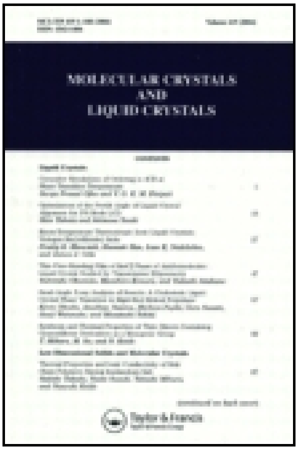

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High-quality carbon nanotubes production using plasma-chemistry deposition method

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HIGH-QUALITY CARBON NANOTUBES PRODUCTION USING PLASMA-CHEMISTRY DEPOSITION METHOD

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Catalyst assisted chemical vapor deposition (CVD) is one of the most viable routes in production of carbon nanotubes (CNTs), but purification and deposition in oriented position still remain an open question. This contribution presents a method to deposit high-quality nanotubes, using RF-plasma assisted CVD and catalytic decomposition of a ferrocene-toluene mixture in a quartz tube reactor. The most important phenomena that have been encountered are that the iron released from ferrocene play catalyst role only on a characteristic length, being removed after that by plasma etching. Raman spectroscopy and Transmission Electron Microscopy (TEM) characterized the obtained carbon structures.

Keywords: catalyst; CVD-plasma assisted; nanotube synthesis; plasma etching.

1. INTRODUCTION

Remarkable results have been obtained using carbon nanotubes in areas like gas storage tanks [1], supercapacitors [2], batteries [3], emitters for field emission [4] etc. Since Ijima [5,6] reported first observation of carbon nanotubes, a series of methods have been developed such as laser ablation, arc discharge [7], and catalytic methods using iron group nanometric powders and ferrocene like metaloorganics [8]. Important roles have the precursors and CVD configuration in all experimental techniques [9]. CVD deposition assisted by catalysts for hydrocarbon precursors is actually large exploited in mass production of nanotubes, particularly nanotubes soot. A continuous improvement run to obtain well-aligned nanotubes with tight control of theirs dimensions. None of the methods rises to satisfy both requirements

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direct from synthesis. The synthesis of nanotubes with high degree of purification and precise geometry is more appropriate for first aims. The next step is their manipulation and positioning by precise control using nanotechnology discoveries such as: precise polymerization, AFM, electric field [10].

The paper deals with an improved method to grow nanotubes simultaneous with branched fibrils with a strange constitution (Y-shapes). The method consists of a RF plasma assisted CVD coupled with an external heater to assure an optimum for chemical transport reaction (CTR). Another contribution of this paper is to show the role of synthesis parameters combined with plasma etching. The pyrolysis of the initial precursors, assisted by plasma, CTR and etching in time of the nanotube deposition prove that those are viable from the point of view of mass production and especially of high aligned, high quality NT synthesis.

The role played by metal in nanotubes synthesis is crucial as regards of yield and purity but these are in close dependence with the temperature and the pressure of the plasma. By optimizing these parameters results deposit of high-quality nanotubes, where the catalyst is removed by plasma etching.

2. EXPERIMENTAL

Pyrolysis apparatus (Fig. 1) consists from a quartz tube (900 mm × 70 mm I.D.) placed horizontally in a RF generator (2.57 MHz). In the tube entrance was attached a syringe solution injection system and a preheater furnace. The other end was placed into an electronic controlled furnace. The pressure was maintained at 10 torr during the experiment. Ferrocene-toluene mixture (10 wt.%) was injected at rate of 0.075 ml/min in the plasma RF zone by

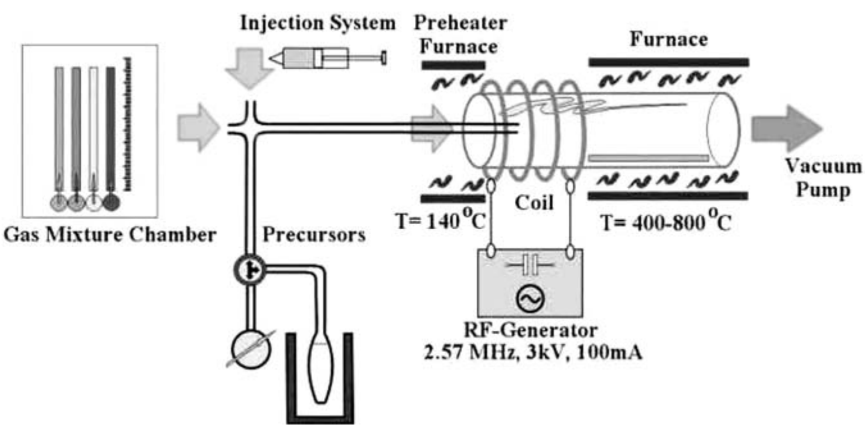

FIGURE 1 Schematic representation of the installation.

the syringe injection system with preheating at 140°C. The carrier gas was argon, at a flow rate of 150 ml/min. At this temperature, the precursors from the injection system were immediately volatilized and swept into RF plasma discharge area and then to the reaction/deposition zone of the furnace. The hydrocarbon decomposition, activated by plasma, occurred on catalyst particles located either in the reaction zone or on iron clusters as results of the ferrocene decomposition. Carbon deposits were formed on the quartz tube walls in the furnace area. The deposits were weighed before and after each run to determine the quantities of nanotubes produced at different sites within the reactor. Raman spectroscopy (R-2001, Ocean Optics, 780 nm laser diode) and TEM (Philips CM120ST) characterized the samples.

3. RESULTS AND DISCUSSIONS

All experiments took place for the same deposition time, pressure, plasma characteristics, and liquid injection speed. A black powder layer was found to cover the quartz plate in the high temperature zone. We observed that in the middle of the furnace the deposit was grown in thick and vertical

FIGURE 2 Growth of the vertical formations.

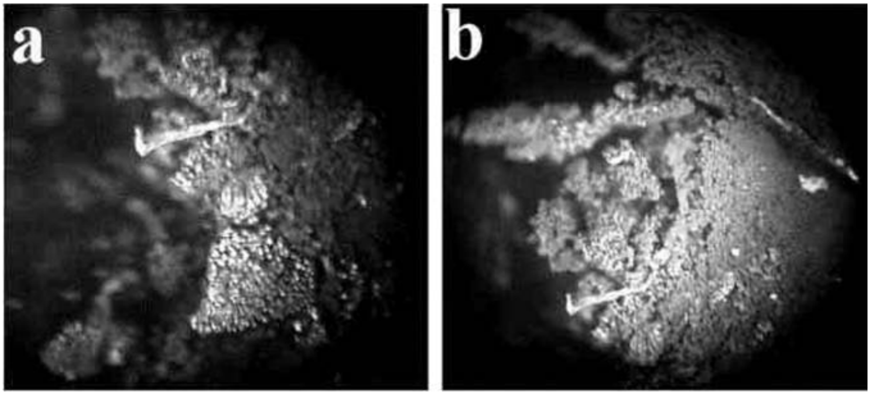

FIGURE 3 Bouquet like forms; (a) – 10× magnification, (b) – 8× magnification.

formations (Fig. 2). Branches of carbon, grown in bouquet-like forms, mainly composed the powder. Depending of temperature these branches are either spherical structures at 400℃ or nanotubes for higher temperatures (800℃). Optical microscopy images of the carbon structures obtained from a typical reaction are shown in Figure 3, optical microscopy – transmission, Figure 4, optical microscopy – reflections. TEM microscopy

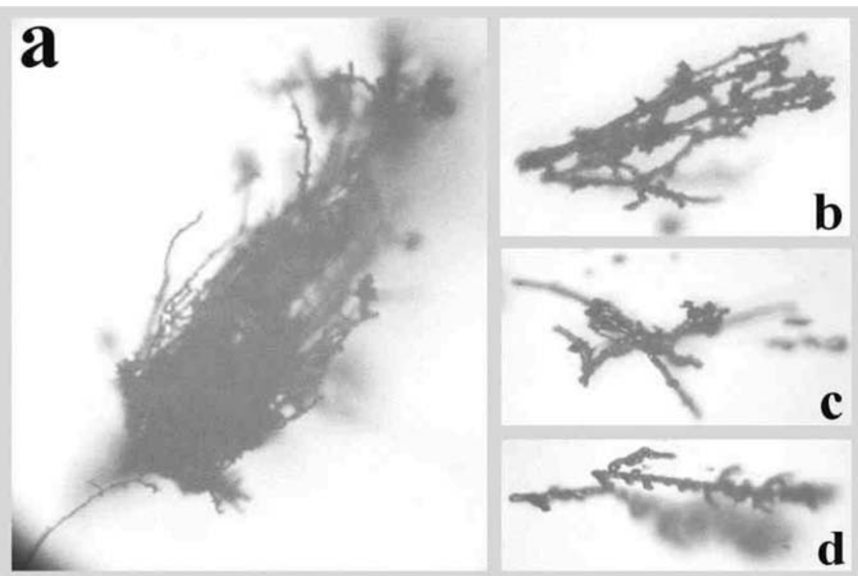

FIGURE 4 Fibrils of carbon; (a) – 10× magnification, (b) – 16× magnification, (c) – 22× magnification, (d) – 22× magnification.

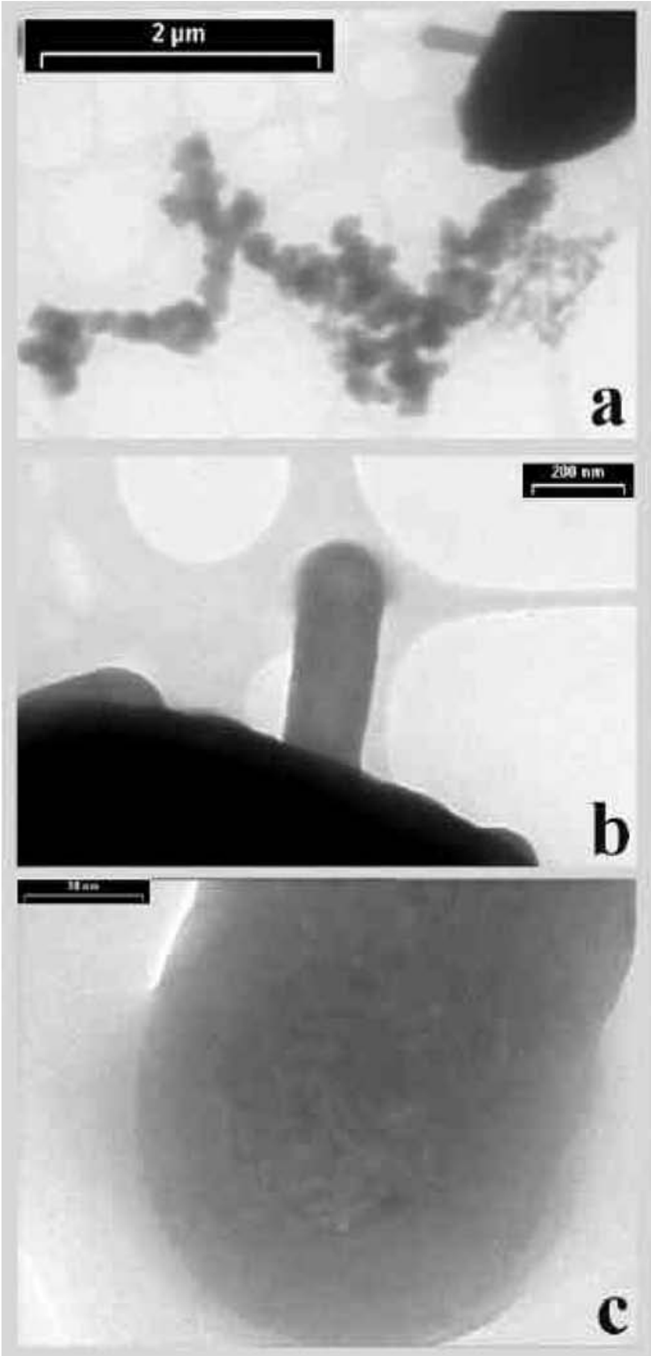

FIGURE 5 TEM; (a) – spherical structure, (b) – multi-walled nanotube, (c) – metal free closed nanotube.

TABLE 1 Effect of the Pyrolysis Temperature

Temperature (°C)	Powder layer thickness (mm)	Vertical formations diameter(mm)/height(mm)	Carbon yield (wt.%)
400	1	4/4	4.2%
500	1.5	5/10	5.4%
600	1.8	5/14	9.7%
800	4	8/40	21.4%

images (Fig. 5) shows multi-walled nanotubes with metal free and closed ends.

Independent of the reaction parameters, the carbon nanotubes found in the collected powders had lengths in the range of 0.5 μm to 5 μm. The influence of pyrolysis conditions in the carbon nanotubes production is shown in Table 1.

Raman spectrum of carbon nanotubes shown in Figure 6 is in close concordance with other reports. There are two important peaks in Raman analysis. The peak at 1321 cm^{-1} is a little defective D-line that indicates the defects and carbonaceous particles on the external walls of carbon

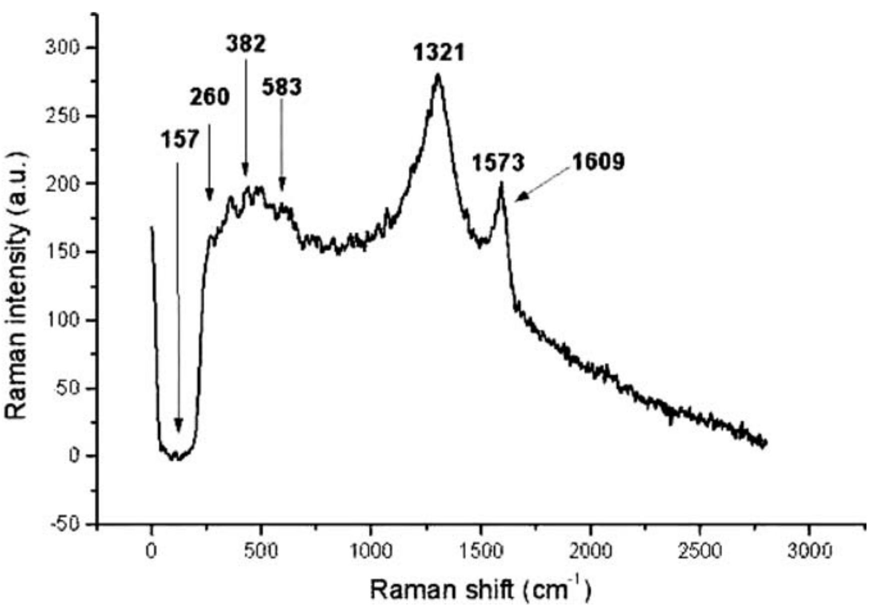

FIGURE 6 Raman spectrum of carbon nanotubes.

nanotubes. The typical G-line, 1572.7 cm^{-1}, reveals a multi-walled structure [11]. The intensity of the D-line and G-line proves that CNs are structurally stable and have a defective graphene sheets on the external walls. The low frequency modes are clearly observed located around 400 cm^{-1}. These represent the out-of-plane modes, RBM (radial breathing mode), corresponding to tubes with particularly small diameter. In general are characteristic of single-walled but it could be observed in multi-walled structures when coaxial structures occur.

The peak at 382 cm^{-1} is close to the Raman-active frequency of 377 cm^{-1} for (9, 9), (10,10) nanotubes [12,13]. The low frequencies profile is believed to emerge from a large number of closely packed nanotubes bundles, but could not be determined from this image.

In the RF zone was observed a thin polymer film as result of non-reacted toluene. We observed that a different type of polymer-like film was deposited in the rear end of the quartz tube indicating that there is a possibility to optimize the reactor geometry.

4. CONCLUSION

The nanotubes are growing simultaneously with fibrils at low temperatures. Nanotubes have metal free ends. A high carbon nanotubes yield with high purity was observed at 800°C. We have confirmed that CVD is a practical method for growth of CNTs directly in bulk or on a substrate surface.

This plasma-assisted method with ferrocene-toluene precursors is a good perspective for CNTs purification and production, in the same time. Our method allows integration of the nanotubes growth into the fabrication of electronic devices based on carbon nanotubes.

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