



Growth of carbon nanotubes by fullerene decomposition in the presence of transition metals

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Abstract

Carbon nanotubes were formed on HOPG when the graphite faces were exposed to a stainless steel C₆₀ evaporator heated to 450°C. No nanotubes were found on gold under the same conditions or when a quartz oven was used as the C₆₀ evaporator. Interesting conical nanostructures were found in the insoluble residue from the stainless steel oven. We interpret the nanotube formation to be due to the presence of small carbon fragments produced by the catalytic decomposition of C₆₀ in the oven. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon nanotubes are a family of nano-objects with remarkable physical, chemical and mechanical properties [1,2]. Macroscopic quantities of nanotubes are routinely produced by the arc discharge method [3], laser vaporisation at elevated temperatures [4] or the catalytic decomposition of small hydrocarbon molecules [5] and there is a rapidly growing interest in understanding their growth mechanisms and electronic properties. For example, scanning tunnelling

spectroscopy measurements [6,7] have conclusively demonstrated an excellent agreement of experimental gap values for semiconducting and metallic carbon nanotubes with earlier theoretical predictions [8] and experimental evidence was recently reported for the feasibility of carbon nanotube based nanoelectronics [9]. Recently, the growth of mixed C–B–N tubes was achieved [10].

In order to be able to synthesise nanotubes with predetermined characteristics, i.e. for the ‘engineering’ of these nanostructures, it is very important to understand and control the mechanisms which govern the growth of carbon nanotubes. An extensive analysis of the growth mechanisms for nanotubes using the electric arc procedure, the catalytic decomposition of hydrocarbons, and carbon vapour deposition on a cold substrate has been given recently by

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Gamaly.² The crucial importance of *asymmetry* in the velocity of the carbon atoms arriving at the growth site was strongly emphasised for all these growth processes.

The decomposition of fullerenes in contact with transition metal atoms has been observed in several experiments: sticking and disintegration of neutral C₆₀ colliding with Ni(110) at 10–50 eV collision energy was reported [12]. Evidence for the formation of metal carbide was found when depositing Ti or Cr on C₆₀ films [13]. Clusters composed of fullerene molecules and transition metal atoms undergo a laser-induced transformation to metal carbide and metallo-carbohedrene clusters [14]. The decomposition of C₆₀ on Ni(110) at 760 K was reported [15], and the authors predicted a similar behaviour for all the other transition metals. C₆₀ monolayers were found to be very strongly bound to Ni(111). They resist nanosecond laser desorption until the ablation threshold of the Ni substrate is reached and decomposition occurs. This decomposition then takes place at a rate considerably faster than that expected for thermal decomposition at the surface temperature of 3000 K [16].

In the present Letter, we report the observation of carbon nanotubes which are produced on highly oriented pyrolytic graphite (HOPG) substrates from material emerging from a stainless steel oven, loaded with C₆₀, and heated at 450°C. This growth procedure is similar to some extent to the procedure based on the quasi-free condensation of carbon vapour generated in an electric arc reported by Ge and Sattler [17]. Nanotubes were also found in the residue collected from the oven. Scanning tunnelling microscopy (STM) was used to show evidence for the nanotubes on the HOPG substrates. Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and STM were used to study the nanotubes in the residue from the oven. When performing a similar experiment with a quartz oven, no nanotubes were found either on the substrates, or in the residue from the oven. Mass spectrometric measurements of the vapour phase, under similar heating conditions, yielded strong peaks corresponding to

small carbon fragments C_n with $n < 20$. A test experiment for reactivity carried out by heating a 1:1 mixture of C₆₀ (99.99%) with iron powder (99.99%) in an evacuated and sealed quartz tube at 450°C confirmed the production of iron carbide that could be unambiguously evidenced by X-ray measurements. However, no nanotubes were observed by TEM examination, although amorphous carbon was found in this experiment.

2. Experimental conditions

2.1. Deposition onto the substrates

The stainless steel ovens used in the experiments were manufactured from X6CrNiMoTi17122 steel (with a nominal content of 17% Cr, 2% Mo, 12% Ni, and up to 0.8% Ti). They consisted of an outer stainless steel container and an inner cartridge of the same material which could be easily removed or replaced with a similar cartridge of a different material (e.g. quartz). The oven temperature was computer controlled. The [60]fullerene material in the oven was heated at 300°C for 60 min in order to remove volatile impurities. Once the oven reached the desired temperature, the deposition was started by exposing the substrate together with a previously calibrated quartz crystal thickness monitor. The duration of the deposition was regulated according to thickness calculations based on the density of fullerenes. Experiments were performed in the range of equivalent [60]fullerene layer thicknesses of 5–24 Å. After the end of the deposition cycle, the residue from the cartridge was removed and analyzed. Each deposition was started with a fresh [60]fullerene filling of a washed and cleaned cartridge. The main experimental results were cross-checked using two different kinds of [60]fullerenes, no differences were found on loading the oven with Hoechst ‘gold grade’ [60]fullerene, or ‘home-made’ [60]fullerene. Experiments under the same preparation, heating and deposition conditions were carried out using a quartz cartridge of the same geometry.

2.2. Substrates

Two kinds of substrates were used during the depositions. Freshly cleaved HOPG and commercial

² E.G. Gamaly, Growth Mechanism of Carbon Nanotubes, in Ref. [2], p. 163.

Au on mica ('Pico' substrates). Nanotubes were found on every HOPG substrate, while no nanotubes were found on any of the Au substrates. The Au substrates showed a deposit which covered the original terraces of the Au and did not reveal any regular structure. After deposition, annealing the Au substrates in vacuum for 12 h at 250°C, restored the characteristic terraced structure. When imaging with STM in high resolution on some of the annealed Au substrates, it was possible to observe a structure with local order consisting of maxima spaced at distances slightly larger than 1 nm. These maxima can be interpreted as C₆₀ molecules which were deposited on the Au, while the structureless cover which was hiding the terraces after the deposition may be partly due to amorphous carbon like material.

We could only identify structures in the recorded STM images corresponding to fullerenes from the 24 Å thick deposit on HOPG, not on the thinner films. Taking into account that the interaction of C₆₀ with graphite is rather weak [18], this is probably the consequence of displacement of the fullerene molecules by the strong, non-uniform electric field surrounding the STM tip. Some of the C₆₀ molecules were regularly picked up by the tip. These molecules could be deposited onto clean Au substrates by cycling the voltage applied to the STM tip from -4 to +4 V.

2.3. STM imaging

STM images were recorded in an ambient atmosphere using a Nanoscope IIIA combined STM-AFM operated in constant current mode. Commercial, mechanically prepared Pt-Ir tips were used (Nanotips TT). The tip quality was checked by controlling the atomic resolution on unexposed regions of HOPG and by imaging steps with a height of a few atomic layers [19]. The deterioration of the tip, which cannot be excluded when scanning objects with random conductivity variations such as the irregular stacks of nanotubes, was minimized by using low scan frequencies, typically in the range of 1 Hz. It should be noted that on samples with low coverage, equivalent to 5 Å of C₆₀, blunt tips with R_{eff} of several hundred Å, may be helpful to locate the nanotubes due to the convolution of the tip shape with the nanotube [20].

2.4. Sample preparation from the material collected from the oven

The residue of the fullerene material, which was found in the oven after the deposition run, was dissolved in 1,2-dichlorobenzene (oDCB). The solution was filtered through a PTFE membrane (pore size, 0.2 μm). The soluble fraction was analysed by HPLC (Cosmosil PBB analytical column, eluent oDCB, UV detection at 320 nm). The insoluble residue was placed on HOPG for STM, on a graphite membrane for SEM and on grids covered by amorphous carbon for TEM studies.

3. Results and discussions

3.1. STM results

In the case of deposits equivalent to 24 Å [60]fullerene thickness, irregular 'haystack' like structures consisting of carbon nanotubes were found on HOPG. Due to the random way these tubes interconnect electrically it is not possible to acquire images with good resolution in the central regions of these structures. However, in the region where the lowermost layer connects to the HOPG, satisfactory resolution can be achieved. An image acquired in such a region is shown in Fig. 1. One can note the parallel arrangement of the carbon nanotubes, which may be related to the growth mechanism proposed by Gamaly, according to which the transition from fullerene growth to nanotube growth takes place due to asymmetry. Two kinds of nanotubes are clearly visible in the image: nanotubes with conic termination (A and C), and nanotubes with a spherical cap (B). On object A – and on several others, not so clearly visible – one can note the step-like change in the diameter, this region is shown in more detail in the small image at the right-hand side. The average line-cut taken in the area denoted by the white rectangle is shown. The height difference corresponding to the two markers is 0.357 nm, i.e. the distance between two graphene sheets in graphite or carbon nanotubes. In the group of nanotubes at B, all tubes have diameters in the 5 nm range. With a regular arrangement of objects of similar radius, the determination of the diameter can be done independently of convolution effects. The largest nanotube, object A, has an apparent diameter of 20 nm. In this case, some contribution from

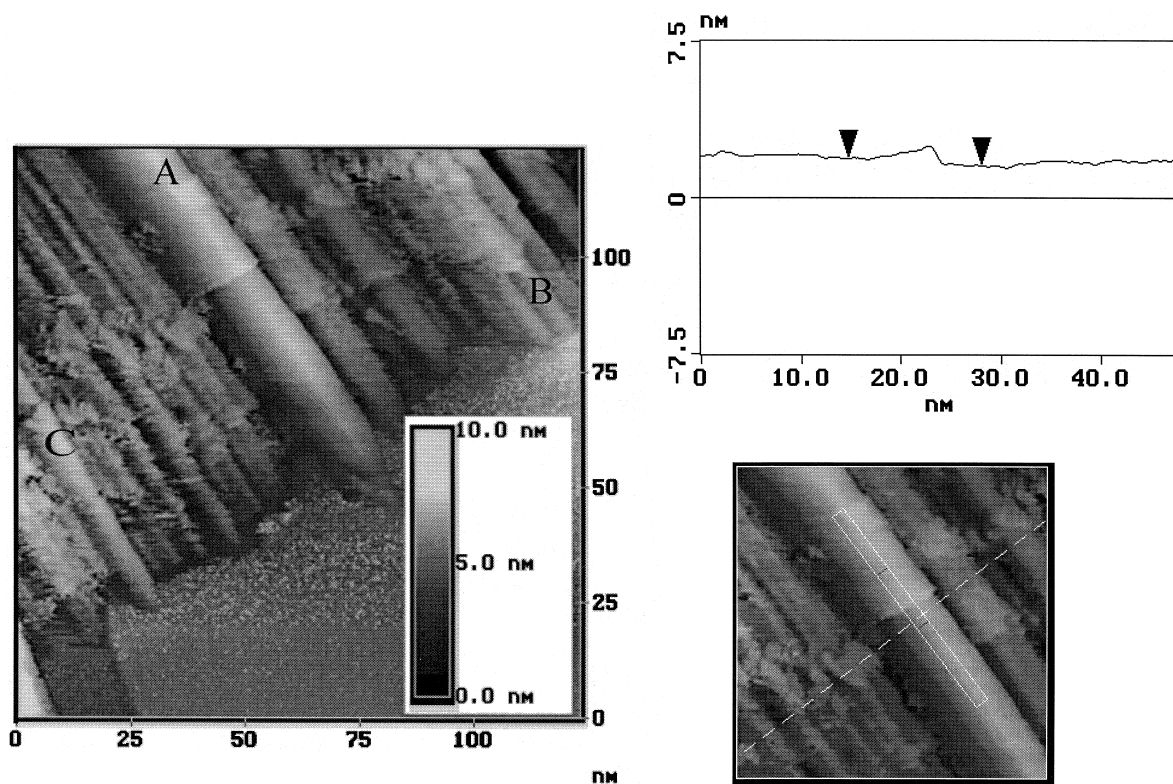


Fig. 1. STM image of carbon nanotubes produced by depositing the vapour from a stainless steel oven containing [60]fullerene at 450°C on a room temperature HOPG substrate. Note that the conical ending of nanotubes labelled A and C while the group of nanotubes labelled B has a different, hemispheric-like termination. The body of the tubes as shown in the detail is also clearly tubular.

convolution effects cannot be excluded as the neighbouring tubes have less than half of this diameter.

In the case of lower coverage, corresponding to 10 Å of equivalent [60]fullerene thickness the ‘nuclei’ of the haystacks could be identified. These have a structure of intercrossing carbon nanotubes in a herringbone arrangement. At even lower coverage, 5 Å equivalent [60]fullerene thickness, the typical structures are long, individual nanotubes; their occurrence is of the order of 10^{-2} per μm^2 . No nanotubes were found in the films deposited on the Au on mica substrates from a stainless steel oven. Also, no nanotubes were found in the films deposited on HOPG from the quartz oven.

3.2. TEM and SEM results

The TEM images revealed three distinct types of material in the insoluble residue from the stainless

steel oven: (i) spherulitic particles, (ii) nanotubes with conical ends and (iii) large conical structures. Examples of the first two structures are shown in Fig. 2. (i) The clusters of spherulitic particles consist of amorphous carbon, this result was confirmed by a detailed analysis with an electron microprobe. (ii) The 4.8 μm long, hollow object is a carbon nanotube with a conical tip. The exterior diameter in the constant diameter range is 83 nm. SEM examination of the insoluble residue placed on graphite found similar objects. (iii) The large conical structures retain their conical shape over several microns. A cone with a height of 6 μm and a base diameter of 0.8 μm is shown in Fig. 3. The STM observation of fullerenic cones was reported earlier under the conditions of quasi-free vapour condensation [21]. The TEM observation of carbon nanocones produced by the pyrolysis of hydrocarbons was reported by Krishnan et al. [22].

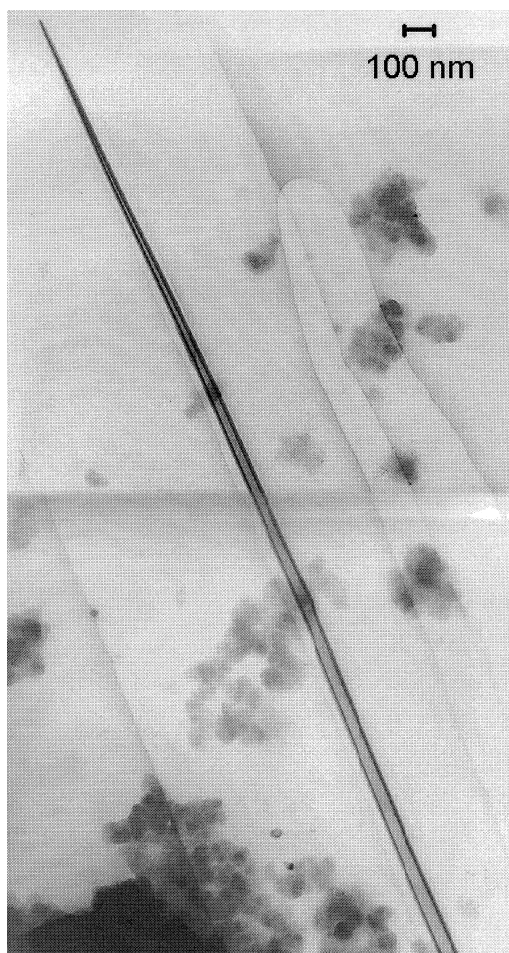


Fig. 2. TEM image of carbon nanostructures found in the stainless steel oven residue. The irregular clusters of spherulitic particles are amorphous carbon. The long tubular object crossing the image from the left upper to the right lower corner is a typical structure with tubular body and elongated conical termination.

3.3. Solubility and HPLC results

The solubility tests of the oven residue in oDCB gave an insoluble fraction of about 1–5% of the material recovered from the stainless steel cartridge. The residue from the quartz cartridge appeared to be practically completely soluble. The results of an HPLC analysis of the solutions are shown in Fig. 4a. The C_{60} peak appears at a retention time of about 4 min. The small peak at 5.5 min which was also observed in the unheated $[C_{60}]_2$ fullerene material corresponds very likely to traces of $(C_{60})_2$, which was

shown to have the same retention time in additional experiments under the same HPLC conditions. A new component, eluted as a broad fraction, was found in the soluble part of the heated material at a retention time of about 8 min. The new component was isolated (see bottom trace of Fig. 4a) and investigated by laser desorption/ionisation mass spectrometry using an excimer laser at 308 nm wavelength with 20 ns pulses. The mass spectrum in Fig. 4b shows molecular ion peaks of C_{60}^+ and higher mass species from C_{110}^+ to C_{118}^+ with even numbers of atoms. The poor signal-to-noise ratio of the mass spectrum was due to the low laser fluence which was used in order to avoid fullerene aggregation [23]. It is

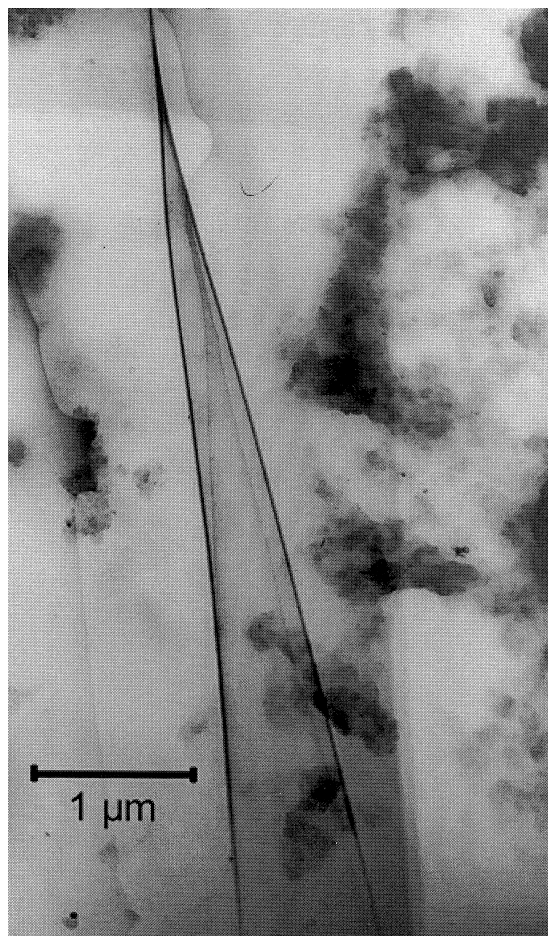


Fig. 3. TEM image of a conical nanostructure found in the stainless steel oven residue. The cone has a height of 6 μm and a base diameter of 0.8 μm .

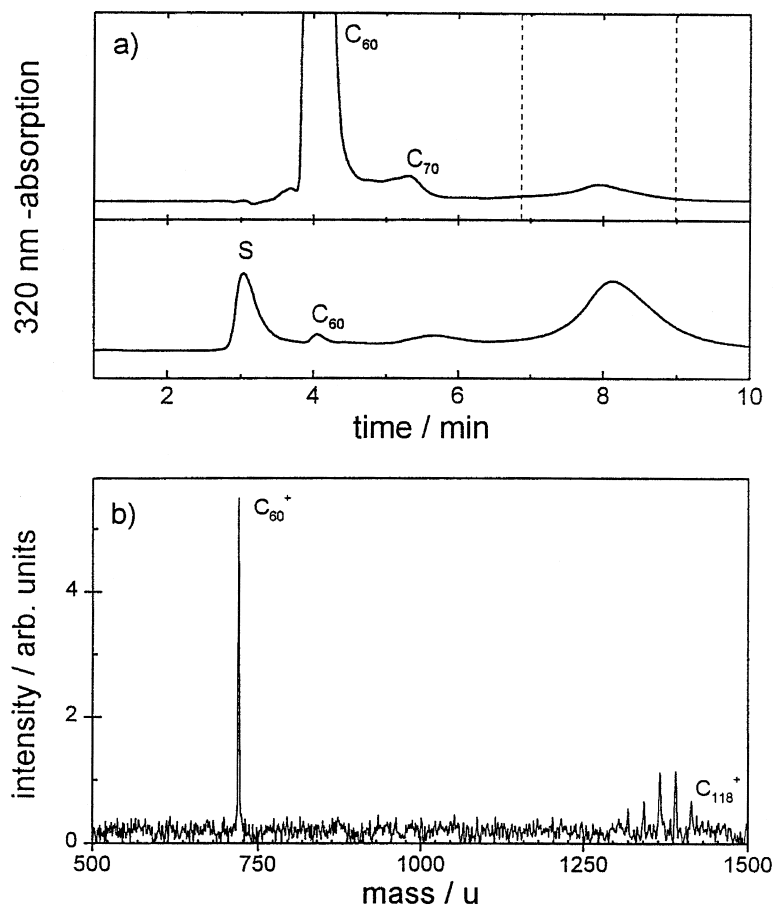


Fig. 4. (a) (top) HPLC analysis of the soluble material from the stainless steel oven after heating [60]fullerene at 450°C for several hours: (bottom) HPLC analysis of the purified fraction which was collected at a retention time between 6.5 and 9 min. (b) Laser desorption time of flight mass spectrum of the purified fraction.

remarkable that C_{58}^+ is not a significant fragment species in Fig. 4b. This was always found in laser desorption studies of C_{60} coalescence with a relative intensity comparable to or higher than that of the aggregation products [24]. The new HPLC fraction is thus interpreted as being due to aggregates of fullerene fragments with intact C_{60} upon heating in the oven under the catalytic effect of the cartridge material.

3.4. X-ray results

In order to check the effect of the cartridge material on the [60]fullerenes, we performed a control experiment in which pure iron (99.99%) was me-

chanically mixed with the same [60]fullerene material used for loading the stainless steel cartridge and evacuated, to the same pressure (2×10^{-6} mbar) used for the deposition experiments, in a quartz tube. The sealed tube was heated at 450°C for 3 days. After opening the quartz tube, the material was analysed by X-ray diffraction. Eleven lines of iron carbide were identified. The pure iron and the C_{60} material was checked but no other lines except for C_{60} and α -Fe were found. Although a quantitative determination was not made, it can be estimated that the amount of iron carbide exceeded 5 weight %. No nanotubes or related nanostructures were found in this experiment indicating that the presence of at least one of the other transition metals present in our

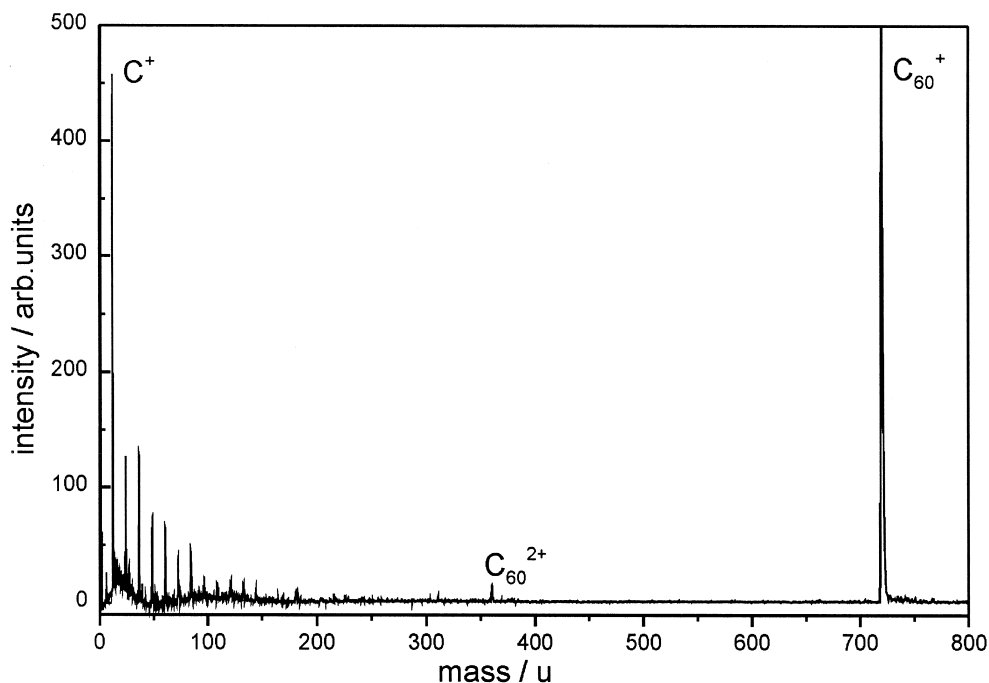


Fig. 5. Laser ionisation (100 fs) time-of-flight mass spectrum of the vapour from a stainless steel oven filled with [60]fullerenes at 450°C. The small carbon clusters are due to the catalytic decomposition of fullerenes in the oven (see text for details).

stainless steel is essential for the formation of the structures found in the insoluble residue from the stainless steel cartridge (Section 3.2).

3.5. Mass spectrometric investigations of the oven vapour

The vapour produced from the oven at 450°C was ionised using 100 fs laser pulses at 800 nm and the ions were mass analysed in a time-of-flight mass spectrometer. Femtosecond laser pulses have the advantage of leading to fragmentation free direct multiphoton ionisation mass spectra at low fluences. This is in contrast to nanosecond laser pulses with photon energies below the ionisation potential which lead to a rapid heating of the fullerenes accompanied by thermal electron emission and significant fragmentation [25]. A typical mass spectrum is shown in Fig. 5. The spectra consisted of C_{60}^+ and small carbon fragments C_n^+ ($n < 20$). No fullerene-like fragment species (C_{2n}^+ , $n > 16$) were observed at the low laser intensity employed for the measurements. At least five photons are necessary for the ionisation of C_{60}

and about eight photons are necessary for the ionisation of the small carbon clusters. We assume that the small carbon clusters originate from C_{60} which was decomposed in the stainless steel oven rather than from photofragmentation of C_{60} in the gas phase because fullerene-like fragments such as C_{58}^+ were not observed at the low fluences applied here. Normally the entire range of fullerene like fragments down to C_{32}^+ is observed in photofragmentation spectra before the small non-fullerene geometry fragments appear [25]. It thus appears that there are practically no decomposition products larger than C_{20} vaporised from the oven.

4. Conclusions

The decomposition of [60]fullerene in a stainless steel oven at 450°C was demonstrated. Carbon fragments C_n , with $n < 20$, were observed in the oven vapour. The low temperature carbon beam emitted from the oven condensed to form carbon nanotubes on HOPG surfaces with diameters in the range of

5–20 nm. No nanotubes were found from a heated quartz cartridge or on gold substrates. The HOPG surface thus appears to be required as a template for the nanotube formation under the low temperature. Carbon nanotubes and amorphous carbon were identified in the residue collected from the oven. HPLC, solubility and X-ray measurements provide additional evidence for the proposed growth scenario.

This procedure, of generating the carbon beam by [60]fullerene decomposition, has a number of advantages: (i) the process is a low temperature one, it can be more easily monitored than a process in an electric arc, or during laser ablation; (ii) no other atomic species (e.g. H, He, N) are involved in the catalytic process; (iii) the substrate temperature can be varied over a very large temperature range without influencing the generation of the carbon beam. In conclusion, we believe that this growth method, although it uses an expensive material like [60]fullerene, can be helpful in achieving the controlled growth of carbon nanotubes. We would also like to point out that this work should serve as a warning to groups who routinely use stainless steel ovens to sublime fullerenes either for film deposition purposes or for gas phase experiments.

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