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Synthesis of carbon nanotubes from bulk polymer

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Carbon nanotubes have been synthesized by heat treating the polymer at 400 °C in air which was obtained by polyesterification between citric acid and ethylene glycol. Transmission electron micrographs and an electron diffraction pattern showed the formation of carbon nanotubes. The diameter of the tubes ranged from 5 to 20 nm, whereas the lengths were less than 1 μ m. © 1996 American Institute of Physics. [S0003-6951(96)04528-7]

The recent discovery of carbon nanotubes¹ has stimulated intensive scientific investigations aiming at elucidating the formation mechanism,²⁻⁶ properties,⁷⁻⁹ and potential applications^{10–14} of the new material. Clearly, experimental tests for understanding of the unique properties, as well as the technological applications, demand a large quantity of the material. By far the most successful way to date for producing carbon nanotubes is the arc-discharge method.¹¹⁻¹³ The following typical experimental conditions must be controlled in the arc discharges to produce nanotubes efficiently; the current density, the interelectrode distance, and the pressure of inert gas filled in the discharge chamber. However, it is relatively expensive, and only a small quantity is formed, because the carbon-arc experiments are done with the low yield in a closed reaction vessel through which an inert gas flows at a controlled pressure. Carbon nanotubes have also been prepared by the plasma decomposition⁶ of benzene in a chamber filled with a gas mixture of Ar/He at a pressure of 50 Torr or the high-temperature (>600 °C) catalytic decomposition^{2,15} of organic vapors such as acetylene or benzene on a metallic catalyst such as Co, Fe, or Ni in N₂ and H₂ gases. The experimental complexity and high capital equipment required for the processes make carbon nanotubes expensive. If carbon nanotubes are ever to achieve widespread application, some simple and inexpensive fabrication route must be found. One possibility is to introduce a chemical route using polymers, which mainly consist of carbon. The essential point is that the bonds between the carbon and other elements can be removed by simple thermal treatment. We have attempted to heat-treat the polymer obtained by polyesterification between citric acid and ethylene glycol. Here we report that carbon nanotubes can be formed by heat treatment of polymer in air.

Carbon nanotubes were synthesized as follows. One mole of anhydrous citric acid (HOOCCH₂C(OH) (COOH)CH ₂COOH) was first dissolved into 4 mole of ethylene glycol (HOCH₂CH₂OH). The mixture was stirred for 2 h at 50 °C until it became transparent. The pale yellow solution thus prepared was heated at 135 °C for 5 h to promote polymerization and remove excess solvents. With continued heating at 135 °C, the solution became more viscous, and gelation occurred. The resulting gel was a transparent brown resin. Charring the resin at 300 °C for 2 h in an electric furnace resulted in a black solid mass, which was lightly ground into a powder with a Teflon rod. The powder thus obtained is referred to as the "precursor" hereinafter. The precursors was heat treated at 400 °C for 8 h in air on an Al_2O_3 boat followed by natural furnace cooling to room temperature. The samples were dispersed in ethanol, placed on a microgrid and observed using a transmission electron microscope (JEM-2010F, JEOL) at 200 kV.

The general morphology of the samples obtained by heat





FIG. 1. (a) Transmission electron micrograph showing bundles of carbon nanotubes. (b) Transmission electron micrograph showing an enlarged carbon nanotube.



FIG. 2. Electron diffraction pattern taken from a multishell nanotube about 10 nm in diameter.

treatment of the precursor at 400 °C for 8 h is shown in Fig. 1. The tube-like samples had the structures reported by Iijima:¹ multiwalled cylindrical nanotubes. The diameter of the tubes in our samples ranged from 5 to 20 nm, whereas the lengths were less than 1 μ m. The spacing between tube walls was about 0.34 nm. This well agrees with the wall separation of conventional multiwalled nanotubes. Figure 2 shows an electron diffraction pattern taken from a multishell tubule. The ring-like patterns originated from $h \neq 0$ spots, and the spots indicated by the arrows corresponded to 0 0 2n, as was found previously for conventional carbon nanotubes.¹ The tip shapes were similar to the tips of the tubes formed by arc-discharge method, as shown in Fig. 1(b). These results indicate that carbon nanotubes form by the present method. Besides the tubes, we also observed small carbon graphitic particles and amorphous sheet-like carbons.

The question remains what the mechanism for the growth of the nanotube is. The fact that nanotubes have been found by heating the polymer at 400 °C indicates that the treatment temperature is critical for their formation. We assume that there exist several kinetically competing processes such as the reactions forming CO, CO_2 , nanotube, graphitic particles, and amorphous sheet-like carbons during the heat treatment. At 400 °C carbon nanotubes were successfully

synthesized in spite of the existence of other competing reactions. The decomposition of polymer might generate dangling bonds of carbon at the temperature, then they will be reconstructed. Thus, nanotube growth seems to take place as a nonequilibrium reaction during the processes.

The ability to simply produce carbon nanotubes is of importance in materials science and applications. Furthermore, it is noteworthy that carbon nanotubes can be formed by the heat treatment of the polymer in air. Thus, such a simple method makes the overall process more feasible and enables us to mass-produce nanotubes. We confirmed that carbon nanotubes could also form by heat treatment of the polymer even in a vacuum chamber. Therefore, quantity and quality of nanotubes would be controlled by the vacuum state or inert gases under atmospheric pressure. The fact that the nanotubes can be formed by the mild heat treatment without electrons, plasmas, ions, metallic catalyst, etc. will provide a powerful clue to elucidate the formation mechanism and possibilities of the synthesis of new type fullerenes as well as those^{16,17} already known. In summary, the novel method is easily accessible to other researchers with an interest in the new materials, and should offer exciting opportunities for fundamental research and potential applications in fullerenes science.

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