Macroscopic synthesis and characterization of giant fullerenes

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Abstract

Thermal treatment of carbon soot produced by arc evaporation of nickel-filled graphite rods in 500 Torr of helium gives giant fullerenes showing characteristic IR, Raman, NMR and powder XRD signatures. Transmission electron micrographs show faceted structures with pentagonal, hexagonal and spherical shapes. The simplicity and similarity of the IR spectrum with those of smaller fullerenes suggest that the material is a form of large fullerenes. Chemical treatment of the material gives carbon onions. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Diverse forms of carbon have been the subject of intense research for the past several years. Chemistry, physics and materials science of fullerenes have been investigated thoroughly well over a decade [1]. Carbon nanotubes [2,3] and related forms have been the focus of recent interest due to their novel electrical, mechanical, chemical and spectroscopic properties as well as potential applications [4–11]. They have been characterized by a number of tools, dominant being transmission electron microscopy (TEM). From Raman spectra, it is possible to deduce the diameter and helicity of the nanotubes [12–14]. Carbon is also known to form other structures such as onions [15]. It is possible to convert one carbon form to the other and sometimes this could be achieved within the molecular carbon structures as has been shown recently by the conversion of amorphous carbon into diamond within onions [16]. Many

researchers have observed that arc discharge of carbon results in the formation of nanotubes, onions and several fullerene-like particles. The shapes of the formed carbon materials depend mainly on the growth conditions [1]. For structures having fewer number of carbon atoms, small closed molecules are more stable than the planar graphitic structure. Spherical shells have no dangling bonds and are stable even under electron bombardment [15,17]. In the case of three-dimensional graphite, a large number of dangling bonds leads to the instability of the structure and under extreme conditions new materials are formed. For example, intense electron beam irradiation of carbon nanoparticles with faceted shapes results in the formation of concentric graphitic spheres [18,19]. Under strong irradiation conditions or at high temperatures these concentric spherical shells are favored over tubule structures for small numbers of carbon atoms [18]. Room-temperature irradiation leads to a large number of defects whereas at 700°C, perfectly coherent shells are formed [20]. Annealing and self-compression of carbon onions

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under electron bombardment were also observed. Annealing nanodiamonds at temperatures of 1100–1500°C [21], exposing carbon soot to a plasma torch [22], and laser melting of carbon at a pressure of 50–300 kbar [23] result in the formation of carbon onions. Carbon soot on shock wave treatment leads to the formation of multilayer carbon shells [24]. The diversity and variety of carbon chemistry outlined above suggest that many other forms exist which could be the subject of future investigations. Herein we suggest the possibility of synthesizing larger fullerenes and onions on a macroscopic scale, which was recently encountered in the course of our investigations on metallocarbohedrenes [25].

2. Experimental method

While investigating the possibility of making metallocarbohedrenes in the solid state by a modified arc evaporation method [25], we decided to look at the presence of tubules, fullerenes and other forms of carbon in the soot. In the method finally arrived at, metal-filled graphite rods of 6 mm diameter (holes of 3 mm diameter were drilled for this purpose) were evaporated by an AC arc of 20 V and 100–200 A in an atmosphere of 500 Torr of helium. Most of the experiments were done with Ti-filled rods, but interesting observations pertaining to this Letter were made when the rods were filled with Ni. All the metals were of commercial quality powders. Both the electrodes used were similarly prepared. The apparatus was similar to a conventional arc evaporation set-up used for the preparation of fullerenes [1,26]. The chamber was originally evacuated to 10^{-2} Torr and was back-filled with helium at 500 Torr. The pressure was measured with a mercury manometer. After 10–15 min of evaporation, the soot, collected on a water-cooled copper vessel, was scraped off and made in the form of a pellet and was subsequently heated in air at $\sim$ 700°C for a period of 12 h. Almost all the carbon was oxidized and a black to brown residue was left behind. It was $\sim$ 1% of the original soot in weight. This was refluxed in nitric acid for $\sim$ 12 h and was filtered. The residue was washed repeatedly with water and was dried in an oven at 110°C. The yield was $\sim$ 0.1% of the original soot. Typically in one run, we got $\sim$ 10–20

mg of the product. It was grey-white in color. In absence of nickel, under the same experimental conditions, the yield was low but the products were the same as in the presence of nickel. This was confirmed by the infrared spectrum. Both samples, namely after heat treatment (**a**) and subsequent reaction with HNO$_3$ (**b**), were subjected to analyses.

Transmission electron microscopy was done in a 200 kV JEOL JEM 2000EX microscope at Purdue University. IR spectra were obtained with a Bruker IF 66V FT–IR spectrometer. Raman spectra were measured with lab assembled Raman microscope having a 532.5 nm excitation from an argon ion laser. X-ray powder diffractograms were recorded with a Siemens instrument with Cu Kα radiation. ^{13}C-NMR (MAS 2.2 kHz) spectra were obtained with Bruker 300 MHz instrument. The NMR spectrum of (**b**) could not be measured due to an inadequate sample. A VG ESCALAB MK II spectrometer with Mg Kα radiation was used for XPS studies.

3. Results and discussion

Transmission electron micrograph (Fig. 1) of sample **a** shows structures of various kinds. Different shapes such as pentagons (inset), hexagons (a) and
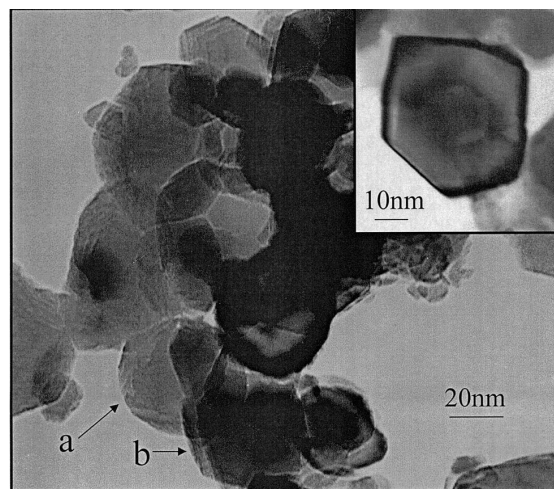

Fig. 1. TEM images of soot after thermal treatment showing faceted structures of giant fullerenes. Spheroidal (a) and hexagonal (b) structures are marked. Inset shows a pentagonal structure which also demonstrates the three-dimensionality of the object.

spherical (b) structures are observed. The three-dimensional nature of the object is quite clear in TEM. Some structures indicate that they could be similar to onions. According to the carbon nucleation scheme proposed by Kroto et al. [27], C_{240} and C_{540} could exist in pentagonal and hexagonal shapes, respectively. The occurrence of pentagonal, hexagonal, and spherical structures is in agreement with theoretical predictions also. According to a calculation [28], when I_h–C_{240} is viewed from C_2 and C_3 symmetric axes, faceted structures are seen. When viewed along the C_5 axis, it is spherical. Therefore, the presence of different shapes in TEM is due to the observation of higher fullerenes from a different axis. EDAX analysis of the selected regions did not show nickel.

The soot after acid treatment (sample **b**) shows onion structures (Fig. 2). Several onions with diameters in the range of ∼ 20 nm are seen in Fig. 2A. An expanded onion structure (Fig. 2B) shows a cavity of ∼ 2.0 nm diameter. The interlayer spacing of the graphitic planes in the onions is ∼ 0.3 nm. The different types of structures (pentagon, hexagon, and sphere) observed after thermal treatment (Fig. 1) were all converted to spherical onions after acid treatment. It is shown below that the material after thermal treatment and that after acid treatment have the same chemical nature. In certain regions, graphitic sheets of nanodimension were also observed (not shown). Thus it appears that irreversible conversion of molecular carbon to graphite can also occur chemically.

In Fig. 3A we show the FT–IR spectra of the soot after heating in air (a) and the material after the chemical procedure (b) in KBr matrices. Both the spectra are very similar, but different from that of tubules; no predicted frequencies of tubules are observed [29]. The spectra are also different from the experimental Raman spectrum of armchair tubules [12,14]. However, there are similarities with the infrared spectrum of fullerene, C_{60}, which shows four characteristic T_{1u} modes in the mid-IR region [1,30]. The C_{60} peaks are observed at 1430, 1136, 575, and 527 cm^{-1}. The intense peak around 1100 cm^{-1} can be assigned to C–C vibration mode. The peak around 1600 cm^{-1} can be assigned to –C=C– modes and the remaining peaks can be attributed to the cage vibrations similar to those of C_{60}. In closed-cage spherical fullerenes, it is shown that upon increasing
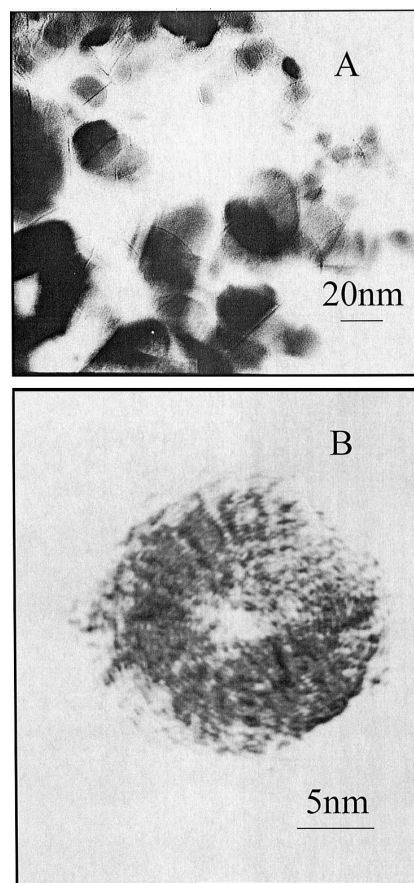

Fig. 2. (A) TEM image of the sample after acid treatment showing giant fullerenes or carbon onions. (B) An expanded view of an onion.

the cage dimension, new structures appear at frequencies above 1430 cm^{-1} [31]. Many of the degeneracies get lifted and the peaks cluster around the C_{60} vibration frequencies. All the peaks are broad with multiple structures, implying that there are different kinds of molecular species. Since the infrared spectrum is similar to that of C_{60} with less number of peaks, the formed higher fullerenes are highly symmetric in nature. The similarities of the two infrared spectra confirm that molecular structures of the two carbon samples are similar. Moreover, in the XPS investigations, the only elements observed were carbon and oxygen and therefore the vibrations have to be assigned to giant fullerenes.
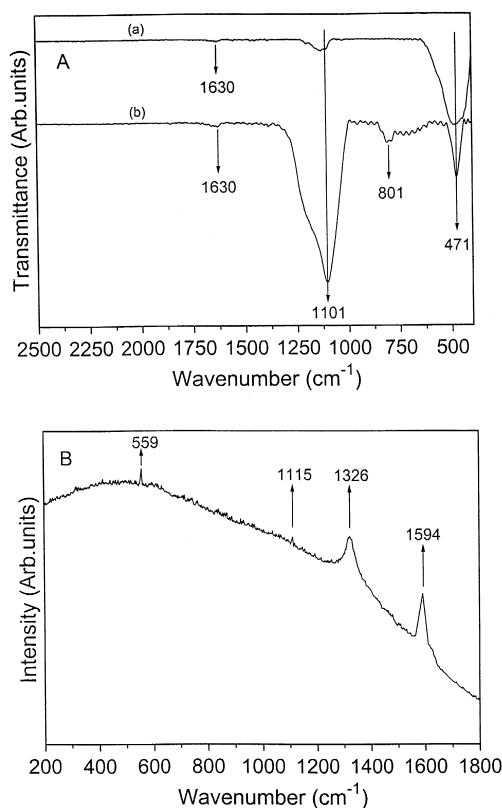
Fig. 3. (A). FT–IR spectra of sample **a** (a) and **b** (b). (B) Raman spectrum of chemically treated sample. The peak positions are labeled.

First-order Raman lines for carbon nanotubes are observed at 830, 1350, and 1590 cm^{-1} [1]. Second-order features are observed around 2950 and 2650 cm^{-1}. Depending on the nature of the tubes, whether single shell or multishell, drastic changes are seen in the Raman spectra. The Raman spectrum (Fig. 3B) of sample **a** shows a broad peak at 1594 cm^{-1}. There is also a broad peak centered around 1326 cm^{-1}. Two sharp lines with weak intensities at 1115 and 559 cm^{-1} are also present in the spectrum. In the case of highly oriented pyrolytic graphite, there is an intense peak at 1580 cm^{-1} [32] which has been assigned to a vibrational mode in which two neighboring carbon atoms in the graphite sheet move in opposite directions. In giant fullerenes, the same peak is shifted to ∼ 14 cm^{-1} and appears at 1594 cm^{-1}, probably due to the closed graphitic structure in them. The other band at 1326 cm^{-1} is also similar

to the carbon forms studied. In samples containing nanotubes [32] a similar band occurs at 1350 cm^{-1} which is attributed to the presence of nanoparticles in the soot.

The powder X-ray diffraction pattern of sample **b** is shown in Fig. 4. The sharp peak at $27.4 \pm 0.2°$ (2θ) corresponds to a d spacing of 0.32 nm ((002) reflection) which is consistent with TEM. This value is to be compared with the 0.335 nm interlayer spacing of graphite. For pure graphite, the peak occurs at 26.5° and for slags it is at 26.1°. Peaks at 44° (101) and 77° (110) are totally absent in both the thermal and acid-treated samples, suggesting that pure graphite and carbon slags are not present as impurities (*hkl* values in parentheses). For nickel carbide, an intense reflection is expected at 44° (2θ) which is not present in both the thermal and acid-treated samples. NiO peaks are, however, present in sample **a** (inset of Fig. 4). This shows that the Ni content is removed by the acid treatment and subsequent washing. The 19.6° peak of sample **a** may be compared with the ∼ 21.5° (222) peak of C_{60} [1]. These evidences again confirm that both **a** and **b** are composed of molecular carbon materials.
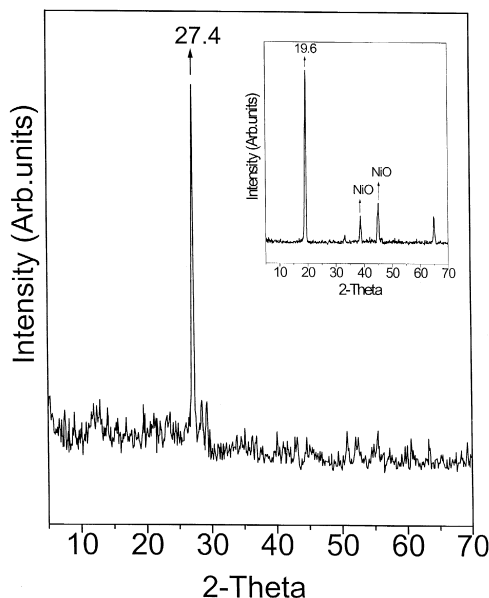

Fig. 4. Cu Kα powder X-ray diffraction pattern of sample **b**. The XRD pattern of sample **a** is shown in the inset. The impurity lines are indicated. The peak at 65° has not been identified.
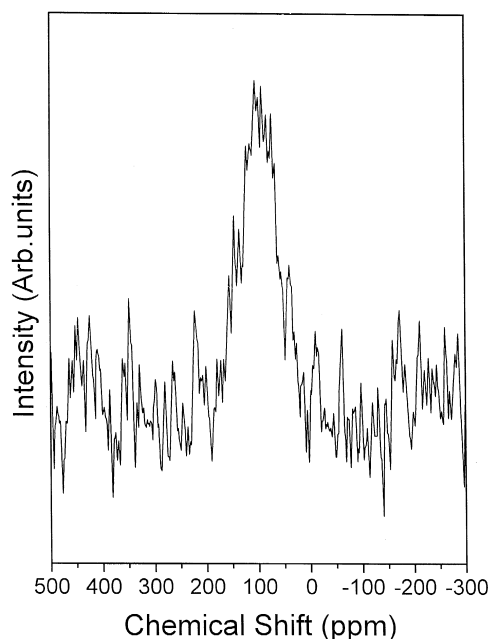
Fig. 5. Solid state ^{13}C-NMR of sample **a**.

studies show that the formed giant fullerenes have faceted structures. Infrared and Raman studies suggest that the material is molecular in nature and has high symmetry. Solid state NMR confirms the presence of sp^2-hybridized carbon atoms. Reaction of the sample with HNO$_3$ results in the formation of carbon onions and the graphitic layers are readily observable in XRD. TEM provides identical information. The mechanism of chemical transformation of large fullerenes to onions is unclear at the moment.

Solid state ^{13}C-NMR (Fig. 5) of sample **a** shows a broad band centered around 100 ppm. FWHM of this peak is 117 ppm. This peak is attributed to the presence of sp^2 carbons present in the higher fullerene. For pure graphite a band occurs at 179 ± 10 ppm [33]. The absence of a peak at 38 ppm implies that there are no sp^3 carbons as well as hydrocarbon impurities in the sample. In the case of solid C$_{60}$ a single narrow peak is observed at 143 ppm [1]. As an increasing number of benzenoid rings are incorporated into the fullerene structure, an upfield shift is observed (compared to C$_{60}$) [34]. It may be noted that the number of paracylene and corannulene resonances are the same in all fullerenes. In agreement with this, a broad band is observed at 130 ppm for nanotubes [35] which resembles the structure observed here. Since the molecules are likely to be non-rotating, spectral broadening is expected.

4. Conclusions

Large fullerenes are synthesized in macroscopic quantities by arc evaporation of Ni-filled graphite rods followed by heating of the collected soot. TEM

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