nanotube (inset in Figure 2d) also confirms the characteristic of identical chirality. To measure the chiral angle accurately, we adopted the method in ref 18. The detailed structures of other chiral nanotubes have been also studied (see Supporting Information).

We have performed the characterization of chirality for a large number of the as-prepared nanotubes; ~80% of them have nearly

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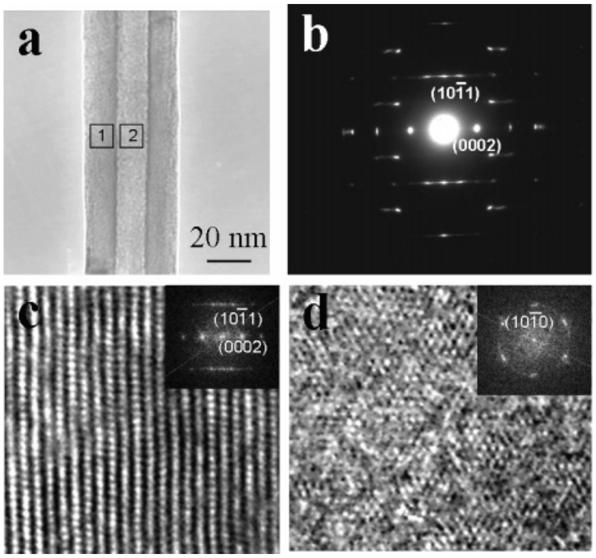

Figure 2. Structural analysis of the monochiral MWCNTs. (a) TEM image. (b) Electron diffraction pattern. (c) and (d) High-resolution TEM images corresponding to the areas marked by B and C in (a), respectively. FFT images (inset in (c) and (d)) reveal the consistent pattern with the experimental.

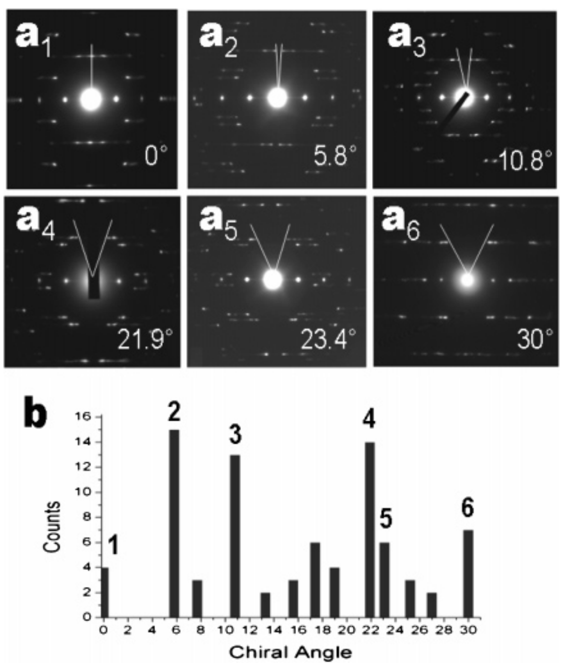

Figure 3. (a) Series of typical electron diffraction patterns of MWCNTs with chiral angles of 0°, 5.8°, 10.8°, 21.9°, 23.4°, and 30°, respectively. (b) Statistic histogram showing the distribution of the chirality for the 82 as-prepared MWCNTs; the columns marked by 1−6 correspond to a_1−a_6 in (a), respectively.

identical chiralities, whereas another ∼20% have two or more chiralities or poor crystallinity. In Figure 3 a_1−a_6 show a series of typical electron diffraction patterns. Figure 3b presents the statistical distribution of chiral angle for 82 monochiral nanotubes, in which histogram columns marked by the numbers 1−6 correspond respectively to a_1−a_6 in Figure 3. It is noted that some specific chiral angles, 5.8°, 10.8°, and 21.9°, are detected with a higher probability.

Diffraction simulations were carried out. The results indicated that the monochiral MWCNTs are formed by nested concentric graphite shells with the same chiral angles (not by scrolling up a graphite sheet) and that the ordered AB stacking sequence for the carbon atoms in the monochiral MWCNTs is also confirmed (see Supporting Information). Considering the nested Russian doll model, geometrically, it is reasonable that the statistically dominant chiral angles have been found. In this study, the growth under higher temperature (>650 °C) usually resulted in multichiral nanotubes (see Supporting Information). The growth mechanism of optimistic energy is under study. We believe that the plasma environment of the CVD process, which can lower the growth temperature and produce a special electric condition, could benefit the growth of MWCNTs with nearly identical chiralities.

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Supporting Information Available: Experimental conditions and SEM images of products; details of chirality analysis for chiral MWCNTs; diffraction simulations showing that monochiral MWCNTs are made of monochirality graphite shells and have AB stacking tendency. This material is available free of charge via the Internet at http://pubs.acs.org.

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