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Synthesis and characterization of amorphous carbon nanowires

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By heating a pressed tablet of graphite powder mixed with nickel in a quartz tube mounted inside a high-temperature tube furnace at 1200 °C, amorphous carbon nanowires were formed on the inner wall of the quartz tube near a copper cooling finger. Bright-field images of transmission electron microscopy show that the diameters of the nanowires are around 40 nm. Selected-area electron diffraction and Raman study reveal that the nanowires have an amorphous structure. © *1999 American Institute of Physics.* [S0003-6951(99)05045-7]

Nanoscale carbons, such as C_{60} (Refs. 1 and 2) or fullerenes,[3] nanotubes,[4] and onions,[5,6] have stimulated great interest among scientists. In terms of chemical bonding, all these carbon nanoscale materials possess sp^2 hybridized bonds.[7] Besides the sp^2 bond, *sp* and sp^3 are the other two types of C–C bonds in carbon materials.[8] The sp^2 bond corresponds to the graphite material. The *sp* and sp^3 correspond to carbyne and diamond bonding, respectively. Carbon nanotubes can be conceptualized as cylinders rolled from a graphite sheet and capped at both ends by hemispheres of fullerenes. They are hollow one-dimensional (1D) nanoscale materials possessing sp^2 bonds. The 1D materials with sp^3 bonds are particularly interesting since they correspond to diamond-like nanowires. Although this material has not been synthesized, nanoscale material with sp^2 and sp^3 bonds is also of interest. This sp^2/sp^3 material corresponds to amorphous carbon nanowire (CNW). In general, amorphous carbon material contains a highly disordered network of carbon atoms that are predominantly sp^2 bonded and more than 10% sp^3 bonded.[9] CNWs have not been reported so far. In this letter, we report the synthesis of CNWs by a thermal evaporation technique.

The evaporation apparatus used in the present experiment is similar to that used to synthesize Si nanowires (SiNW).[10,11] 8 g of graphite powder (mean size: 30 μm, purity: 99.85%, impurities: O) mixed with 0.1 wt % Ni powder was pressed into a tablet by a hydraulic press at room temperature. The tablet was then put into a quartz tube mounted inside a high-temperature tube furnace. After pumping down to a pressure of 4×10^{-2} Torr, high-purity argon (99.99%) was then passed through the quartz tube at a flow rate of 50 sccm near atmospheric pressure. The quartz tube was then heated to 1200 °C and kept at this temperature for 24 h. A little black soot was collected from the inner wall of the quartz tube near the copper cooling finger. A Mo grid for transmission electron microscopy (TEM) observation was put in advance inside the quartz tube at a position where the soot was expected to deposit. After removal from the tube, the grid was simply blown by a stream of nitrogen to remove the loosely bound particles and then observed directly with TEM (Philips CM20).

Figure 1(a) shows a TEM bright-field image of the nanowires. The diameters of most nanowires are around 40 nm. Some nanowires with diameters less than 10 nm can also be seen from this image. Unlike carbon fibers which are straight,[12] these nanowires are smooth and curvy. The inset in Fig. 1(a) gives a selected-area electron diffraction (SAED) pattern taken from an individual nanowire. The diffuse diffraction ring clearly shows that the nanowire is amorphous.[13] It is noticeable that the pattern differs from that of carbon

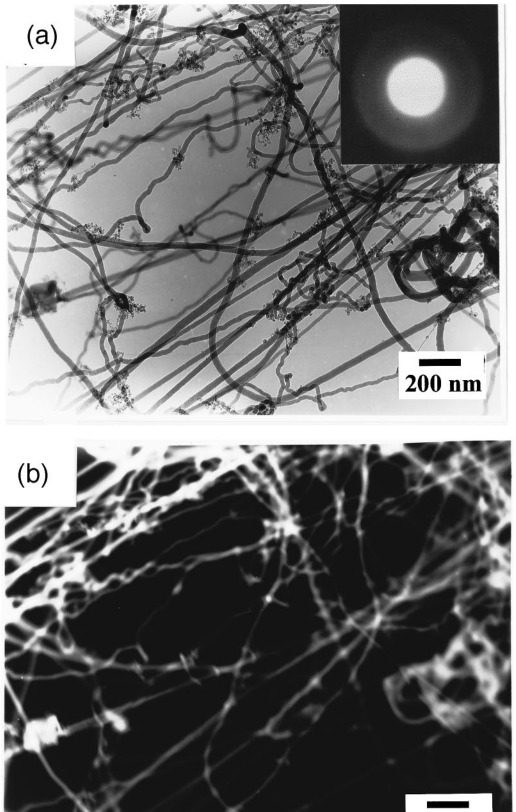

FIG. 1. Morphologies of the carbon nanowires and SAED pattern. (a) TEM bright-field image. The inset is the SAED pattern of a single nanowire. (b) TEM dark-field image.

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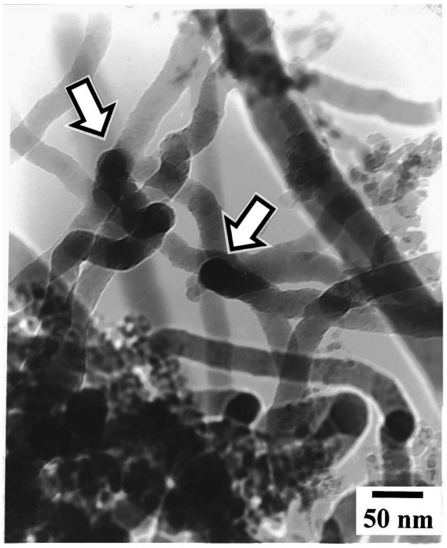

FIG. 2. TEM micrograph of the cross section of the nanowires.

nanotubes, in which several diffraction spots of $(hk0)$ appear in the pattern.[4,14] Figure 1(b) shows the corresponding dark-field image of the same region in Fig. 1(a). All nanowires have a bright contrast which is opposite to that in Fig. 1(b). The complementary contrast of Figs. 1(a) and 1(b) further supports that the nanowires are not crystalline.

As the nanowires change their growth directions, their cross section can be observed at the turning points which are marked by arrows in Fig. 2. It can be seen from the image that the nanowires have a circular solid cross section. This is a common characteristic of nanowires, such as SiC nanowires[15] and Si nanowires.[16,17]

Raman spectroscopy offers an effective method to identify the structure of carbon materials. We used a Renishaw 2000 micro-Raman system with 1 cm^{-1} resolution and 0.4 cm^{-1} reproducibility to study the nanowires. The excitation source was the 514.5 nm line of an argon-ion laser with a spot size of 10 μm in diameter and a power of 4 mW. The measurement was performed at room temperature. The Raman spectrum, shown in Fig. 3, revealed the characteristic bands centered at 1352 and 1586 cm^{-1}, which are the typical Raman peaks of amorphous carbon materials.[18]

Metallic catalysts (Ni) were found to play an important role in the growth of the nanowires. CNW could not be formed without Ni. The diameters of the nanowires were dependent on the concentration of Ni powder in the tablet. This phenomenon can be seen in Fig. 4. When the concentration of Ni was high enough (1 wt %), irregular shapes of nanoparticles were observed on the tips of the nanowires. These nanoparticles are composed of C and Ni as detected by energy-dispersive x-ray (EDX) spectroscopy mounted on the TEM. It should be noted that nanowires with smaller diameters have no catalyst balls on the tips (pointed to by the arrow in Fig. 4). When the concentration of Ni in the graphite powder is below 1 wt %, the nanowires are of a smaller diameter and the metallic particles were less abundant. We speculate that the small-diameter nanowires might also have metallic particles on their tips initially. The disappearance of the metal particles was due to a metal-consuming process during growth, so that the size of the metallic ball shrinks gradually as the nanowire grows in length.

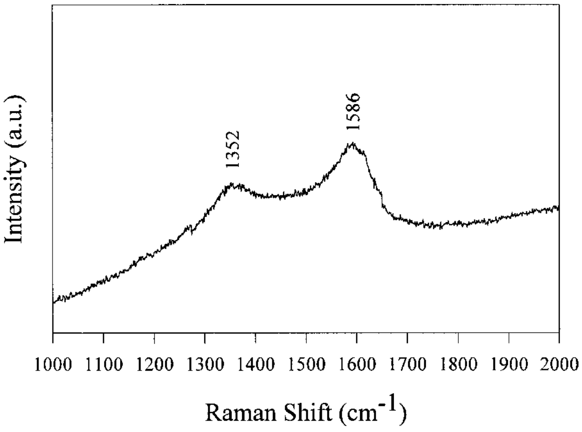

FIG. 3. Raman spectrum of the carbon nanowires.

FIG. 4. TEM image of metallic catalysts on the tips of the nanowires.

Baker[19] reported the gasification of carbon using Pt catalysts, and discussed the formation of carbon whiskers. Similarly, a CO-assisted growth model of carbon nanowires is proposed in this work, which is schematically shown in Fig. 5. In this model, graphite reacts first with the oxygen or water trapped in the graphite tablet at high temperature:

$$2C+O_2\rightarrow 2CO,$$

and

$$C+H_2O\rightarrow CO+H_2.$$

Then, the CO molecule was carried by the Ar gas to the colder finger where it decomposes into graphitic atoms and carbon dioxide molecules at the surface of the metallic catalyst:

$$2CO\rightarrow C+CO_2.$$

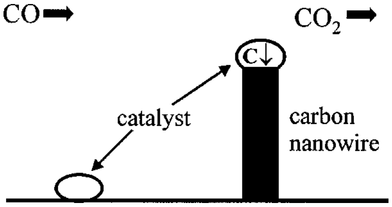

FIG. 5. CO-assisted growth model of amorphous carbon nanowires.

The gaseous CO_2 was then evacuated by the mechanical pump. The temperature of the colder finger was about 100 °C. The temperature of the substrate where CNWs grew was between 800 and 900 °C. The Ni nanoparticles could transport to the substrate possibly due to the following reaction:

$$\mathrm{Ni}+\mathrm{CO}\rightarrow\mathrm{Ni(CO)_4},$$

since the product $Ni(CO)_4$ is volatile. The graphite atoms entered the catalyst solution and joined the carbon nanowire at the other edge of the solution according to the vapor–liquid–solid (VLS) growth mechanism.[20,21] With the help of CO as an intermediate product, the whole growth process can be sustained. This growth mechanism is supported by the sintering experiment of the tablet. After sintering at 1200 °C for 72 h, the tablet was put into another quartz tube and the thermal evaporating experiment was repeated. However, no carbon nanowires could be obtained. In this case, nearly all the oxygen trapped in the tablet was removed by sintering at high temperature for a long time. So the intermediate material CO could not be formed and the growth process could not start.

In conclusion, amorphous carbon nanowires with diameters around 40 nm have been synthesized at 1200 °C by thermally heating graphite mixed with a Ni catalyst. The diameters of some nanowires are smaller than 10 nm. SAED and Raman study show that these carbon nanowires are in an amorphous state. A CO-assisted growth model is proposed to explain the growth process. The experimental results provide a kind of nanoscale carbon material synthesized by simple thermal evaporation.

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