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Preparing Carbon Nanotubes and Nested Fullerenes from Supercritical CO_2 by a Chemical Reaction

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The discovery of carbon nanotubes (CNT) in 1991[1] has led to extensive research activities in this field due to the unique properties of the CNT.[2] CNT have potential applications as superconductors,[3] single-molecular transistors,[4,5] and, when the CNT are filled with metals or metal oxides, as part of magnetic recording devices.[6,7] The various methods of preparation of CNT have recently been reviewed.[8] They can be classified into two categories: physical methods and chemical methods. The physical techniques are characterized by low nanotube yield, technical complexity, and a very low energetic efficiency that makes them unsuitable for mass production. They include electric arc synthesis, laser ablation, resistivity vaporization, electron or ion beam vaporization, and sunlight-induced vaporization.[9] The chemical methods are aimed at mass production with reasonable yields and low energy consumption. However, they usually result in nanotubes of lower quality. The chemical reactions employed include the catalytic pyrolysis of hydrocarbons,[10] catalytic disproportionation of CO,[11] the reduction of perfluorinated hydrocarbons by an alkali metal amalgam,[12] hydrothermal growth from amorphous carbons,[13,14] and the catalytic reduction of CO,[15,16] oxidation of C_2H_2,[17] polymerization of C_6H_2,[18] a metathesis reaction,[19] and the thermal decomposition of $Fe(CO)_5$ in a heated flow of CO.[20]

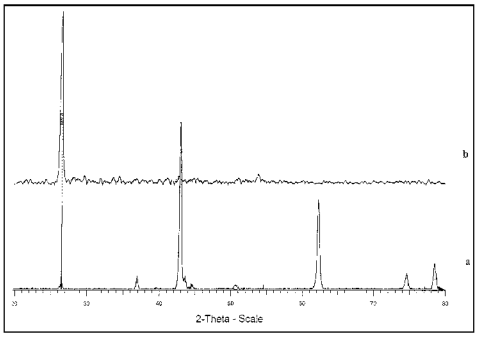

Figure 1. XRD diffraction patterns of the (a) as-prepared sample and (b) after HCl treatment.

We report herein that when we react carbon dioxide with Mg in a closed cell for 3 h at 1000 °C, it produces MgO and carbon. The MgO is removed by treating the reaction products with aqueous HCl. The solid precipitate, which remains, contains CNT and nested fullerenes. The total yield of carbonaceous materials (relative to the CO_2 starting material) is about 15.5%. CNT account for 10% of this material, and nested fullerenes are estimated at 1−2% (both estimates are based on visual inspection of HRTEM micrographs).

The XRD (X-ray diffraction) of the as-prepared products as well as that of the posttreated HCl sample are presented in Figure 1. It shows that MgO is the major product in the as-prepared sample and that it disappears after the HCl treatment. The only diffraction peak detected after digestion with HCl is that assigned to graphitic [002] carbon at $2\theta = 26.380$.

The HRTEM (high-resolution transmission electron microscopy) micrographs in Figure 2 present the major structures obtained after the HCl treatment. Figure 2a shows CNT with a length of 500−600 nm and a width of 30−40 nm. The walls are built of 10−20 graphitic layers. The fringes of these walls are observed through the whole width of the NT. EDAX (energy-dispersive X-ray analysis) measurements using an electron beam focused on the whole width of the tube reveal a minute amount of oxygen (less than 1%) as the only contaminant; the rest is carbon.

Nested fullerenes are depicted in Figure 2b. The EDAX measurements of these onions detect no element other than carbon. No fringes are observed in the darkened center. This suggests that they are filled with amorphous carbon. To demonstrate the three-dimensional nature of the nested fullerenes, the HRTEM measurements were conducted at three different tilt angles (+200 and −200). The picture remained unchanged at all three angles. Finally, we also see highly aggregated, elongated, carbon rods. They are not crystalline. They are 0.5−3 μm long and 15−30 nm wide, and contain impurities of Mg and Fe.

The Raman spectrum of the posttreated reaction product is depicted in Figure 3. The spectra taken at different points in the sample are similar, with only slight variations in the relative intensity of the small D-band at around 1350 cm^{-1}. The peak at 1581 cm^{-1} (G-band) is much stronger and very sharp, with a full width of 15 cm^{-1}. The peak is assigned to an E_{2g} mode of graphite and is related to the vibration of sp2-bonded carbon atoms in a 2-dimensional hexagonal lattice, the same as in a perfect graphitic layer.[21] The D-band is associated with the presence of defects in the hexagonal graphitic layers. The intensity of the D-band is known to be high for badly graphitized materials. The inverse of the ID/IG intensity ratio of the G and D bands serves as a measure

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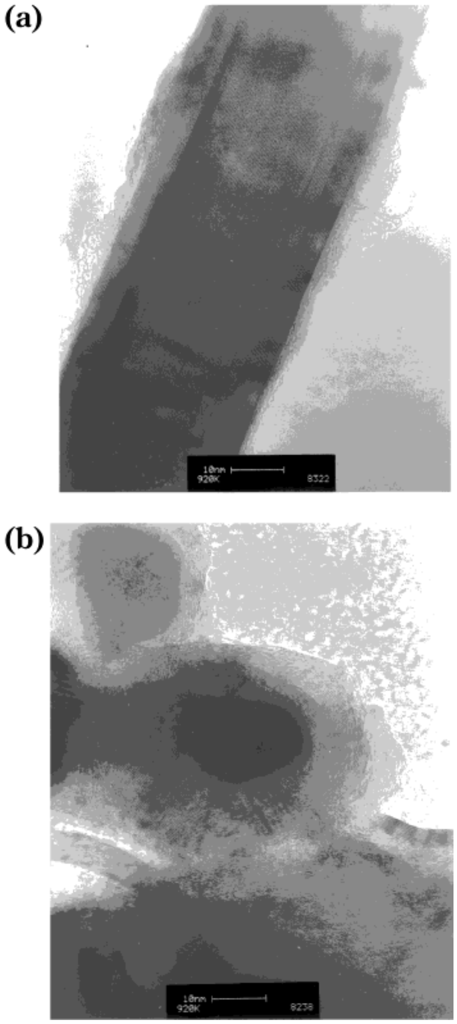

Figure 2. HRTEM pictures of the product after the HCl treatment. (a) An individual nanotube, b) nested fullerenes.

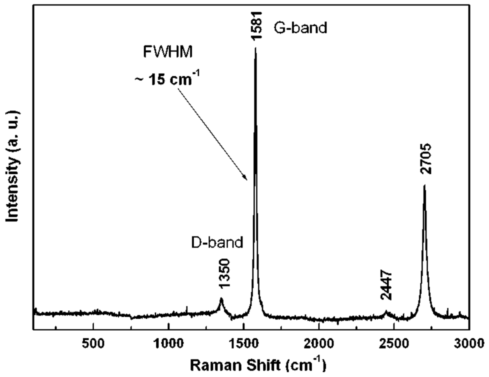

Figure 3. Raman spectrum of the sample after the HCl treatment.

of the graphitic ordering and indicates the approximate crystalline size in the hexagonal plane, La,[21−23] which is related to the length of pristine (defect-free) graphitic multiwalls in the CNTs and nanorods. The calculation using the relationship La = 44(ID/IG) −1 yields values > 2 μm for the treated sample, in good agreement with the observed length of the MWCNT (see Figure 2a). The Raman spectrum is characteristic of a single crystal lattice, without lattice edges within the analyzed area. Therefore, the concentric graphitic shells forming the nanotube walls are highly crystalline. The absence of carbon atoms with dangling bonds, associated with plane edges and terminations, indicates that the nanotubes have closed-end multiwalls. The Raman spectrum is in good agreement with the lattice images of the nanotubes observed in the HRTEM studies.

Our interpretation of the chemical reactions that occur at the operating temperature of 1000 °C is based on the work of Shafirovich and Goldshleger.[24]

$$Mg_{(g)} + CO_{2(g)} \longrightarrow MgO_{(s)} + CO_{(gas)} \qquad (1)$$

$$Mg_{(l)} + CO_{(g)} \longrightarrow MgO_{(s)} + C_{(graphite)} \qquad (2)$$

Their work suggests that the first step is a homogeneous gas-phase reaction, followed by a heterogeneous reaction occurring on the surface of the liquid magnesium. Magnesium melts at 650 °C, and its normal boiling temperature is 1090 °C. The vapor pressure of magnesium at 1000 °C is 350 mmHg. The CO_2 is in its supercritical state, and the calculated pressure at 1000 °C is approximately 10 kbar. From the balance of materials we conclude that 59% of the gases leak out due to this high pressure. As pointed out by Shafirovich,[24] and observed in our measurements as well, the reaction is exothermic. The temperature of our cell is raised at the start of the reaction, above the oven temperature by at least 100 °C.

It is not clear whether this reaction is catalyzed by any of the components of the stainless steel (SS) cell. We can only say that within the detection limits of the EDAX and XRD measurements we could not find any evidence for any transition metal in either the CNT or the nested fullerenes. However, the diffraction patterns at $2\theta = 43.7$ 0 and 50.6 0 detected for the as-prepared material are assigned to an FeNi alloy (JCPDS 47-1405). As a control reaction we have introduced the same amount of dry ice into the cell without magnesium. After 3 h at 1000 °C, no products are found. To further examine the catalytic role of the SS walls, the reaction was conducted in a closed ceramic crucible within the SS cell. The same products are obtained in the crucible. Despite these findings, we cannot rule out the possibility that vaporized metal atoms from the cell walls catalyze the formation of CNT.

The different shapes of nested nanocarbons observed are a result of reaction kinetics and cluster size at the initial stages of growth. The growth of the hexagonal sheets along the nanotube axis is quicker, while the nested fullerenes structures are thermodynamically favored for big carbon cluster sizes due to the elimination of energetic dangling bonds. Optimization of the experimental conditions of this new method is likely to increase yields of NT above 15 wt %. In existing methods of NT production in the gas phase, CNT are found initially in much lower yields, as a byproduct of fullerene synthesis.

This research demonstrates that structures of graphitic concentric shells can be grown by a simple chemical method. We have obtained well-crystallized nanotubes from dry ice in the presence of Mg by heating the precursors in a closed vessel at the autogenic pressure of the mixture. We avoid the complexities of using a flowing gas at controlled pressures and high temperatures and require no technically complex equipment. We simplify considerably the existing production methods for CNT.

Experimental Section. A typical reaction is performed in a SS cell containing 2.6 g of dry ice and 0.3 g of magnesium. The cell is cylindrical, having an inner diameter of 15 mm and a length of 30 mm. The cell is sealed with a flat copper gasket. The filled cell is heated for 3 h at 1000 °C. At the end of the reaction the cell is cooled to room temperature, and its screw-cap is opened. No release of pressure was detected when the cell was opened. Solid product (1.217 g) is collected at the end of the reaction. The product is collected and dissolved in 8 M HCl aqueous solution at 70 °C for 1 h. It is then left in the HCl solution at room temperature, overnight. A microfilter is used to filter the solid product from the solution. It is then washed with ethanol and dried in air to yield 110 mg of product.

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