# Synthesis of multishell fullerenes by laser vaporization of composite carbon targets

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Multishell fullerenes 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 ($C_{60}$, $C_{70}$, $C_{84}$, $C_{102}$, etc.), multishel fullerenes have a cage-inside-cage concentric structure such as double-shell $C_{60}@C_{240}$ or triple-shell $C_{60}@C_{240}@C_{560}$. We report the synthesis of multishell fullerenes by laser vaporization of $C_{60}$-containing composite carbon targets. Transmission electron microscopy, Raman scattering spectroscopy and other methods have been used for the product characterization. The yield of the process reaches up to 40%, which permits production in gram amounts even in laboratory conditions.

Multishell fullerenes are the smallest among other multishell carbon clusters such as bigger graphitic onions [1,2] or multiwall nanotubes [2,3]. 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 concentric structure such as double-shell $C_{60}@C_{240}$ or triple-shell $C_{60}@C_{240}@C_{560}$. These cage-inside-cage structures were foreseen by Kroto et al. [4] as early as in 1988, i. e. shortly after his pioneering discovery of the basic buckminster fullerene $C_{60}$ [5]. The first observation of several double-shell and triple-shell molecules was however reported only recently [6,7]. In the works [6,7], the double-shell $C_{60}@C_{240}$, double-shell $C_{240}@C_{560}$ and triple-shell $C_{80}@C_{240}@C_{560}$ were found in the products of 3000°C high temperature treatment of laser pyrolysis carbon blacks. The content of multishell fullerenes was less than 0.01%, while most of the material was dominated by hollow graphitic particles of $\sim 20$ nm size and ordinary, single-shell fullerenes.

Though the multishell fullerenes possibly possess interesting and attractive properties [7], no measurement could have been done until these fullerenes were isolated in milligram amounts, at least. So the first priority of the research in this field was to find an efficient synthetic route to production of multishell fullerenes.

It is hard to improve the method of high temperature treatment of laser pyrolysis carbon black [7]. Also, it seems reasonable to suggest that actual growth of additional shells around $C_{60}$ cores took place not during 3000°C treatment but during the cooldown after the heat treatment. If this suggestion is correct, a successful synthetic route should comprise at least two steps: (1) formation of carbon vapour which contains many $C_{60}$ molecules; and (2) cooling down at the appropriate substrate. A hypothetical growth sequence is shown in Fig. 1. We realized that the method of laser vaporization would meet the above conditions. Another attractive feature of this method is that it allows flexible control of different key apramenters of the process.

The purpose of the present work was to find effecient synthetic route to multishell fullerenes by use of laser vaporization method.

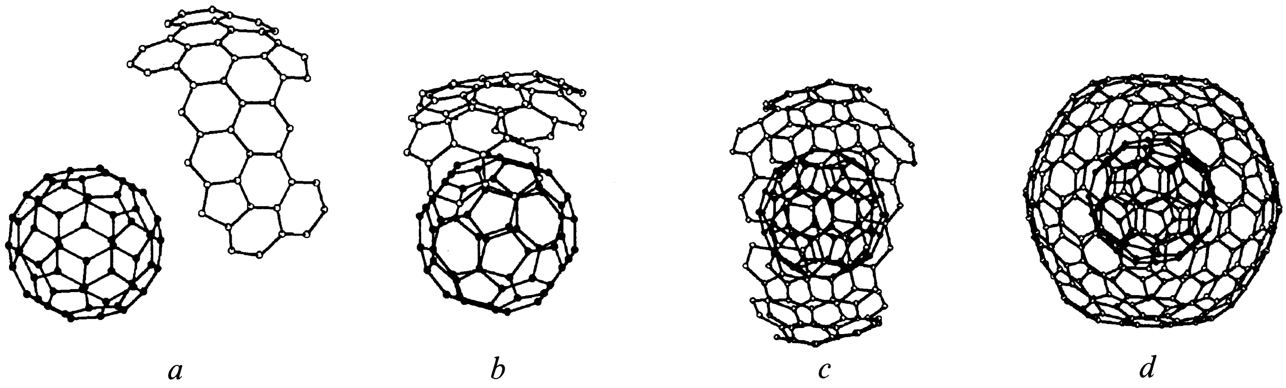

**Figure 1.** Hypothetical growth sequence of multishell fullerene evolving from: (*a*) a fullerene molecule and a fullerene/nanotube fragment, through (*b*) and (*c*) in which the shell fragment deposited onto a fullerence forms an embryo in which the second shell is forming. The sequence leads in a natural way to multishell fullerens (*d*).

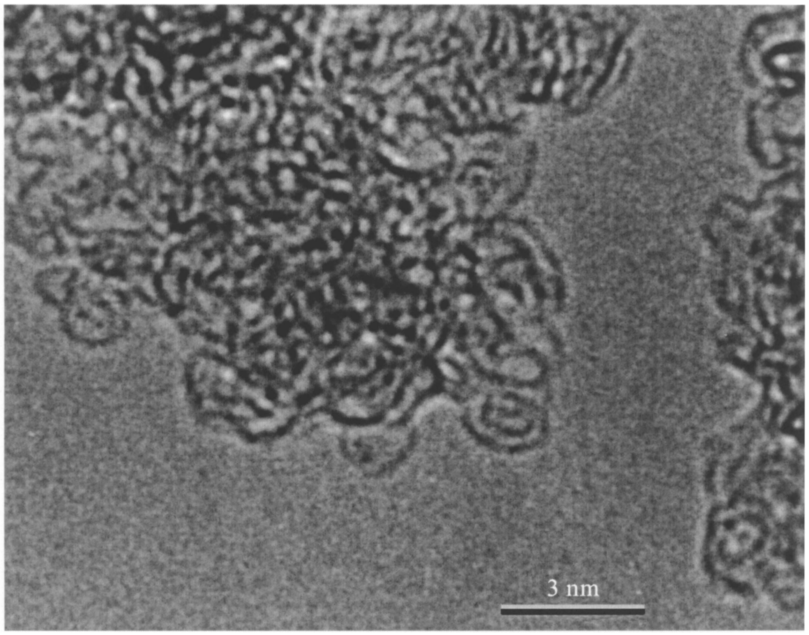

**Figure 2.** TEM images show multishell fullerenes in large amounts. The concentric dark rings are the electron images of multishell fullerenes.

## 1. Experimental

For laser vaporization, a KrF excimer pulse laser ($\lambda = 248\,\mathrm{nm}$) was used. Typical laser fluence and repetition rate were $1.5\,\mathrm{J/cm^2}$ and 10 Hz, respectively. Two different targets were used for vaporization. Both targets contained 40 wt% of fullerene $C_{60}$, but the rest was different: amorphous laser pyrolysis carbon black or, alternatively, carbon nanofibres. The carbon nanofibres were vapour grown carbon fibres with nanotube-like concentric multishell structure [3]. The experiment was performed in He atmosphere, with He pressure varying in the range from 1 to 200 Torr. The substrates of stainless steel SUS304, quartz glass and pyrolytic graphite were used to collect the deposit. The substrate temperature was 300°C. The deposits were studied by transmission electron microscopy (TEM), Raman spectroscopy and other methods. Vacuum sublimation was used to separate fractions of the deposit. The details of the vacuum sublimation technique may be found elsewhere [7].

## 2. Results and discussion

The deposits obtained by vaporization of either of the targets at different He pressures were yellow thin films ($\sim 500\,\mathrm{nm}$ thick after 20.000 pulses). The films could not be dissolved in organic solvents such as toluene, xylene or chloroform. Though the yellow colour implies the absence of graphite or graphitic particles, TEM study showed that the latter actually did occur in small amounts in the deposits.

The main result of the TEM study was, however, the observation of large amounts of double and triple fullerenes. The yield was higher at lower He pressure, in the range

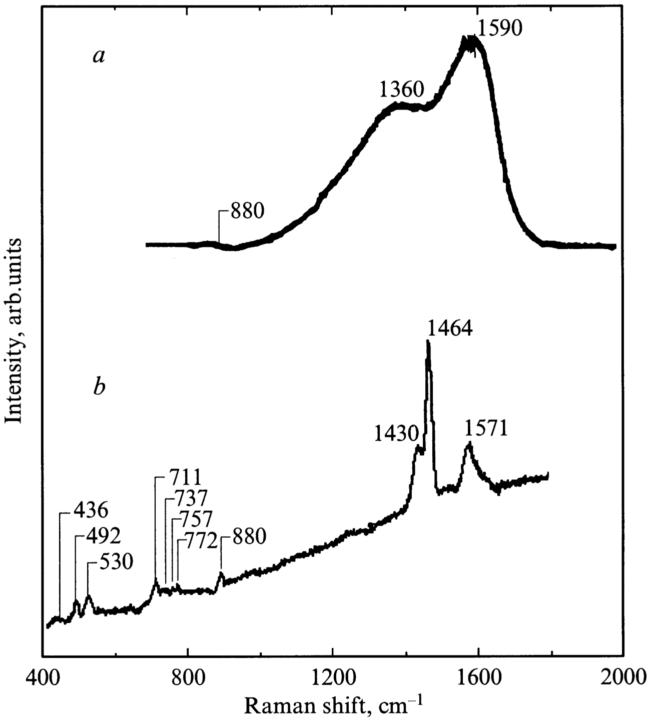

**Figure 3.** Raman scattering spectra: (*a*) laser vaporization deposit on stainless steel; (*b*) sublimated film. The spectrum of the deposit (*a*) is dominated by two overwhelming "disordered graphite" features: the peak at $1590\,\mathrm{cm^{-1}}$ is identified with the well-known $E_{2g}$ vibrational mode of graphite, upshifted by $\sim 10\,\mathrm{cm^{-1}}$ from the position $1582\,\mathrm{cm^{-1}}$ reported for single-crystal graphite [2]; the peak at $1360\,\mathrm{cm^{-1}}$ is identified with symmetry-forbidden modes associated with the maximum in the graphite density of states, activated lattice disorder and/or small crystalline size [2]. As for features at the (*b*) spectrum, see comments in the text.

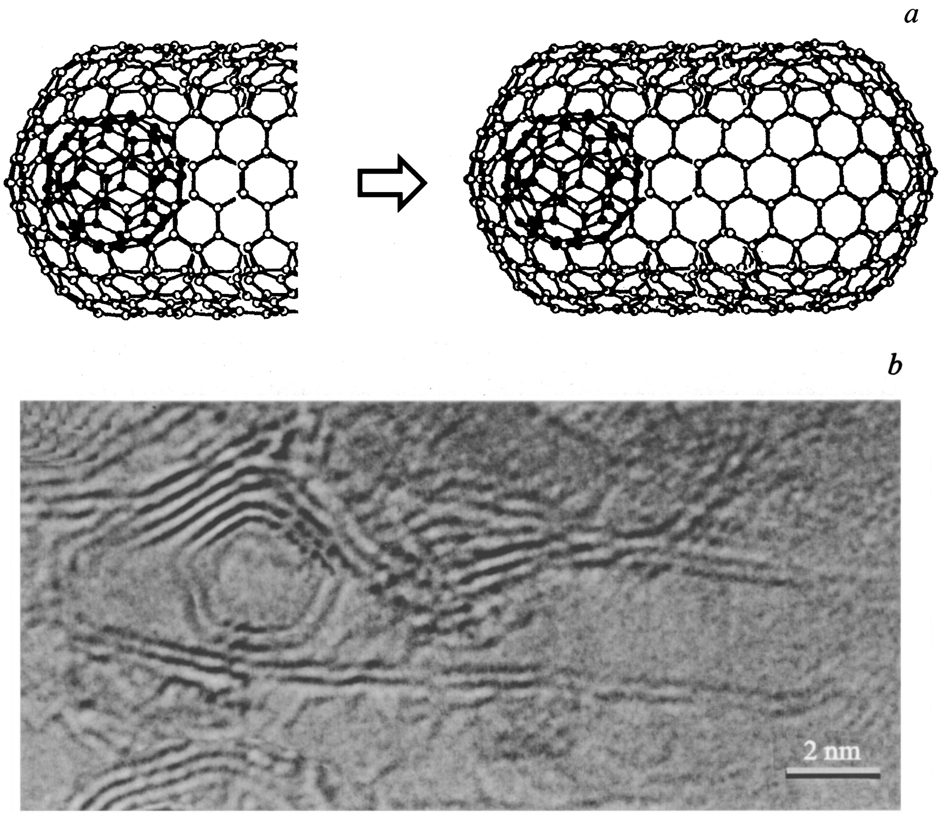

**Figure 4.** A "buckyshuttle" (fullerene molecule enclosed in a tubulene) as a result of deviation from the normal growth sequence of multishell fullerene: (*a*) hypothetical growth sequence after deviation from the path which is shown in Fig. 1, *c*, *d*; (*b*) TEM image of a deposit, showing a "buckyshuttle".

of 1–4 Torr. Vaporization of $C_{60}$/nanofibre targets always gave 3–5 times higher yield than that of $C_{60}$/carbon black targets. The best samples, recieved by vaporization of a $C_{60}$/nanofibre target at 1 Torr, contained 40% of multishell 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 Fig. 2. From a fullerene diameter it is possible to calculate its mass [2], though uncertainty in carbon–carbon bond length and other factors produce an inevitable error, which we estimate as ±5%. As a result, it is possible to assign the following chemical formule to the observed fullerenes: $C_{60}@C_{240}$ to the double 14 Å size, and $C_{60}@C_{240}@C_{560}$ to the triple 20 Å size.

The multishell fullerene fraction can be easily separated by vacuum sublimation though it requires at least 1200°C in a vacuum of $10^{-7}$ Torr. So high sublimation temperature is in sharp contrast with that of $C_{60}$ which can be easily sublimated at 400°C. The sublimates film has yellow colour and contains predominantly the multishell fullerenes.

The comparison of Raman scattering spectra of laser vaporization deposits and the sublimated films (Fig. 3) shows how the strong "disordered graphite" features at 1360 and 1590 $\mathrm{cm}^{-1}$ disappear after sublimation. The sublimated film does not contain graphitic nanoparticles with their strong, overwhelming spectral lines, and its spectra (Fig. 3, *b*) clearly display three strong broad peaks at 1430, 1464, and 1569 $\mathrm{cm}^{-1}$ and a number of weaker peaks below 1000 $\mathrm{cm}^{-1}$. This pattern is very similar to that of $C_{60}$ (1426, 1469, and 1573 $\mathrm{cm}^{-1}$ features) [8]. Four of the weaker peaks: 530, 737, 757, and 880 $\mathrm{cm}^{-1}$ — cannot be identified with the vibrations of $C_{60}$ molecule, though the peaks at 730 and 757 $\mathrm{cm}^{-1}$ were earlier observed in the spectra of "phototransformed" $C_{60}$ solid [8], i. e., the $C_{60}$ solid after photoinduced immobilization of $C_{60}$ molecules in the polymer network.

It is reasonable to suppose that the most of peaks in Fig. 3, *b* are produced by the core $C_{60}$ molecules immobilized inside the multishell fullerenes. No peaks, with possible exception of 530 and 880 $\mathrm{cm}^{-1}$ features, can be assigned to the outer shells, because the latter produce many weak Raman peaks due to their generally lower symmetry, larger number of degrees of freedom and/or possible isomers. Also, it was predicted by Iglesias-Groth et al. [9] that the strongest vibrational lines of the outer shells lie at much lower frequencies of 65–120 $\mathrm{cm}^{-1}$.

The growth of the outer shells is probably determined by the mechanism which is shown in Fig. 1 and discussed above. This hypothesis is supported by the above-mentioned fact, that laser vaporization of the $C_{60}$/nanofibre targets gave much higher yield of multishell fullerenes than that of

$C_{60}$/carbon black targets. Indeed, the difference between the targets is in the presence of nanofibres. Those nanofibres, comprised of multiple curved shells, are a good source of shell fragments to initiate the multishell fullerene growth process according to Figs. 1, *a, b*. On the other hand, the vaporization of the $C_{60}$/carbon black target cannot produce the shell fragments, — hence even if the embryos of multishell fullerenes do appear, this happens due to much less probable process of spontaneous nucleation of corannulene-like carbon networks from carbon vapour, as was suggested by Kroto et al. [4].

Apparently, the uncertain stage of the hypothetical growth mechanism is the shell closure (Fig. 1, *c, d*). The growth may well lead to elongation of the outer shell with formation of a tubulene, as it is shown in Fig. 4, *a*. Indeed, we observed such objects more than once in the laser vaporization deposits — see, for example, Fig. 4, *b*. This kind of nanocluster called "buckyshuttle" represents a nanometre-size two-level system which can be used as computer memory element and was recently discovered in the products of heat treatment of nanodiamond [10]. We have a good reason to believe that the laser vaporization method can be controlled in a way to synthesize selectively the buckyshuttles with high yield.

In conclusion, a method of the large-scale synthesis of multishell fullerenes has been found. The method of laser vaporization of composite $C_{60}$-containing carbon targets gives the yield of up to 40%, which permits production in gram amounts even in laboratory conditions. The results suggest that the method can be controlled in a way to synthesize selectively certain types of multishell fullerenes and other multishell carbon clusters.

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