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Condensation of Carbon Vapour in the Microwave Oven

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ABSTRACT

This work is devoted to microwave heating of graphite for studying the processing of carbon nanotubes (CNTs) by graphite vaporization. We have applied heating by microwaves (MW) (power 800W, frequency 2.45 GHz) in air at 20-90 min. The oven temperature was approximately 1200°C. The condensed material was collected on a fused silica target. After deposition, the morphology of carbon nanotubes was studied by Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), and Transmission Electron Microscopy (TEM). The samples were found to contain nanotubes, nanoparticles and fibers (at 1.30-2.80 micrometers to 6-11 micrometers) which appeared to be highly graphitized. It was observed that multi-walled nanotubes (MWNT´s) were produced by this method.

INTRODUCTION

Multi-walled carbon nanotubes (MWNT´s) were first discovered in 1991 [1]. The walls of this kind of nanotubes consist of multi-layered coaxial cylinders of carbon atoms. In 1993, the other kind of nanotubes, called single-walled carbon nanotubes (SWNT´s), was discovered by NEC and IBM, respectively. Unlike MWNT´s, the walls of SWNT´s have only a single-layer of carbon atoms. Composed of pure carbon, carbon nanotubes are hollow cylinders with a few nanometers in diameter. The honeycomb structure of carbon atoms on the cylinder walls is similar to that of graphite. Due to such special arrangement of carbon atoms, several distinctive properties of carbon nanotubes have been extensively studied. Numerous potential applications, such as flat panel displays [2], chemical sensors [3], hydrogen storage [4], etc., have been proposed. A number of methods such as arc discharge [5], laser vaporization [6], pyrolysis [7,8], plasma-enhanced [9,10] or thermal chemical vapor deposition (CVD) [11,12], have been developed for the production of CNTs.

The synthesis of CNT´s is often accompanied by the formation of other forms of carbon, such as fullerenes, polyhedral particles and amorphous forms of carbon. In many instances purification of CNT´s (removal of side products) is necessary [13].

The microwave (MW) irradiation technique is widely applied in some areas of chemistry [14] and technology to produce or degrade various materials and chemical compounds [15], as well as in the study of chemical processes. Some of its advantages are: a) rapid heating is simply achieved; b) the energy is accumulated in the material; c) the environment do not need to be heated, so energy savings are possible; d) there is no direct contact between the energy source and the material; e) the heating can be easily automated.

A new synthesis method of fullerenes using microwave-induced naphthalene-nitrogen plasma at atmospheric pressure was reported in 1995 [16]. Some positive results were reported in 1999 by MW-heating of chloroform in presence of argon[17].

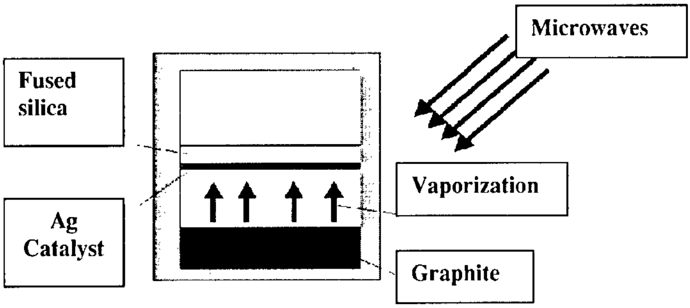


Fig.1. Experimental scheme of heating by microwaves.

The objective of this work is to obtain nanotubes using MW-heating and performe their characterization by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM).

EXPERIMENTAL DETAILS

Preparation of nanotubes was carried out in a domestic MW-oven (power 800 W and frequency 2.45 GHz). The MW-action allows the graphite heating without direct contact with the energy source; the process control is achieved varying the power and heating time from 20 to 90 min. The samples were prepared from powdered graphite (99 %) and put into a crucible, allowing the heating up to approximately 1200°C. Silver was used as a catalyst simplifys the condensation of carbon vapor and accumulation of nanoparticles. This catalyst was used on the fused silica targets. Fig.1 illustrates the scheme of the experiment.

The obtained samples were characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). The AFM images were recorded in the contact mode in air at room temperature.

RESULTS AND DISCUSSION

It is well-known that materials absorb microwaves in different manners. In particular, graphite does not need a preliminary heating to absorb microwaves, so it can be directly MW-heated (Fig.2).

Table I. Heating time of the samples.

Sample number	Time (min)	Target	Observation
1	20	Fused silica	No CNT´s
2	20	Fused silica and Ag	Few CNT´s
3	30	Fused silica	Few CNT´s
4	30	Fused silica and Ag	CNT´s
5	40	Fused silica	CNT´s
6	40	Fused silica and Ag	CNT´s
7	60	Fused silica	CNT´s
8	60	Fused silica and Ag	CNT´s
9	90	Fused silica	Crucible was melted.

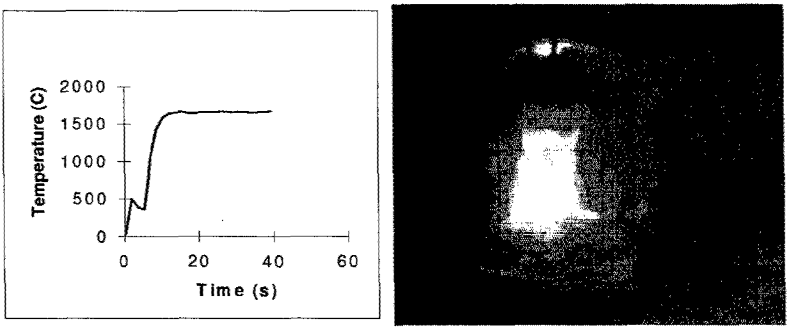


Fig.2. Microwave heating of graphite.

Various graphite samples with weight of 8 g were heated for 20, 30, 40, 60, and 90 min. As it is shown in Table I, the condensation was carried out through carbon vaporization and the process was completed in 60 min. The next step was the deposition of Ag catalyst on the fused silica targets; a series of similar experiments was carried out (Table I). It was established that, when using use of Ag as a catalyst, the deposition time averaged 30 min (Fig.3). The SEM observation of the obtained samples allowed to conclude that the size of the nanotubes are increased with heating time.

The diameter of formed CNTs about is10 nm; others investigators have reported that when using a coating with Co/SiO_2, the diameter may reach up to 0.5 μm [18]. In our experiments, the surface was covered with silver; the diameter of nanotubes increases from 168 nm to 400 nm (Fig.3(b)). The diameters of nanotubes slightly increases with increasing growth time in the range 30-60 min. Since the microwave energy is selectively absorbed by the different materials, the absorbed energy increases with the heating time.

The average growth rate calculated is about 0.3 μm/min. After heating for 20 min, cracks appear in some parts of the surface of the fused silica target, its surface even can be destroyed when the heating is applied for 60 min. Fig.4 shows a TEM image of the CNTs. Most of the carbon nanotubes are closed at both ends. The TEM images are coincident with the images of SEM. The tubes have a bamboo-like structure (Fig.4(b)).

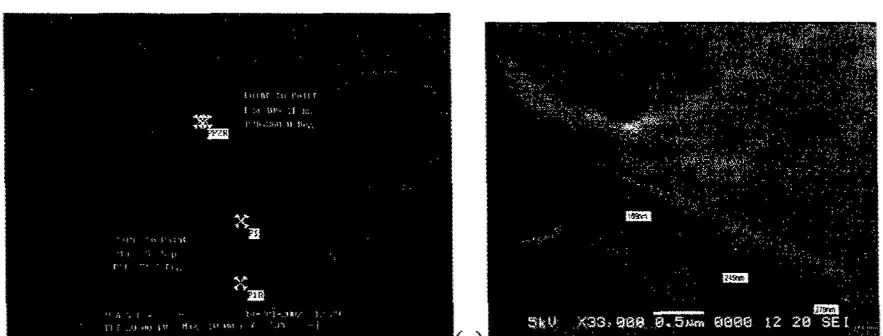


Fig.3. (a) SEM image of MWCNT´s on the target heated for 60 min with catalyst; (b) Image for the bamboo-like structured CNT´s grown on the target heated for 30 min with catalyst.

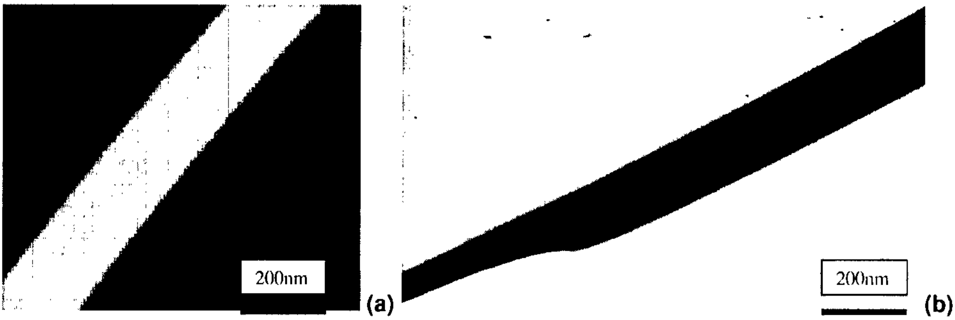


Fig.4. (a) TEM image of CNT on the target heated for 30 min with catalyst; (b) a CNT with a bamboo-like structure.

We measured TEM images of the CNTs to investigate the structure dependence on the catalyst (Table II). The CNTs exhibit exclusively a multi-walled bamboo-like structure for the Ag calatyst. The CNTs have a closed tip without not encapsulated catalyst particle and open tip without encapsulated catalyst (Fig.5). The tip with the particle is open. The tubes are the result of tip growth and metal particles are lifted-up as the tubes grew. This phenomenon has been observed and it has been postulated that the metal nanoparticles were in liquid state during nanotube growth [19].

To investigate the structure of nanotubes obtained by microwaves heating, CNT's were analyzed by AFM. According to AFM studies (Fig.6), carbon vaporization via microwave treatment produces multi-layer nanotubes (thickness 117 Å). As it is seen, the catalyst increases the diameter of tubes (Table II). The tube contains approximately 20 graphite wall layers. This result agrees well with the results of Zhang et.al. [19].

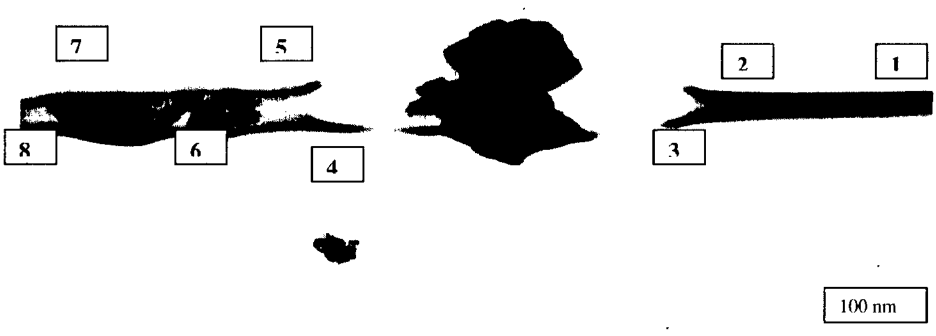


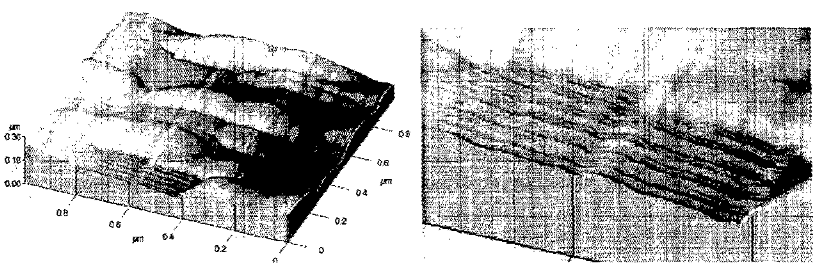
Fig.5. TEM image of CNT tip with a Ag particle in the tube and opened tip (the numbers correspond to entries in Table II).

Table II . Dependence of the diameter of CNT on presence of Ag catalyst.

Entry	Diameter of CNT, nm	Graphite sheets, nm	Channel diameter, nm	Observations
1	55 nm	18.5 nm	17 nm	Without catalyst.
2	66 nm	20 nm	26 nm	Without catalyst. Close to the open tip.
3	99.2 nm	19 nm	61 nm	Open tip.
4	110.3 nm	19 nm	82 nm	Open tip.
5	82.2 nm	20 nm	42.2 nm	With catalyst. Close to the open tip.
6	103.7 nm	17.7 nm	68.3 nm	With catalyst.
7	112.5 nm	18.5 nm	75.5 nm	With catalyst.
8	71.1 nm	19.7 nm	31.7 nm	With catalyst. Far from the Ag particles.

An easy way was reported for improving the purity of nanotubes using a domestic multimode microwave oven [20]. In the present investigation, we noted that the CNTs appeared to be highly graphitized. The nanotubes, obtained by this technique do not require further purification. The diameter of hollow CNT is constant over a long distance.

The SEM analysis of crucible surfaces allowed to observe that the heating for 60 min provokes the formation of carbon fibers with diameters up to 11.87 μm (Fig.7).



(a) (b)

Fig.6. (a) AFM image of the CNT´s with a one open MWCNT , (b) image of the CNT layer.

CONCLUSIONS

The vaporization technique by microwaves allows to produce nanotubes. The optimal time is 60 min. The presence of silver as a catalyst permits to decrease heating time to 30 min. As a contribution of this method, the aligned multi-layer carbon nanotubes were obtained. Their diameter is from 50 to 400 nm and the length is from 1 μm to 10 μm. Layer size is about 117 Å.

The CNTs have bamboo-like structure with empty closed compartments inside the nanotube. When we use silver as a catalyst, carbon nanotubes contain Ag particles inside and one tip is open. When nanotube diameters decreased, the layers between compartments appear more compressed. In some cases, the CNT´s are aligned in fibers up to a diameter of 5-12 μm.

Fig. 7. SEM images of a fiber on a crucible´s surface after heating for 60 min.

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