Behavior of C$_{60}$ under Hydrothermal Conditions: Transformation to Amorphous Carbon and Formation of Carbon Nanotubes

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The behavior of fullerenes C$_{60}$ under hydrothermal conditions between 200 and 800°C, and under 100 MPa pressure, in the absence and in the presence of nickel is reported. The highest temperature of fullerene stability in water was 400°C after a 48-h-long treatment. Increasing the temperature and/or time of the hydrothermal treatment resulted in transformation of fullerene to amorphous carbon. At 700°C, high-quality open-ended multiwalled carbon nanotubes were formed in the vicinity of nickel particles. These nanotubes typically had an outer diameter of 30–40 nm and a wall thickness of 5 nm, with a graphitization level similar to that of carbon nanotubes prepared by chemical vapor deposition. The potential for large-scale synthesis of the carbon nanotubes by the hydrothermal technique is discussed. Since the present study was conducted under conditions which are common in the geological environment, our results imply that carbon nanotubes may form in natural hydrothermal systems. © 2001 Academic Press

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1. INTRODUCTION

Fullerenes (1) and fullerene-related materials, such as carbon nanotubes (2), have many potential applications and thus have attracted great interest of researchers all over the world. Fullerenes can be synthesized under extreme conditions, which rarely occur in nature, for example the electric arc method (3), carbon vaporization by pulsed lasers or in focused sunlight, direct inductive heating of carbon, or sooting hydrocarbon flames (4). The major synthesis routes for carbon nanotubes are the carbon arc method (5), laser ablation (6), and chemical vapor deposition (CVD) (7–14). All these techniques require high temperatures (usually at least 700–800°C for the nanotubes and 1000°C for the fullerenes), vacuum systems, gas flow, and complicated equipment. Yields are relatively low and the products often require purification.

With the current synthesis of fullerenes and carbon nanotubes being still very expensive and in the absence of known large-scale natural deposits of these carbon allotropes, their low-temperature, high-yield synthesis would be of great scientific and technological importance. Carbon nanotubes have been synthesized by electrolysis in molten salts (15). It has also been shown that amorphous carbon (16) and even diamond (17) can be prepared under hydrothermal conditions. Hydrothermal synthesis of carbon filaments, including well-aligned arrays on a substrate (18), demonstrated the potential of the hydrothermal technique for growing complex carbon structures. However, these filaments contained periodic conical cavities and were thicker than typical carbon nanotubes (18). Taking into account the advantages of hydrothermal synthesis in materials processing (19, 20) and the fact that various forms of hydrothermal carbon can be prepared in the temperature range of 300–800°C (100–140 MPa) (16, 17), this method seems to be potentially very promising for synthesis of the new carbon allotropes.

It is also worth mentioning that interactions between fullerenes/nanotubes and water have recently attracted attention due to efforts to increase the efficiency of extraction/purification of these carbon allotropes. Therefore, a study of the hydrothermal behavior of the fullerenes and the carbon nanotubes could give unique information about their formation/stability/transformation conditions, which is of great importance for mastering purification and synthesis techniques of these materials. Moreover, such a study could be very useful for geologists looking for natural

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deposits of fullerenes and carbon nanotubes, because naturally occurring hydrothermal systems are widespread in the Earth's crust.

2. EXPERIMENTAL

Fullerene powder (C$_{60}$, purity 99.95%, Science Laboratories Co., Japan) was used in all experiments. Small samples of this powder (≈ 0.020 g) were inserted into golden capsules of 3 mm diameter (volume of ≈ 0.1–0.2 cm^3), which were subsequently filled with double-distilled water. The capsules were then sealed, placed into autoclave tubes (Tuttle-Roy type), and heated at 200, 400, 500, 600, 650, 700, 750, and 800°C for periods between 20 min and 48 h under 100 MPa pressure. Water was used as the pressure transfer medium. The nickel powder (purity 99.8%, Nilaco Co., Japan) was added to some capsules in the amount of 3 wt%. The Ni-containing capsules, where amounts of water were between 30%–100% (by weight), were treated at 400, 500, 600, and 700°C for 168 h under 100 MPa pressure. After the synthesis, the autoclave tubes were rapidly quenched in water. All the hydrothermal experiments were conducted at the Tokyo Institute of Technology. Materials were characterized at the Tokyo Institute of Technology by X-ray diffraction (XRD, 40 kV/40 mA, CuKα radiation, MAC Science Co. Ltd., Tokyo, Japan) and by Raman spectroscopy. A Raman spectrometer (T64000, Atago-Jobin Yvon, France-Japan) with an Ar$^+$ laser with an excitation wavelength of 514.5 nm has been used. The laser power was low to avoid transformation of the fullerenes to amorphous carbon during the measurements. The materials were characterized also by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) at the Research Resources Center of the University of Illinois at Chicago. The FESEM used was a JSM-6320F with magnification up to 500,000 $\times$. High resolutions at low accelerating voltages are possible with this instrument due to its objective lens design. The microscope is also fitted with a Noran Voyager EDX system with a light element X-ray detector analyzer, which was used for elemental analysis of nanotubes. The TEM used was a JEOL 3010 (300 kV) with a lattice resolution of 0.14 nm (point resolution 0.17 nm).

3. RESULTS AND DISCUSSION

Selected Raman spectra of the hydrothermally treated fullerene powders are shown in Fig. 1. The Raman spectrum denoted "as received" corresponds to the fullerene powder, which did not undergo any hydrothermal treatment. This spectrum is characteristic of C$_{60}$, showing clearly all 10 Raman-active modes (21). Raman spectra of the C$_{60}$ acquired after the hydrothermal treatments in pure water at 200–400°C (0.3–48 h) were almost identical to as-received
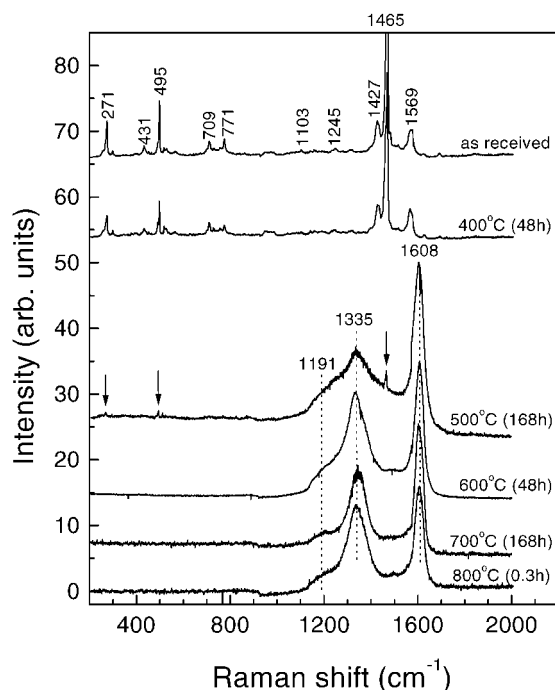

FIG. 1. Selected Raman spectra of the C$_{60}$ powder after hydrothermal treatments in water with or without Ni, under 100 MPa pressure. The temperature and duration of the treatments are marked. Arrows indicate weak C$_{60}$ bands. Amorphous carbon bands at 1608 cm^{-1} and 1335 cm^{-1}, as well as a shoulder band at 1191 cm^{-1}, are marked. All other bands originate from C$_{60}$.

C$_{60}$, indicating that the C$_{60}$ was stable under hydrothermal conditions in this temperature range for these times, as shown in Fig. 1 (in this context the word "stable" is not used in a thermodynamically rigorous sense). In the Raman spectra acquired from the fullerenes hydrothermally treated at 500°C (168 h), or at higher temperatures but for shorter times, e.g., at 600°C (18 h) or 700°C (0.3 h), new bands appeared in addition to weakening of C$_{60}$-derived bands. Two strong and broad bands at about 1335 cm^{-1} and 1608 cm^{-1} can be ascribed to amorphous carbon (16). These positions of bands of amorphous carbon (downshifted D-band and up-shifted G-band) are typical for hydrothermally formed carbon. A shoulder band at about 1200 cm^{-1} has been observed in hydrothermally formed carbon but its origin is not clear. After hydrothermal treatment at 600°C (48 h), 700°C (168 h), or 800°C (0.3 h), the Raman spectra did not show any fullerenes, demonstrating that C$_{60}$ was completely transformed to amorphous carbon (Fig. 1). XRD patterns of the hydrothermally treated fullerene powders supported the Raman spectra. New broad peaks indicating transformation of the fullerenes were observed at 24.5° and 43.5° and could be ascribed to graphitic carbon. Both Raman spectra and XRD patterns of the C$_{60}$ hydrothermally treated in water under different

conditions show that, with increasing temperature and time of the hydrothermal treatment, the C_{60} fullerenes gradually transform to amorphous carbon. The highest temperature of their stability was 400°C after 48-h-long treatment under 100 MPa.

The C_{60} crystals were transformed during the hydrothermal treatment into amorphous carbon, some of which was graphitized (Fig. 2b), without any significant shape changes (Fig. 2a), but sometimes with visible etch textures. The fullerenes, which did not survive any hydrothermal treatment at temperatures higher than 400°C, are known to exhibit quite high temperature stability without H_2O. Molecular dynamic studies show that in the carbon-only system C_{60} is stable up to over 4000°C (22). In an inert gas atmosphere C_{60} crystals transform into amorphous carbon at 700–950°C (23). Our results indicate that water strongly accelerates transformation of fullerenes. The process of hydrothermal transformation of C_{60} to amorphous carbon is kinetically controlled; thus, longer hydrothermal treatments will shift the stability range to lower temperatures.

FESEM analysis of the fullerene crystals after hydrothermal treatment in the presence of nickel revealed formation of carbon filaments in the vicinity of the Ni particles (Fig. 3a). The filaments had a circular cross-section and their outer diameter was in the range of 30–120 nm. The wall thickness of the carbon filaments was in the range of 4–40 nm, which corresponds to a number of graphite layers of 10–100. Some of the filaments appeared to be high-quality open-ended multiwalled carbon nanotubes,
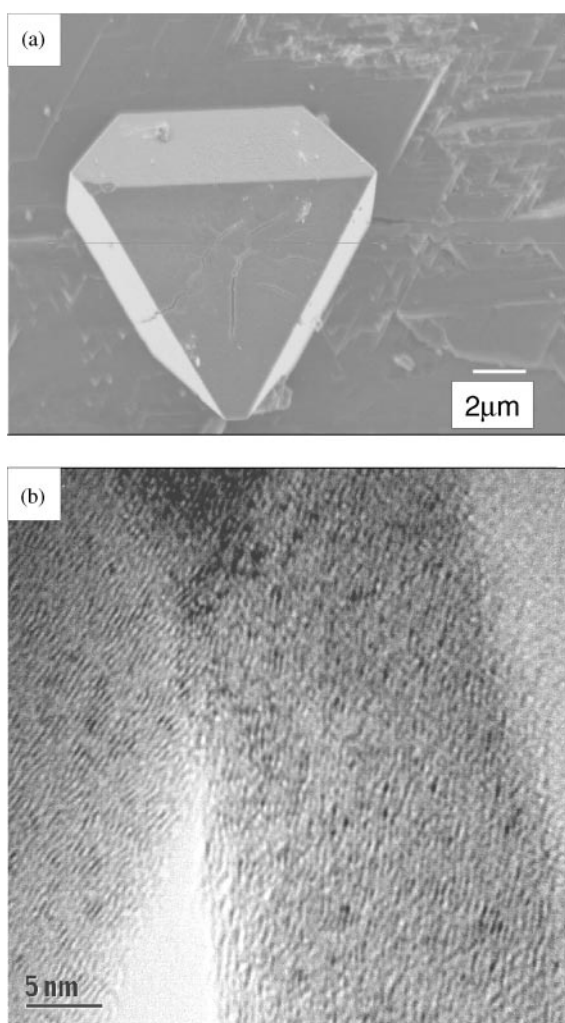

FIG. 2. (a) Typical FESEM micrograph of amorphous carbon formed during hydrothermal treatment (3% Ni, 30% water, 700°C, 100 MPa, 168 h), showing that the shape of the transformate is the same as that of the original C_{60} crystals. Some cracks and etch textures were observed. (b) TEM photograph of the amorphous and graphitized carbon formed in our experiments, revealing the presence of graphite layers.
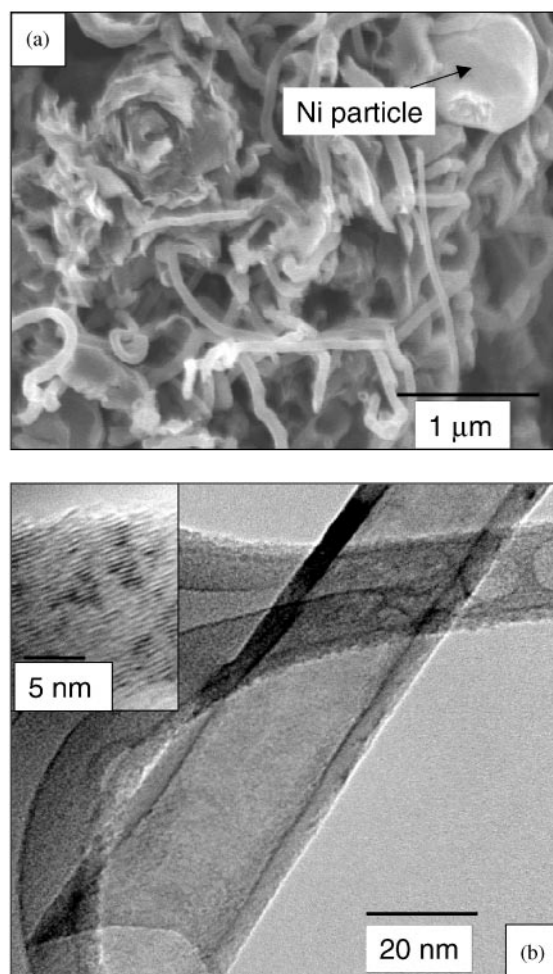

FIG. 3. (a) FESEM photograph showing the carbon filaments in the vicinity of a Ni particle. (b) TEM micrographs of typical carbon nanotubes produced by hydrothermal treatment of C_{60} with 3% Ni, 30% water at 700°C for 168 h under 100 MPa pressure. The inset shows graphite fringes in the nanotube wall.

typically with an outer diameter of 30–40 nm and a wall thickness of 5 nm (Fig. 3b). The high-resolution TEM shows well-ordered but not ideal graphite layers in the wall of the nanotube (Fig. 3b). Generally, there was no obvious or consistent connection of the tubes to nickel particles. In some cases, lattice fringes were inclined relative to the tube longitudinal axis, causing helicity. It is not clear whether the nanotubes were formed directly from C$_{60}$ or from the amorphous carbon, to which C$_{60}$ was transformed under the experimental conditions.

The carbon nanotubes synthesized hydrothermally in this work are open-ended and slightly thicker and moreover have a larger central cavity than typical carbon nanotubes prepared by the carbon arc method (typically 2–25 nm in diameter with an inner hollow diameter of 1–3 nm) (5). They do not exhibit as high graphitization level as the nanotubes prepared in the electric arc (5) but they have a quality comparable to that of carbon nanotubes prepared by the CVD techniques (10, 12–14). CVD synthesis of carbon nanotubes has recently attracted wide attention. This technique has the capability to fabricate at relatively low temperatures nanotube arrays with controlled alignment (10, 13, 14) on patterned catalysts (Ni, Co, Fe, etc.) (7, 13), which is of great importance for flat panel displays due to excellent field emission properties of carbon nanotubes (7, 14). While in the present work we do not provide direct evidence of nanotube alignment, we do demonstrate that hydrothermal processing may have potential similar to that of CVD in this regard. A capability to hydrothermally synthesize aligned carbon filaments has been confirmed elsewhere (18). In addition, deposition and patterning of layers of Ni as a catalytic material can easily be accomplished by the hydrothermal technique (or electrodeposition) on a variety of substrates, even at room temperature (24), which indicates that hydrothermal processing could be applied in this case for the entire device fabrication (24).

An important implication of our results is the possibility of large-scale hydrothermal synthesis of bulk carbon nanotubes. In the follow-up studies, polyethylene (25) and amorphous carbon (26) were used as much cheaper carbon sources under similar hydrothermal conditions. The hydrothermal synthesis of carbon nanotubes from amorphous carbon did not require the presence of metal catalysts. The quality of the carbon nanotubes prepared in those works was similar to ours, while the material cost was reduced significantly. The hydrothermal technique is known to give products with a much higher homogeneity than solid state processing and with higher density than gas or vacuum processing (faster growth rate) (20). Moreover, liquids accelerate diffusion, adsorption, reaction rate, and crystallization (nucleation and growth), especially under hydrothermal conditions (20). Under supercritical conditions, the fluid has some of the advantages of both a liquid and a gas. Diffusion in supercritical fluids is higher than that in liquids and the

viscosity is lower, enhancing the mass transport (19). These phenomena usually contribute to a significantly increased yield of synthesized materials, as compared to deposition from the gas phase (24). Large-scale, low-temperature, and thus low-cost synthesis of the carbon nanotubes would certainly be a great step toward serious applications of these materials.

The results of the present study also have geochemical implications. Hydrothermal solutions with a temperature ranging between 50 and well over 500°C are common and widespread in the Earth's crust (27). The hydrothermal fluids, which circulate below the Earth's surface, participate in a variety of geological processes by leaching, transport, and precipitation of their mineral constituents or by hydrothermal alteration of existing minerals (27). Taking into account these facts, the formation of carbon nanotubes under hydrothermal conditions, demonstrated in our experiments, implies the presence of natural carbon nanotubes in carbon-rich rocks, in the areas of the Earth's crust, which had been influenced by the hydrothermal fluids. It is worth mentioning that very recently Osawa *et al.* discovered carbon nanotubes in coals and carbonaceous rocks (28). Naturally occurring fullerenes (29–32) could also be significantly affected by the geological hydrothermal activities. Since the stability and transformation conditions of C$_{60}$ were established in our work, C$_{60}$ could be useful as a geothermometer. Our hydrothermal experiments with C$_{60}$ were conducted for a very short time on a geological scale (only hours as compared to years in the case of geological processes) but they suggest that the fullerenes might scarcely occur in nature, partially due to the low hydrothermal stability of C$_{60}$. However, while a fullerene mine still seems to be science fiction, the discovery of large-scale natural deposits of carbon nanotubes may be closer to reality.

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