Hydrothermal Processing of High-Quality Multiwall Nanotubes from Amorphous Carbon

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Hollow carbon nanotubes with a multiwall made of well-ordered concentric graphitic layers have been synthesized in the absence of metal catalyst by hydrothermal treatment of amorphous carbon in pure water at 800 °C and 100 MPa. Hydrothermal nanotubes are free of amorphous carbon after treatment.

Multiwall carbon nanotubes can be synthesized at very high temperatures or energy input (>3000 °C) or at lower temperatures, from 500 to 1200 °C, by pyrolysis of gaseous hydrocarbons in the presence of catalytic transition metal nanoparticles. The nanotubes synthesized by catalytic decomposition of hydrocarbons have low crystallinity and are covered by a thick layer of amorphous carbon, difficult to remove.[1−4] They also require a complex purification process to remove metal catalyst particles.[1,5−6] The oxidative effect of hot water on amorphous carbon is currently used for purification of carbon nanotubes by hydrothermal treatment (immersion in water at moderates and high temperatures and pressures),[6−9] but little is known about the possibilities of hydrothermal processing aimed to the synthesis of nano-structured carbons.[10−14] However basic in our environment and experimentally accessible, the chemistry of the C−O−H system is very complex and not well understood.

The aim of the present communication is to introduce hydrothermal synthesis as a new processing method for fabrication of well-crystallized multiwall carbon nanotubes, without the addition of metal catalyst. The homogeneity of hydrothermal processes, cheapness, and availability of amorphous carbon material, without the need of catalyst, are advantages favoring the scaling-up of the new method. The treatment of higher volumes would only require autoclaves with increasing load-bearing capacity.

Hydrothermal experiments were carried out with use of conventional Tuttle-type autoclaves made of stellite superalloy. Initial samples of pure amorphous carbon were placed into golden capsules 3 mm in diameter and 5 cm in length, which were subsequently filled with double distilled water (≈0.3 g). The capsules were then sealed, so no contamination occurred during treatment, placed into the autoclave, and treated at a temperature of 800 °C and pressure of 100 MPa for 48 h. Electron microscopy studies were carried out with a H9000NAR, Hitachi TEM at an operating voltage of 300 kV. Samples were prepared by adding methanol and dispersing the amorphous particles in an ultrasonic bath. After ultrasonication, a drop of the suspension was placed on a microgrid and dried in air before observation.

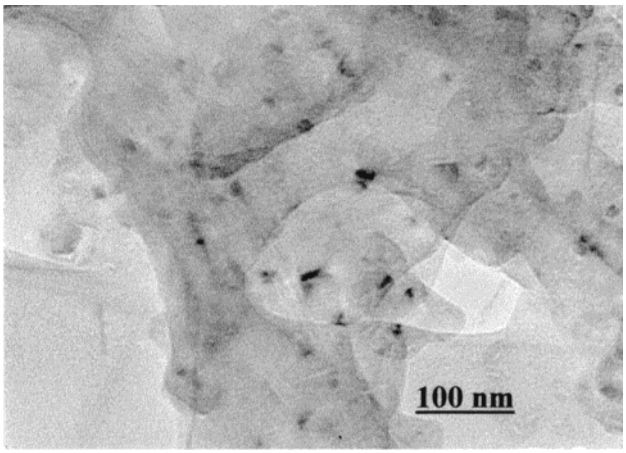

Figure 1. Electron micrograph of the initial sample consisting of amorphous carbon from soot.

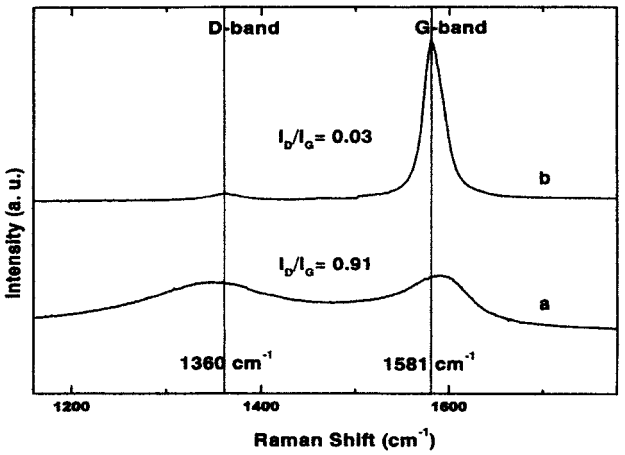

Figure 2. Raman spectra of starting material (a) and after treatment at 800 °C and 100 MPa for 48 h (b).

The microstructure of initial samples is shown by electron microscopy in Figure 1. It is pure amorphous carbon with a porous structure, and abundance of internal surfaces and graphitic clusters embedded in the amorphous matrix. The Raman spectrum is shown in Figure 2a, displaying the characteristic wide D and G bands at around 1360 and 1590 cm^{-1}, respectively, typical of amorphous carbons or disordered graphite.[15,16]

Electron microscopy observations revealed the formation of aggregates of needlelike and polygonal nanoparticles after hydrothermal treatment. No amorphous carbon remained. Observed individually the elongated particles revealed an internal hollow core. These hollow nanotubes have diameters in the range of tens and lengths in the range of hundreds of nanometers. Aspect ratios are between 20 and 100. The outer diameters are between 10 and 50 nm, and the inner diameters are between 2 and 8 nm. Polyhedral particles are between 20 and 50 nm in diameter. TEM observations revealed that the polygonal particles have polyhedral shapes with a hollow core and a multiwall of concentric graphene layers (we shall name them "carbon nano-polyhedrons"). They

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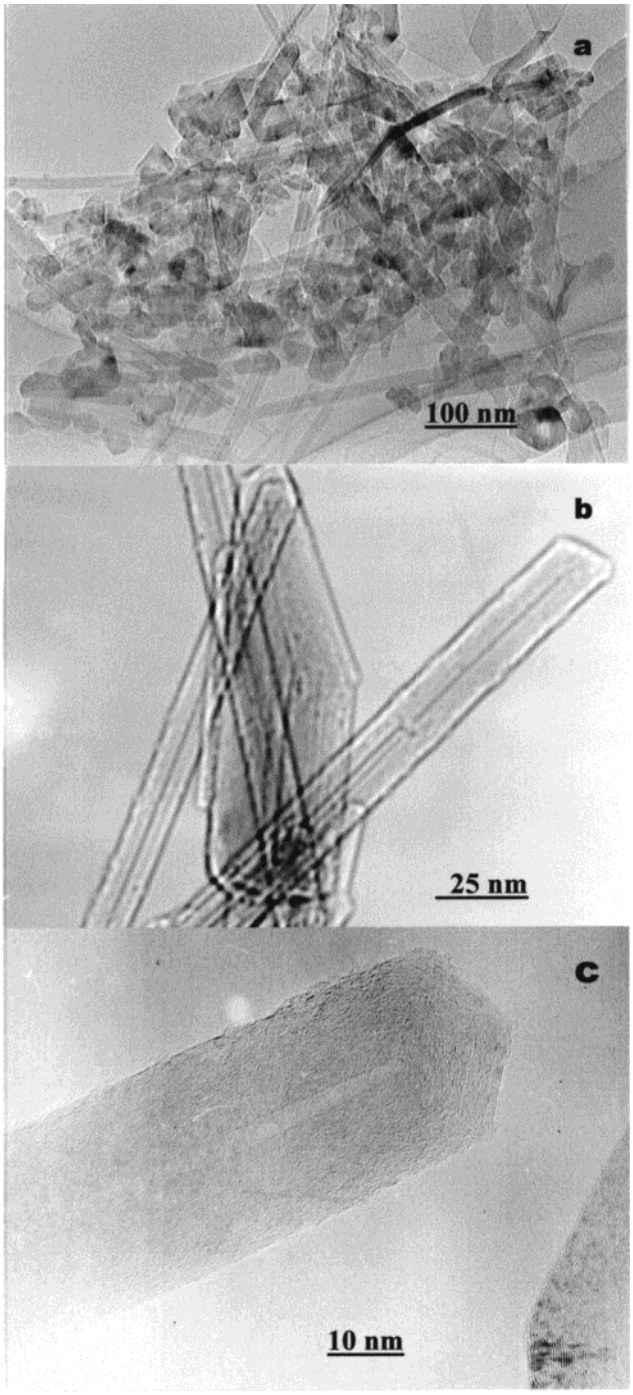

Figure 3. Electron micrographs after treatment showing multiwall nanotubes and graphitic nanoparticles (a); detail at higher magnification showing the hollow cores (b); and HRTEM lattice fringe image of several hydrothermal multiwall nanotubes (c).

can be considered as very short multiwall nanotubes. The micrograph in Figure 3a shows a typical aggregate. The micrograph in Figure 3b at higher magnification shows in detail the tip of several nanotubes and their hollow cores. A thin hollow core can be noticed inside the polygonal particle. It seems to be a shortened nanotube, with a shape similar to the tip of a thicker nanotube. Figure 3c shows the lattice of a nanotube. Bended graphene sheets form the ending caps. The interlayer spacing in the multiwalls, ~ 3.4 Å, corresponds to the 002 distance of graphitic carbon, in the direction perpendicular to the hexagonal graphene layer.

The Raman spectrum after treatment is shown in Figure 2b. The peak at 1581 cm^{-1} (G-band) corresponds to a E_{2g} mode of graphite and is related to the vibration of sp^2-bonded carbon atoms in a 2-dimensional hexagonal lattice, such as in a graphite layer.[15] Nanotubes with concentric multiwalled layers of hexagonal carbon lattice display the same vibration.[17] The D-band at around 1360 cm^{-1} is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite or glassy carbons. After treatment, the D-band nearly disappeared and the G-band sharpened, so the relative intensity of the G-band with respect to the D-band increased very significantly. The inverse of the I_D/I_G intensity ratio between G and D bands is an usual measurement of the graphitic ordering and may also indicate the approximate layer size in the hexagonal plane, L_a,[15,18] which in this case is related to the length of pristine (defect-free) graphitic multiwalls. The I_D/I_G ratio in the treated material is ~0.03, compared to a value of ~0.9 in the starting material. The calculation using the relationship $L_a = 44(I_D/I_G)^{-1}$ yields values of around 1.5 μm for the treated sample, in good agreement with the maximum length of multiwall carbon nanotubes observed in TEM images. The sharp decrease of I_D/I_G indicates that the number of sp^2 bonded carbon atoms without dangling bonds have increased at the expense of disordered carbon. The low ratio I_D/I_G is characteristic of a graphite lattice with perfect two-dimensional order in the basal plane. The spectrum 2b indicates a nearly defect-free lattice ordering, and reveals that the multiwalls forming the nanotubes have a perfect lattice without defects, edges, or plane terminations, as seen in Figure 3c. The crystallinity of hydrothermal nanotubes is similar or higher than in multiwall nanotubes grown using evaporation methods, for which I_D/I_G ratios are typically ~0.10.

The growth of multiwall carbon nanotubes in the absence of metal catalyst is observed for the first time in hydrothermal conditions. Formation of quality multiwall carbon nanotubes has never been observed previously in the C−H−O system at this range of relatively mild temperatures (below 800 °C). Multiwall formation does not take place from the gas phase in these liquidlike experimental conditions. It involves rearranging atomic bonds of amorphous carbon induced by the reactivity of the hot hydrothermal fluid and the enhanced mobility of carbon clusters.

In summary, amorphous carbon transforms into pristine multiwall nanotubes as a result of hydrothermal treatment at 800 °C and 100 MPa. The purity and good quality of nanotubes obtained by hydrothermal treatment make hydrothermal synthesis a promising method for the production of multiwall carbon nanotubes or other graphitic nanocarbons.

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