The Observation of Large Concentric Shell Fullerenes and Fullerene-like Nanoparticles in Laser Pyrolysis Carbon Blacks

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It has been shown that carbon blacks produced by iron carbonyl-catalyzed CO_2-laser pyrolysis of benzene (laser pyrolysis carbon blacks) are characterized by a two-level nanostructure, i.e., they consist of amorphous carbon nanoparticles 30−40 nm in size and fullerene molecules where the fullerenes are predominantly represented by C_{60}. Heat treatment of the blacks at 3000 °C causes restructurization with the appearance of fullerene-like multishell nanoparticles of ∼20 nm in size, higher fullerenes, and multishell fullerenes. Unlike classical fullerenes, which have a cage structure and are known to have been synthesized in a variety of sizes (C_{60}, C_{70}, C_{84}, C_{102}, etc.), multishell fullerenes have a cage-inside-cage structure. Direct transmission electron microscopy observation of the cage-inside-cage clusters shows the occurrence of at least three varieties: two-shell 14-Å-sized $C_{60}@C_{240}$, two-shell 20-Å-sized ($C_{240}@C_{560}$), and also three-shell 20-Å-sized ($C_{80}@C_{240}@C_{560}$).

Introduction

Carbon blacks can be produced by different techniques, low-tech and high-tech, varying from incomplete oxidation of hydrocarbons in flames to laser ablation of composite carbon-containing targets. The variety of synthesis techniques results in many morphological forms of carbon particles with diameters in a typical range of 10−100 nm.[1] In the laser pyrolysis method,[2] a powerful laser beam (usually a CO_2 laser) impacts a flow of a gas containing a carbon source component, such as a hydrocarbon, and a photosensitizer (such as SF_6 or C_2H_4), which absorbs laser irradiation and converts its energy into thermal energy. A black amorphous soot or "laser pyrolysis carbon black" is a product of the reaction.

Bi et al.[2] found that the carbon black formed by the iron carbonyl-catalyzed pyrolysis of benzene consists of globular amorphous nanoparticles of an average size of 30 nm. It was also shown in that work[2] that heat treatment at 2850 °C resulted in the particles losing their spherical shape and developing a new morphology composed of a polygonal outer shell and an empty hollow polygonal center.

Cauchetier et al.[3] reported that toluene extracts of carbon blacks produced by oxidative (i.e., in the presence of O_2 gas) laser pyrolysis of lower nonaliphatic hydrocarbons contain substantial amounts of C_{60} fullerene. The results of this work[3] suggest that the products of nonoxidative laser pyrolysis may also contain fullerenes. There are indications in the literature that high-temperature treatment may lead to the restructurization of lower fullerenes into higher ones, as was shown by Weber et al.[4] for the thermal treatment of arc-discharge soots.

Higher fullerenes, if they are formed, are of particular interest because their synthesis is usually very difficult and laborious. Thus only a few of these interesting carbon cage structures, such as C_{70}, C_{84}, C_{102}, etc., have already been synthesized, whereas many more giant fullerene varieties, such as C_{180}, C_{240}, and C_{560}, have been predicted theoretically only.[5] Recently, we briefly reported the first observation of two kinds of multishell fullerenes: two-shell $C_{60}@C_{240}$ and three-shell $C_{80}@C_{240}@C_{560}$ in the laser pyrolysis carbon black.[6]

In the present work, we report a detailed study of the nanostructure of both as-produced and thermally treated laser pyrolysis carbon blacks that comprise unusual types of nanoparticles and fullerenes, including another variety of multishell fullerene.

Experimental Section

A laser pyrolysis carbon black produced from benzene with the assistance of an iron carbonyl catalyst by the technology described in ref 2 was supplied by Nanogram Corporation. Typical values of the reaction parameters used in the synthesis were as follows: laser frequency, 945 cm^{-1}; laser intensity range, 100−180 W; chamber pressure, ∼300 Torr; and C_2H_4 flow rate, ∼300 sccm. The reactants $Fe(CO)_5$ and benzene were

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(1) Lahaye, J.; Prado, G. In *Chemistry and Physics of Carbon*; Walker, P. L., Ed.; Marcel Dekker: New York, 1978; Vol. 14, p 167.

(2) Bi, X. X.; Jagtoyen, M.; Endo, M.; Das Chowdhury, K.; Ochoa, R.; Derbyshire, F. J.; Dresselhaus, M. S.; Eklund, P. C. *J. Mater. Res.* **1995**, *10*, 2875.

(3) Cauchetier, M.; Armand, X.; Herlin, N.; Alexandrescu, R.; Morjan, I.; Petcu, S.; Voicu, I. *Fullerene Sci. Technol.* **1999**, *7*, 91.

(4) Weber, J. V.; Millon, E.; Kubler, B.; Theobald, J.; Muller, J. F. *J. Anal. Appl. Pyrolysis* **1994**, *29*, 1.

(5) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *Science of fullerenes and carbon nanotubes*; Academic Press: London, 1996.

(6) Mordkovich, V. Z.; Umnov, A. G.; Inoshita, T.; Endo, M. *Carbon* **1999**, *37*, 1855.

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Table 1. Comparison of the Results of the Present Work with that of Work[2] on Structural Properties of Laser Carbon Blacks

material	average particle size (nm)	wall thickness of hollow particles (nm)	interlayer distance (Å) by XRD	interlayer distance (Å) by TEM	concentric structure of particles	graphene sheet stacking ordering from XRD
			As-Produced			
Bi et al.[2]	30	–	3.7	3.8–4.2	yes	slight
this work	40	–	3.63	3.4	no	none
			Thermally Treated			
Bi et al.[2]	30	7	3.5	3.7	yes	none
This work	20	7	3.39	3.4	yes	significant

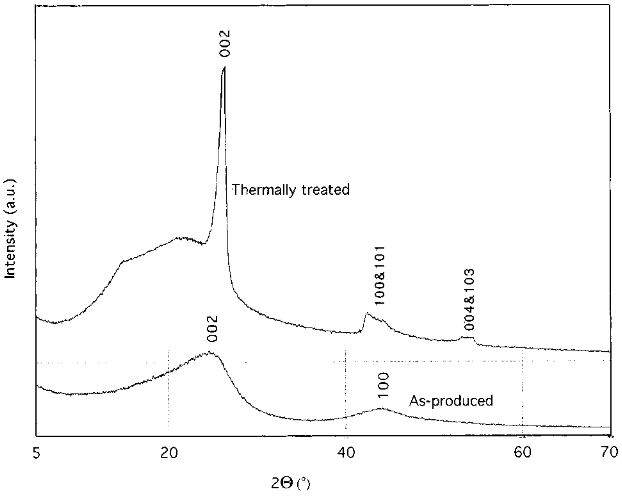

Figure 1. X-ray diffraction patterns (Cu Kα irradiation) of laser pyrolysis carbon black. The diffraction peaks are indexed on the basis of a convention for acetylene blacks.

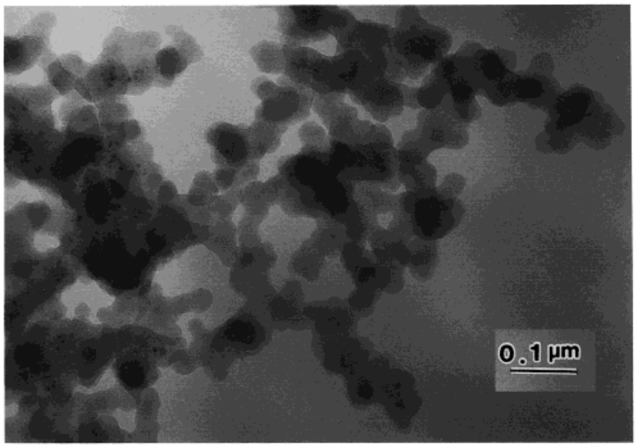

Figure 2. TEM image of as-produced laser pyrolysis carbon black.

introduced into the gas stream by bubbling C_2H_4 through a diffuser into a 2 mol % solution of $Fe(CO)_5$ in benzene.

Thermal treatment of the black for 1 h was performed in a closed graphite crucible in Ar gas atmosphere at 3000 °C. The product after thermal treatment was a black powder.

Vacuum sublimation was used to separate fractions of both as-produced and thermally treated blacks. The vacuum sublimation was performed by heating a sample in a tantalum metal boat at temperatures in the range of 600–1600 °C in a vacuum of 10^{-7} Torr. The resulting sublimated film was deposited onto a quartz glass substrate plate.

Transmission electron microscopy (TEM) was employed to study the material's structure. Also, X-ray diffraction (XRD), Raman scattering spectroscopy, X-ray photoelectron spectroscopy (XPS), and IR spectroscopy were used.

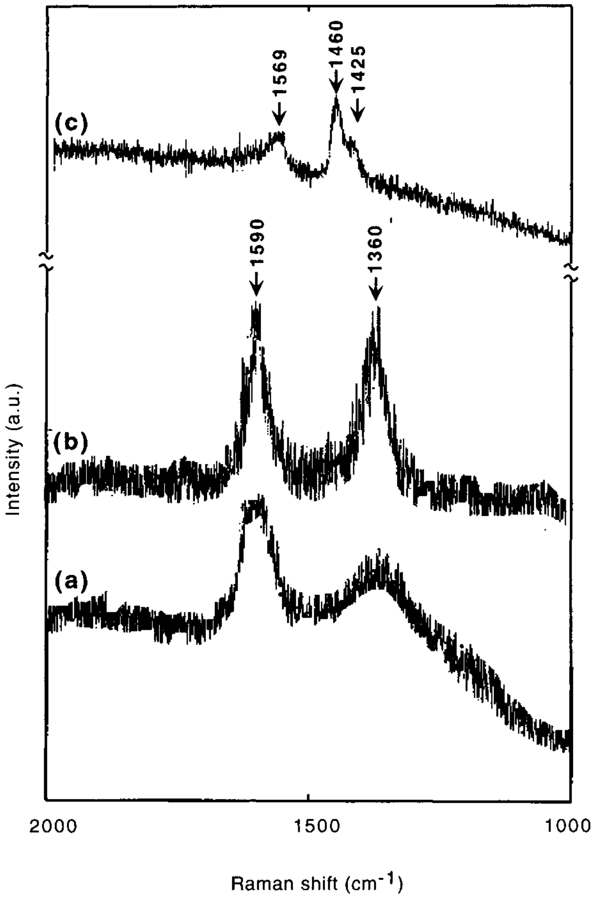

Figure 3. Raman spectra of laser pyrolysis carbon blacks: (a) as-produced powder, (b) thermally treated powder, and (c) film sublimated from the as-produced powder. Both powders show 1360 and 1590 cm^{-1} "disordered graphite" modes, whereas the film shows a typical triplet of a polymerized fullerene C_{60}.[5]

Results and Discussion

As-Produced Black. The X-ray diffraction pattern of the as-produced laser pyrolysis carbon black shown in Figure 1 is typical for highly amorphous graphite-like carbons and manifests the average interplanar distance of 3.63 Å. The diffractogram of Figure 1 is indexed according to the convention for acetylene blacks.[2] The absence of the (101) peak suggests no stacking ordering of graphene sheets. A typical lower-magnification TEM image of this carbon black is shown in Figure 2. Amorphous globular particles with an average size of 40 nm and with size variation limits of 30–80 nm are seen in this Figure.

These results are consistent with the data for a similar material reported by Bi et al.,[2] although there

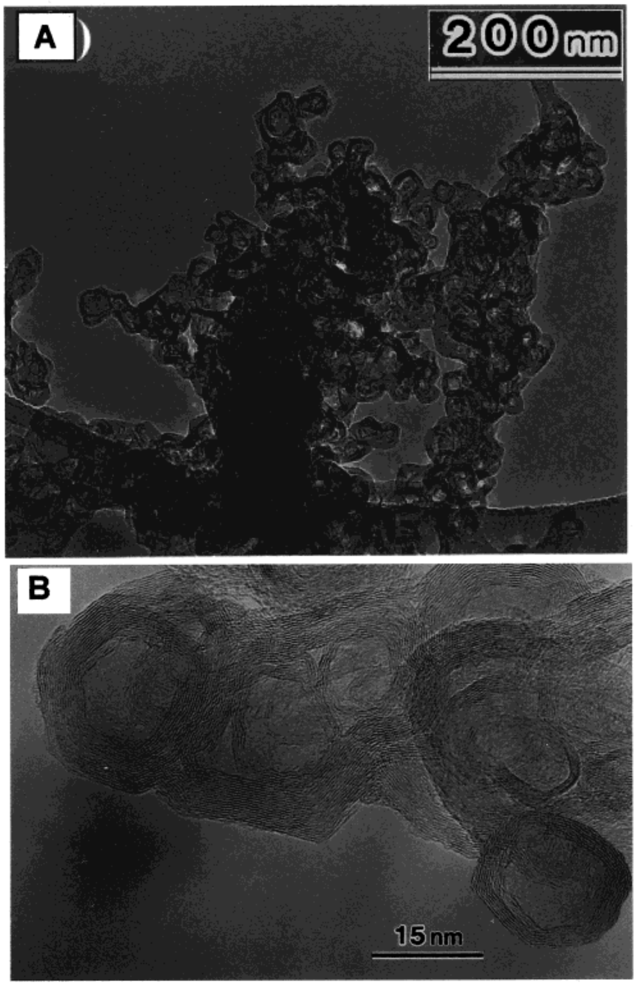

Figure 4. TEM image of thermally treated laser pyrolysis carbon black given at (a) lower and (b) higher magnification. Spherical and polygonal fullerene-like nanoparticles are seen.

are some differences concerning the observation of a concentric orientation of carbon atom layers and of stacking ordering in the X-ray diffractograms (see Table 1). These differences might appear because of variations in the parameters of the laser pyrolysis process; in particular, we observed slight variations of the average particle size for the samples that were reportedly produced with a different laser beam power.

Raman scattering spectra manifested two broad features at 1360 and 1590 cm^{-1}, which is typical for carbon blacks (see Figure 3a). The peak at 1590 cm^{-1} is identified with the well-known E_{2g} vibrational mode of graphite, upshifted by ∼10 cm^{-1} from the 1582 cm^{-1} position reported for single-crystal graphite.[7] The peak at 1360 cm^{-1} is identified with symmetry-forbidden modes associated with the maximum in the graphite density of states, activated by lattice disorder and/or small crystalline size.[7] Al though it is shown below in this paper that the as-produced blacks contain large amounts of fullerene C_{60}, no fullerene-corresponding peaks can be seen in Figure 3a, which is because of the much higher intensity of globular nanoparticle-related modes at 1360 and 1590 cm^{-1}.

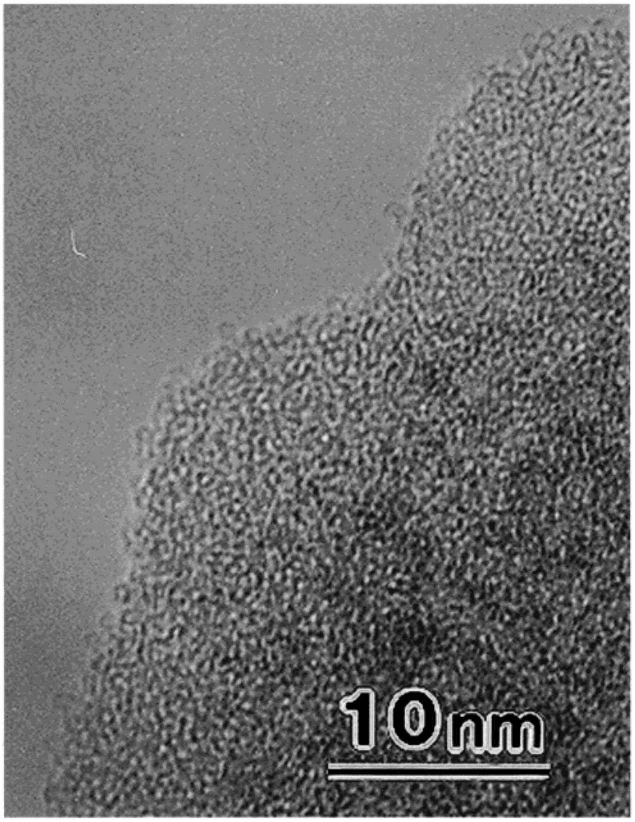

Figure 5. TEM image of the sublimated film obtained by vacuum evaporation of the as-produced laser pyrolysis carbon black. Numerous ring images of C_{60} fullerene molecules (separate rings of 7 Å in size can be seen at the edge of the film) fill the micrograph field.

Thermally Treated Black. After the thermal treatment of the sample, the X-ray diffraction patterns showed obvious signs of graphitization (see Figure 1), such as the appearance of the (104) and (101) peaks and also a change in width and position of the (002) peak. An interplanar distance of 3.39 Å was observed. A typical lower-magnification TEM image of thermally treated laser pyrolysis carbon black is shown in Figure 4. A variety of spherical and polygonal hollow fullerene-like nanoparticles can be seen in this figure. These nanoparticles are characterized by an average size of 20 nm and a size variation within the limits of 10−40 nm. The nanoparticle wall thickness is in the range of 10−30 monolayers (35−100 Å), while the observed interlayer spacing is 3.39 Å. Raman scattering spectra manifested the same features at 1360 and 1590 cm^{-1} as for as-produced blacks, although a decrease in line width due to increased ordering is obvious (see Figure 3b).

Although the phenomenon of the formation of hollow quasi-concentric microparticles is known for different carbon blacks,[2,8] the particles observed in this work are smaller and more perfect and rather resemble the "superfullerenes" recently found in the shungite mineral in Northern Russia.[9] A comparison with the results of Bi et al.[2] is shown in Table 1. The differences can easily

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[7] Kinoshita, K. *Carbon, Electrochemical and Physicochemical Properties*; Wiley: New York, 1998.

[8] Kasatochkine, V. I.; Loukianovitch, V. M.; Popov, N. H.; Tehmutov, K. V. *J. Chem. Phys.* **1960**, *37*, 822.

[9] Kovalevski, V. V. *Zh. Neorg. Khim.* **1994**, *39*, 31.

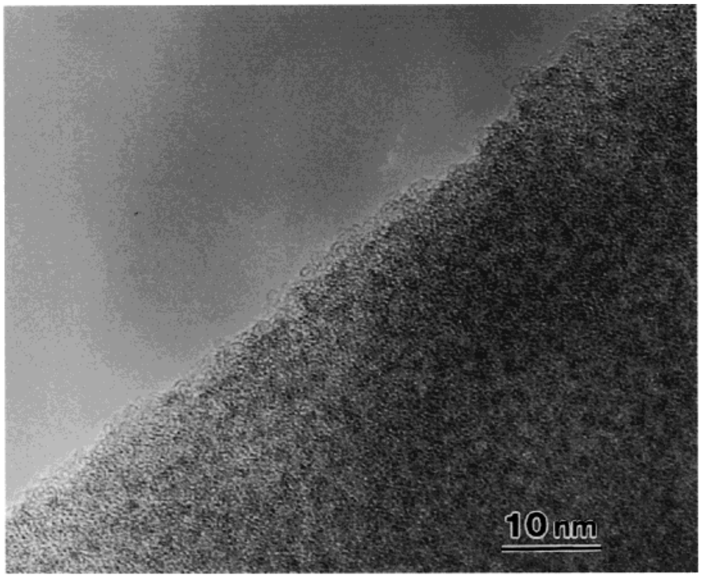

Figure 6. TEM image of the sublimated film obtained by vacuum evaporation of the thermally treated carbon black. Ring images of higher fullerenes fill the micrograph field.

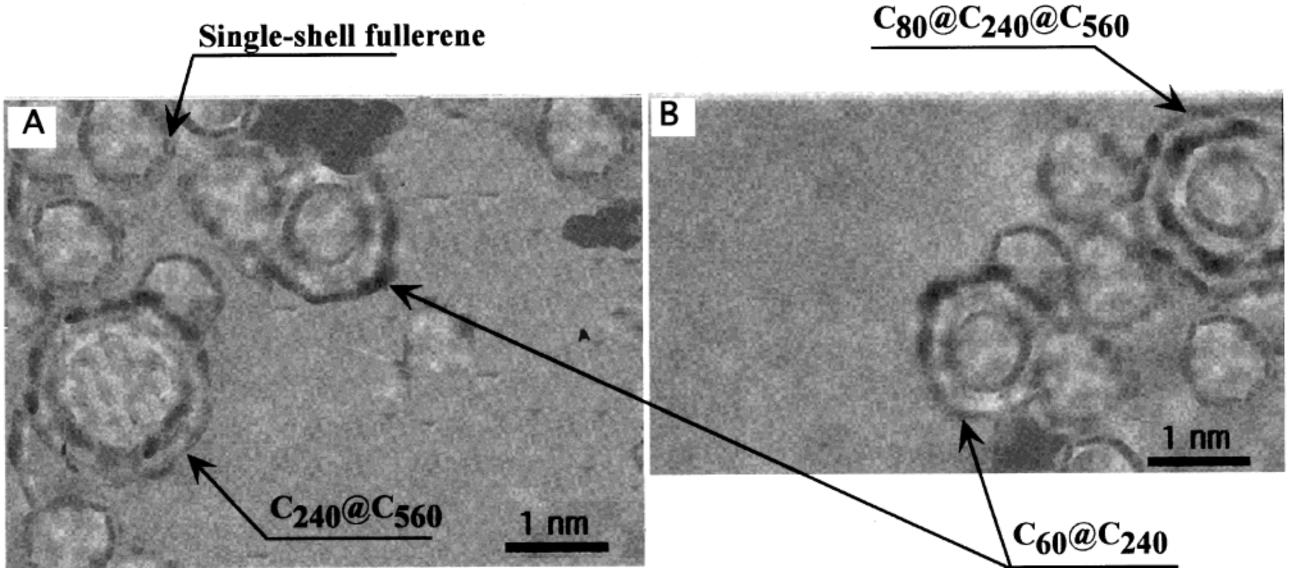

Figure 7. High-magnification TEM images of the sublimated film obtained by vacuum evaporation of thermally treated carbon black. Molecules of two-shell $C_{60}@C_{240}$ and $C_{240}@C_{560}$ are seen in the image a; two-shell $C_{60}@C_{240}$ and three-shell $C_{80}@C_{240}@C_{560}$ are seen in the image b, along with "ordinary" fullerene molecules.

be explained by the higher temperature of the thermal treatment (3000 °C in the present paper vs 2850 °C in the previous work),[2] which caused a higher degree of intraparticle ordering.

At the edges of some nanoparticles (see Figure 4), uneven matted areas can be seen, which suggests the presence of another nanoscale fraction, orders of magnitude smaller. The isolation of that smaller fraction from both as-produced and thermally treated carbon blacks is described below.

Sublimated Films. The separation of the smaller fraction might be accomplished throughan extraction/recrystallization technique. Indeed, we found that toluene extracts up to 50% of the as-produced carbon black (brownish solution is formed) and up to 3% of the thermally treated carbon black (a colorless solution is formed). However, the vacuum sublimation technique proved to be more convenient for small samples and handier for the preparation of thin films.

The sublimation produced brown transparent films that had a metallic shine in the case of as-produced blacks but were dull in appearance in the case of thermally treated blacks. About 30−40% of the as-produced black or 2−3% of the thermally treated carbon black was sublimated, while the residue stayed in the tantalum metal boat and generally preserved the same structure as it had before sublimation.

A TEM image of the film sublimated from as-produced black (Figure 5) shows that the smaller fraction mentioned above actually consists of C_{60} fullerenes whose ring images fill the TEM micrograph field. It is necessary to note that a similar TEM image was observed by Iijima et al. for a soot prepared by laser ablation of graphite at 1200 °C.[10] The authors of the work,[10]

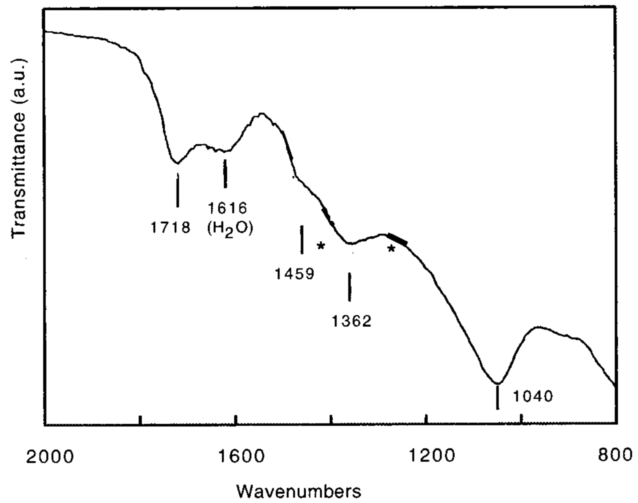

Figure 8. IR spectrum of the sublimated film. Asterisks show the positions of the strongest C_{60} lines at 1424 and 1183 cm^{-1}, which do not appear in this spectrum.

however, found that the ring-filled image did not change after an attempt to extract fullerenes by organic solvents and interpreted their result as the observation of the system of "interconnecting fullerene-like cages". In the present work, the sublimated films could not be dissolved in toluene, either; however, we interpret this fact otherwise, as a typical consequence of polymerization.[5] Indeed, the sublimated films could be easily re-sublimated again, and the presence of polymerized C_{60} fullerene was also confirmed by Raman scattering (see Figure 3c). The sublimation procedure induced the polymerization of C_{60} molecules by excitation of the deposited film either by visible light (so-called "phototransformation" that takes place when a C_{60} thin film is exposed to visible or ultraviolet irradiation in the absence of oxygen)[5] or possibly by heat in the evaporation chamber.

A TEM image of the film sublimated from thermally treated blacks (Figure 6) shows that the smaller fraction mentioned above actually consists of different fullerenes whose ring images fill the TEM micrograph field. The majority of fullerenes observed has sizes of 8.1 or 11.9 Å, which approximately correspond to C_{80} and C_{180}, respectively.

A number of multishell fullerenes have been observed among single-shell fullerenes, as is shown in a higher-manification TEM image in Figure 7. At least three varieties have been observed, all of them present in Figure 7: two-shell 14-Å-sized, two-shell 20-Å-sized, and also three-shell 20-Å-sized structures. We believe that this is the first observation of a cage-inside-cage structure. From a fullerene's diameter, it is possible to calculate its mass,[5] although uncertainties in the carbon–carbon bond length and other factors produce an inevitable error, which we estimate to be ±5%. As a result, it is possible to assign to the observed multishell fullerenes the following chemical formulas: $C_{60}@C_{240}$ to the two-shell 14-Å-sized, $C_{240}@C_{560}$ to the two-shell 20-Å-sized, and $C_{80}@C_{240}@C_{560}$ to the three-shell 20-Å-sized structure.

The film sublimated from the thermally treated carbon black was further characterized by a number of experimental methods. X-ray diffraction showed no diffraction features, and so the film proved to be amorphous. XPS measurements were undertaken in order to confirm the chemical composition of the samples and valence states of the atoms. Lines of three elements were detected in the XPS spectra: carbon, oxygen, and tantalum (one should note that this does not automatically exclude the possible presence of hydrogen because XPS is not sensitive to hydrogen). The chemical shift in the Ta4f and O1s lines shows that tantalum occurs in the form of tantalum oxide Ta_2O_5 and obviously came as stray microparticles from the tantalum sublimation boat. Indeed, the XPS peak intensity analysis showed that the content of tantalum oxide in the samples varied from 2 to 5% only, and occasional microparticles of tantalum oxide were really detected by optical microscopy. Carbon gives a C1s peak with a binding energy of 284.6 eV, which is between the typical values for carbon in graphite (284.5 eV) and in alkanes (285 eV). Raman spectra showed very weak features that proved to be difficult to analyze, and hence, these data are not shown here. IR spectroscopy, however, allowed us to observe rather good spectra on these films. A typical IR spectrum of the film sublimated from thermally treated carbon black is shown in Figure 8. There are four lines in the range 800–2000 cm^{-1}. Three stronger lines at 1040, 1362, and 1718 cm^{-1} can be assigned to vibrational modes of the higher fullerenes C_{80} and C_{180}, which constitute the majority in the film. A weaker 1459 cm^{-1} line usually manifests polymerization of fullerenes[11] and may be of the same origin here, too. The IR spectra also clearly indicate that the film does not contain any significant amount of C_{60} fullerene because the strongest C_{60} lines at 1424 and 1183 cm^{-1} do not appear.

Models of the molecules of $C_{60}@C_{240}$ and $C_{80}@C_{240}@C_{560}$ are shown in Figure 9. These models were produced from the templates of the Fullerene Library of HyperChem Pro software. The comparison of Figure 9a with Figure 9b illustrates that higher fullerenes have complicated shapes and may look very different if viewed from different angles. It explains why the TEM images of the outer shells of multishell fullerenes do not look like perfect rings in Figure 7.

Our model shows that the average interlayer separation between C_{240} and the innermost shell is 3.4 Å for $C_{60}@C_{240}$ and 3.0 Å for $C_{80}@C_{240}@C_{560}$. This is similar to the phenomenon of the interlayer separation shrinking that was observed by Banhart and Ajayan[12] in carbon onions. The spacing between the layers of the onion decreased from 3.4 Å in outer shells to 2.2 Å in the core, indicating, as the authors[12] described it, considerable compression toward the multilayer particle center. The compression might be induced by the stresses in the curved carbon shell. Although carbon onions are much bigger clusters, with tens of shells, a similar mechanism might lead to the observed appearance of C_{80} inside a three-shell fullerene instead of C_{60} inside a two-shell fullerene.

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(10) Iijima, S.; Wakabayashi, T.; Achiba, Y. *J. Phys. Chem.* **1996**, *100*, 5839.

(11) Rao, A. M.; Zhou, P.; Wang, K. A.; Hager, G. T.; Holden, J. M.; Wang, Y.; Lee, W. T.; Bi, X. X.; Eklund, P. C.; Cornett, D. C.; Duncan, M. A.; Amster, L. J. *Science* **1993**, *259*, 955.

(12) Banhart, F.; Ajayan, P. M. *Nature* **1996**, *382*, 433.

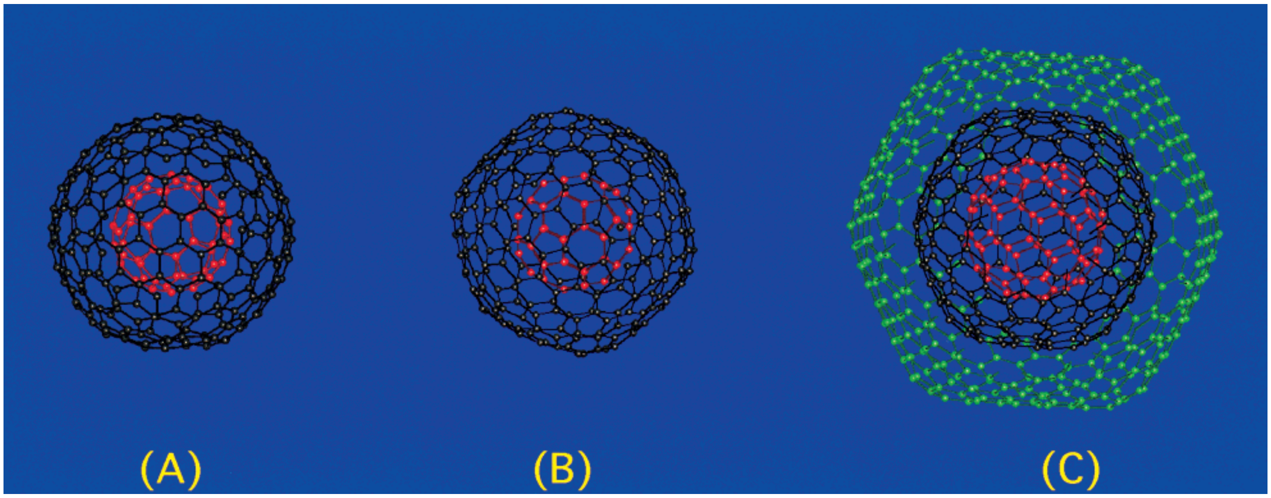

Figure 9. Models of the molecular structures of multishell fullerenes (a) $C_{60}@C_{240}$, (b) the same $C_{60}@C_{240}$ rotated 60° around vertical axis, and (c) $C_{80}@C_{240}@C_{560}$. The front parts of the outer shells of $C_{80}@C_{240}@C_{560}$ are clipped away for a better view into the inner part of the multishell structure.

It is interesting to note that the multishell fullerenes that we directly observed in this work represent an interesting and novel variety of carbon clusters. The multishell fullerenes are essentially different from much bigger and essentially graphitic carbon onions.[5] If it is possible to isolate multishell fullerene crystals, it would be most interesting to compare their properties with the properties of endometallofullerenes $M@C_{2n}$ (where M = La, Y, Sc, and other metals),[13] for which, at the present time, only a something-inside-cage structure known.

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(13) Bubnov, V. P.; Koltover, V. K.; Laukhina, E. E.; Estrin, Ya. P.; Yagubskii, E. B. *Izv. Akad. Nauk. Ser. Khim.* **1997**, *Feb*, 254.