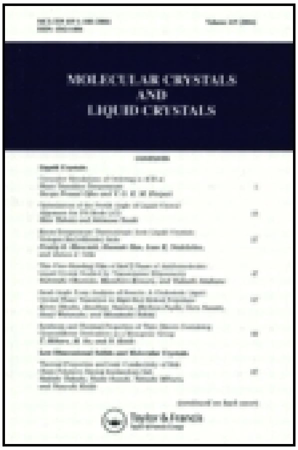

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Formation of multishell fullerenes from vaporized carbons

V. Z. Mordkovich [a], Yosuke Shiratori [a], Hiroyuki Hiraoka [a], Yasumasa Takeuchi [a] & Morinobu Endo [b]
[a] Intl Center for Materials Research, East 601, KSP, Kawasaki, 213-0012, Japan
[b] Shinshu University, Nagano, 380-0922, Japan

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FORMATION OF MULTISHELL FULLERENES FROM VAPORIZED CARBONS

V. Z. Mordkovich, Yosuke Shiratori,
Hiroyuki Hiraoka, and Yasumasa Takeuchi
Intl Center for Materials Research, East 601, KSP,
Kawasaki 213-0012, Japan

Morinobu Endo
Shinshu University, Nagano 380-0922, Japan

Two different processes, which lead to formation of multishell fullerenes, are reported and discussed. The first process is 3000°C high temperature treatment of C_{60}-containing carbon blacks. The second process is laser vaporization of composite carbon targets, containing C_{60} and vapor-grown carbon fibers (VGCF). It has been shown that the laser vaporization technique allows increasing the yield up to 40%. Possible mechanisms of formation of the outer shells are discussed.

Keywords: fullerenes; carbon onions; laser vaporization

INTRODUCTION

Multishell fullerenes, which were foreseen by Kroto *et al.* [1] as early as in 1988, are the smallest among other multishell carbon clusters such as bigger, graphitic onions or multishell nanotubes. 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}, etc.), the multishell fullerenes have a cage-inside-cage structure such as double-shell $C_{60}@C_{240}$ or triple-shell $C_{60}@C_{240}@C_{560}$.

Recently, we reported the observation of double-shell $C_{60}@C_{240}$, double-shell $C_{240}@C_{560}$ and triple-shell $C_{80}@C_{240}@C_{560}$ in the products of 3000°C high temperature treatment of laser pyrolysis carbon blacks [2,3]. The content of multishell fullerenes was less than 0.01%, while most of the

Laser vaporization experiments were carried out through the courtesy of Quantum Design Japan Co. with valuable assistance from Dr. M. Nakamura and Dr. M. Sawada.

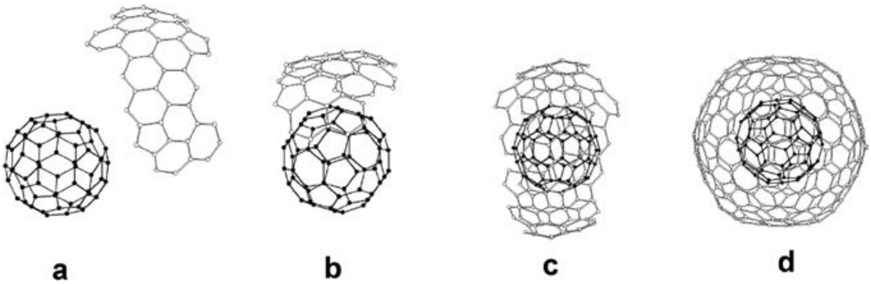

FIGURE 1 Hypothetical growth sequence of a multishell fullerene evolving from: (a) a fullerenes cluster and a fullerene/nanotube fragment through (b) and (c) in which the shell fragment deposited onto a fullerene forms an embryo in which the second shell is forming. The sequence leads in a natural way to multishell fullerenes shown in (d).

material was dominated by hollow graphitic particles of ~20 nm size and ordinary, single-shell fullerenes.

It seems reasonable to suggest that the actual growth of additional shells around C_{60} cores took place not during 3000°C treatment but during cooling down after the heat treatment. This suggestion is supported by the fact that C_{80}, which dominates the product, also is a core of many multishell molecules. If this suggestion is correct, a successful synthetic route should comprise at least two steps: (1) formation of carbon vapor which contains many C_{60} clusters; and (2) cooling down at the appropriate substrate. A hypothetical formation sequence is shown in Figure 1. We realized that the method of laser vaporization would meet the above conditions.

The purpose of the present work was to find an efficient synthetic route to multishell fullerenes by use of the laser vaporization method and to compare the results with those of high temperature treatment of laser pyrolysis carbon black.

EXPERIMENTAL

A laser pyrolysis carbon black for heat treatment was supplied by Nanogram Corporation. Details of the laser pyrolysis technology are described elsewhere [3]. Thermal treatment of the black for 1 h was performed in a closed graphite crucible in Ar gas atmosphere at 3000°C.

For laser vaporization, a KrF excimer pulse laser ($\lambda = 248$ nm) was used. A typical laser fluence and repetition rate were 1.5 J/cm^2 and 10 Hz, respectively. Two different targets were used for vaporization. Both targets contained 40 wt.% of fullerene C_{60}, but the rest of the target was different:

amorphous laser pyrolysis carbon black or, alternatively, vapor-grown carbon fibers (VGCF)[4]. The experiment was performed in a He atmosphere, with the He pressure varying in the range from 1 to 200 Torr. The deposit was collected on heated (300°C) stainless steel substrates. The deposits were studied by transmission electron microscopy (TEM) and Raman spectroscopy. Vacuum sublimation was used to separate fractions of the deposit. The details of the vacuum sublimation technique may be found elsewhere [3].

RESULTS AND DISCUSSION

The fullerene fraction of the heat-treated laser pyrolysis carbon black was separated by vacuum sublimation. TEM investigation of the resulting brownish film showed the presence of multishell fullerenes in small amounts (see Table 1), while most of the material was dominated by the single-shell fullerene C_{80}.

The deposits obtained by laser vaporization of either of the targets at different He pressures represented yellow thin films. The main result of the TEM study was the observation of large amounts of double and triple fullerenes. At least two varieties have been observed: two-shell 14 Å size, and three-shell 20 Å size. The two-shell fullerenes are easily seen in Figure 2. The yield was higher at lower He pressure, in the range of 1–4 Torr. Vaporization of C_{60}/VGCF targets always gave 3–5 times higher yield than that of C_{60}/carbon black targets – see Table 1.

The multishell fullerene fraction can be easily separated by vacuum sublimation. The sublimated film is comprised predominantly of multishell fullerenes.

Raman spectra of the laser vaporization deposit after sublimation (Fig. 3) display three stronger peaks at 1430; 1464 and 1569 cm^{-1} and a number of weaker peaks. This pattern is very similar to that of C_{60} (1426; 1469 and 1573 cm^{-1} features) [5]. Some of the weaker peaks cannot be

TABLE 1 Multishell Fullerene Content in Different Deposits

Method	Content (%)
Sublimation of 3000°C heat-treated carbon black	<0.1
Laser vaporization of C_{60}/amorphous carbon composite at 1 Torr	15
Laser vaporization of C_{60}/VGCF composite at 1 Torr	40

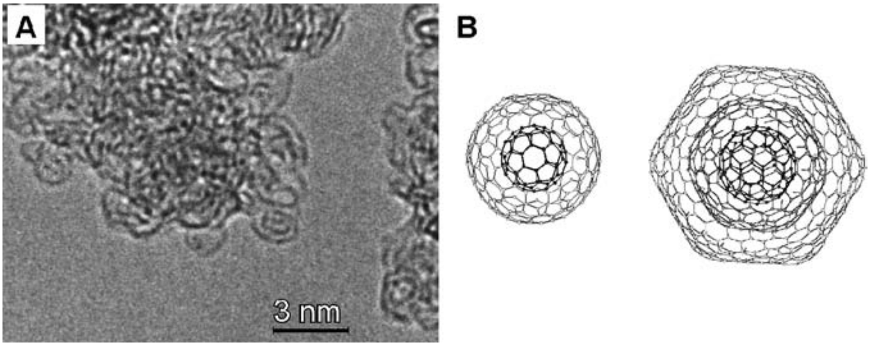

FIGURE 2 TEM images show multishell fullerenes in large amounts: (a) TEM image of a deposit of laser vaporization; (b) models of double shell $C_{60}@C_{240}$ and triple-shell $C_{60}@C_{240}@C_{560}$ fullerenes. The concentric dark rings in the image (a) are the electron images of multishell fullerenes.

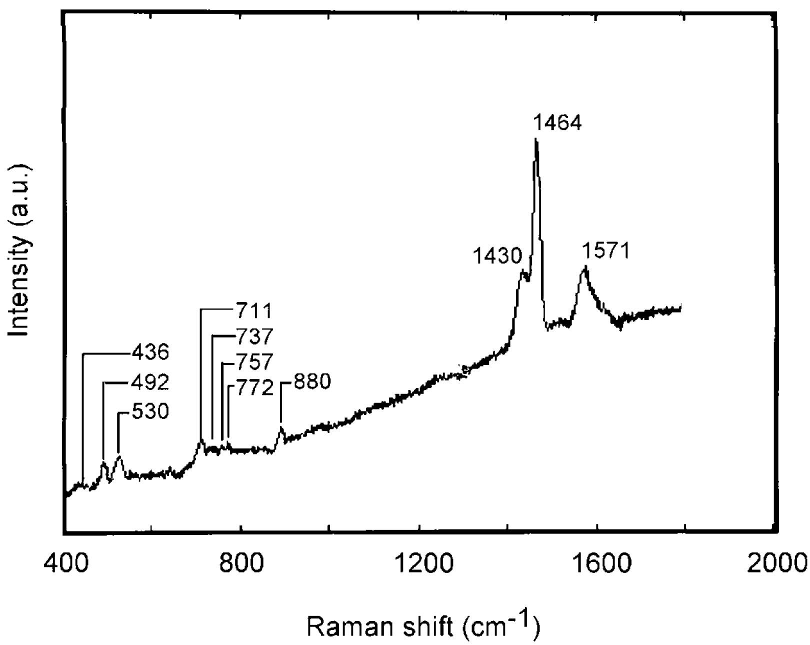

FIGURE 3 Raman scattering spectra of a laser vaporization deposit after sublimation – see comments in the text.

identified with the C_{60} cluster, though the peaks at 730 and 757 cm^{-1} were earlier observed in the spectra of "phototransformed" C_{60} solid [5], i.e. the C_{60} solid after photoinduced immobilization. It is reasonable to suppose that the core C_{60} molecules, immobilized inside the multishell fullerenes, produce most peaks in Figure 3.

The growth of the outer shells is probably determined by the mechanism, which is shown in Figure 1 and discussed above. Indeed, the VGCF, comprised of multiple curved shells are a good source of shell fragments to initiate the growth process according to Figure 1a,b. On the other hand, the vaporization of targets without VGCF cannot produce the shell fragments, – hence even if the multishell embryos still appear, it is due to a much less probable spontaneous nucleation of corannulene-like networks from the carbon vapor, as was suggested by Kroto *et al.* [1]. So, this is how the role of VGCF may be explained.

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