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SYNTHESIS AND MORPHOLOGY OF NANOSTRUCTURES VIA MICROWAVE HEATING

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Abstract. This work is devoted to microwave heating of graphite to produce carbon nanotubes (CNT's). We have applied heating by microwaves (MW) (power 800 W, frequency 2.45 GHz) in vacuum (10^{-5} Torr) at 30-90 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) and Transmission Electron Microscopy (TEM). The samples were found to contain nanotubes, nanoparticles and fibers (1-2.8 micrometers). It was observed that multi-walled nanotubes (MWNTr's) were produced by this method.

1. INTRODUCTION

The new structural form of carbon discovered by Iijima in 1991 [1] attracted the attention of several research groups due to its interesting properties. Numerous potential applications, such as flat panel displays [2], chemical sensors [3], hydrogen storage [4], *etc.*, had been proposed. A number of methods such as arc discharge [5], laser vaporization [6], gas-phase pyrolysis [7,8], plasma-enhanced [9,10] or thermal chemical vapor deposition (CVD) [11,12], had been developed for the production of CNT's.

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 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.

A method of fullerene synthesis using microwave-induced naphthalene-nitrogen plasma at atmospheric pressure was reported in 1995 [16]. Some positive results were also presented in 1999 [17], the authors of the work used MW-heating of chloroform in presence of argon.

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

2. EXPERIMENTAL

Preparation of nanotubes was carried out in a domestic MW-oven (power 800 W and frequency 2.45 GHz) [18]. 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 60 min. The samples were prepared from powdered graphite (99%) and sucrose; calcined sucrose and boric acid. The mixtures of

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Table 1. Heating time of the samples.

Sample number	*Time* (min)	*Target*	*Observation*
1	60	Graphite	nanotubes
2	60	Sucrose	No heating
3	60	Calcined Sucrose	No heating
4	60	Sucrose and graphite	Nanotubes, nanofibers
5	180	Boric Acid and graphite	Nanotubes, nanofibers, and microparticles

each composition were contained under vacuum atmosphere (10^{-5} Torr) into a quartz capsule.

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.

3. 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.1).

As it is shown in Table 1, the condensation was carried out through carbon vaporization and the process were completed in 60 min (180 min to graphite and boron compounds).

SEM observation of graphite samples allowed to conclude that the size of the nanotubes increased with heating time. The diameter of the formed CNT's is about 100 nm; others investigators have reported that using a Co/SiO_2 coating, one can obtain the diameter up to 0.5 mm [18]. In our experiments, a

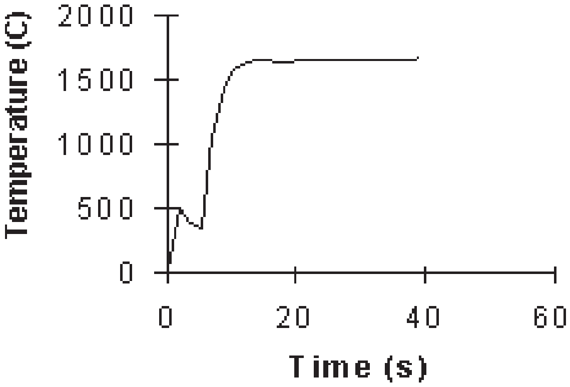
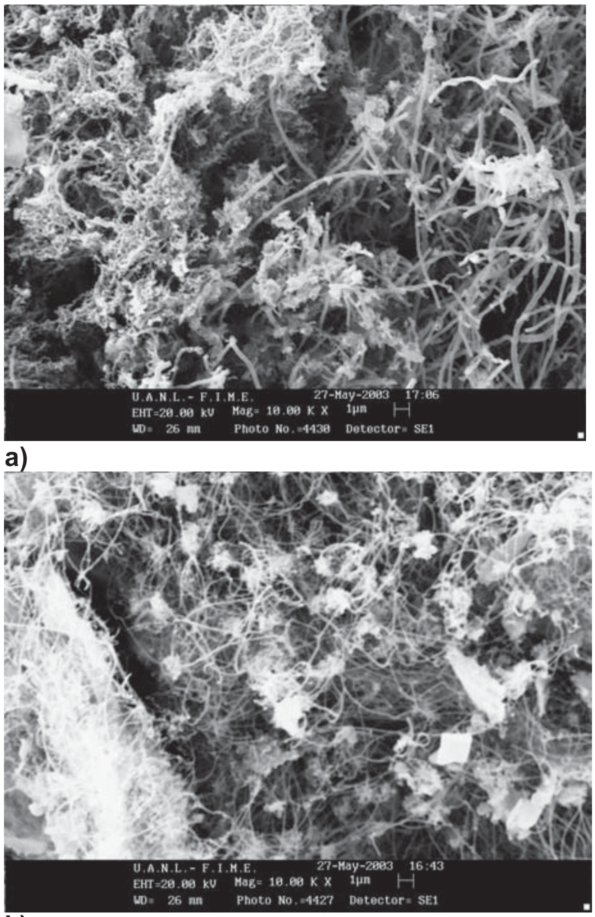


Fig.1. Microwave heating of graphite.



a)

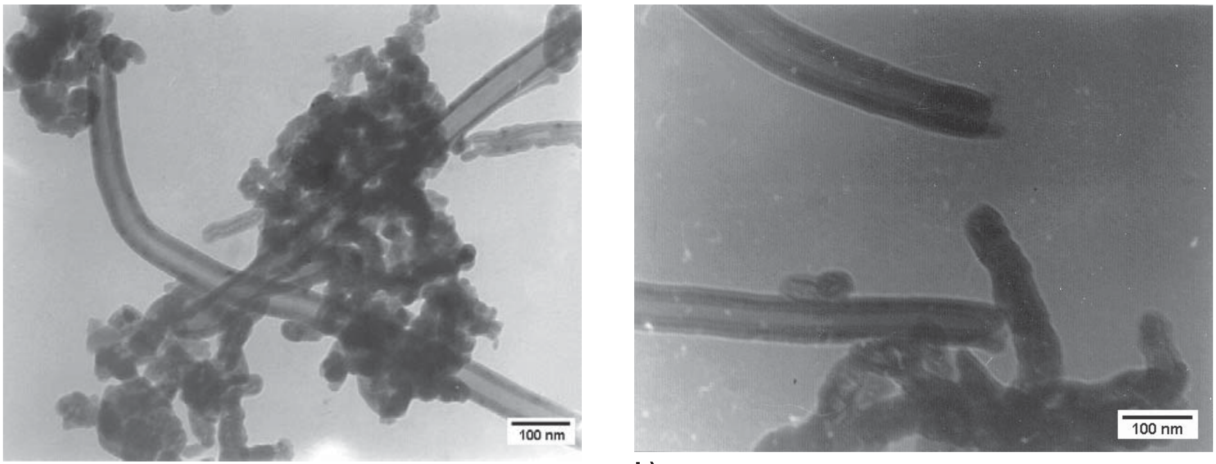
b)

Fig.2. (a) SEM image of MWCNTr's on the target heated for 60 min without catalyst; (b) Image for the CNT grown on the sample heated for 60 min without catalyst.

catalyst is not employed and the diameters of nanotubes are from 100 nm to 200 nm (Fig.2). The diameter of nanotubes slightly increases with increasing time in the range 30-60 min.

Fig.3 shows a TEM image of the CNT's, most of the carbon nanotubes are surrounded by carbonaceous material and smallest particles. The TEM and SEM images demonstrate a good agreement.

We registered TEM images of the CNT's to investigate the structure of the sample. The CNT's



a) b)

Fig.3. (a) TEM image of CNT on the target heated for 60 min with out catalyst; (b) a CNT with the sample heated for 60 min with out catalyst.

exhibit exclusively a multi-walled bamboo-like structure (Fig.4a). Some of the tips are open (Fig. 4b), most are closed, or end on massive carbonaceous particles (Fig. 4c).

To investigate the structure of nanotubes obtained by microwaves heating, CNT's were analyzed by AFM. According to AFM studies (Fig.5), carbon vaporization via microwave treatment produces multilayer nanotubes (thickness 117 Å). The tube contains approximately 20 wall layers. This result agrees with these of Zhang *et al*. [19].

An easy way to improve the purity of nanotubes using a domestic multimode microwave oven was reported in [20]. In the present investigation, we noted that the produced CNT's are highly graphitized, so the nanotubes obtained by this technique do not require further purification.

The SEM observation of the calcined sucrose and graphite samples allowed to conclude that the content of the nanotubes or nanofibers and their size, are smaller than those for nanotubes obtained in the graphite sample (Fig. 6). The TEM study shows the presence of filled nanotubes and nanofibers (Fig.

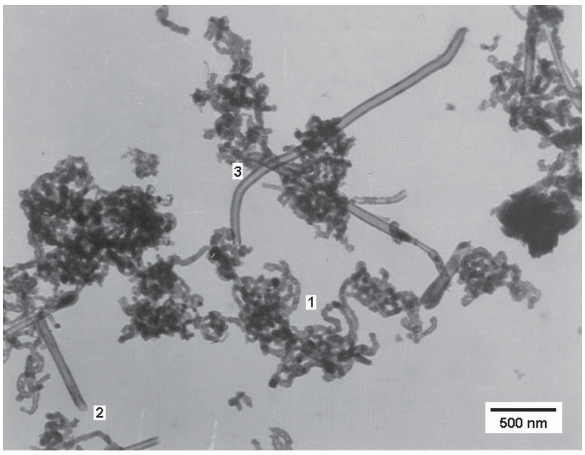
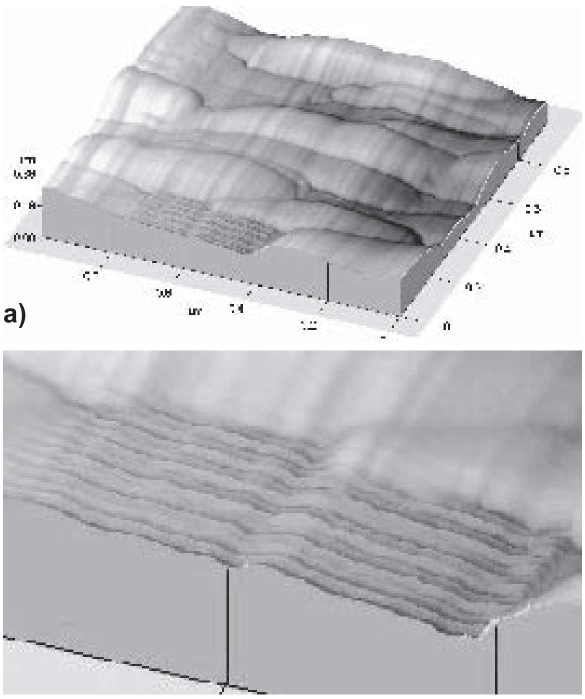


Fig.4. TEM image of a CNT closed tip in the tube and unopened tip.



a)

b)

Fig.5. (a) AFM image of a one open MWCNT, (b) Image of the CNT layer.

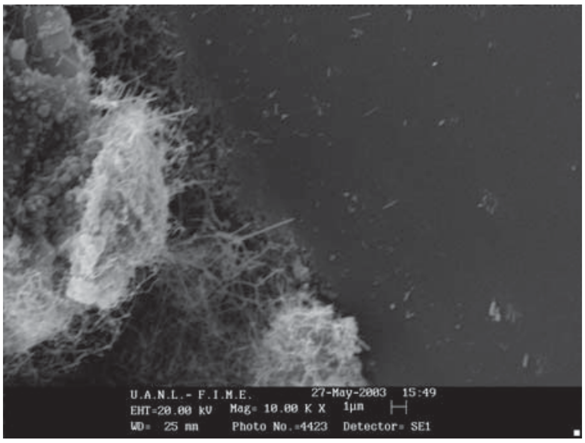


Fig. 6. SEM images of a nanotubes of calcined sucrose and graphite mixture without catalyst, after heating 60 min.

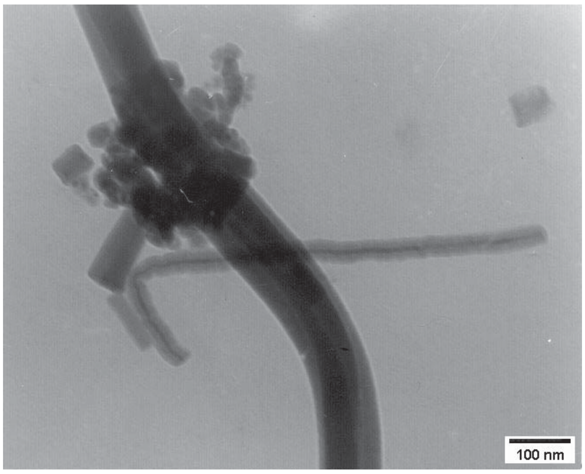


Fig. 7. TEM image of filled CNT and nanofibers from calcined sucrose and graphite sample hated for 60 min without catalyst.

7). In the presence of sucrose the generation of filled nanotubes and nanofibres seems unlikely. The size of nanofibers here is smaller than that typical for the nanotubes of the graphite sample, TEM image of nanoparticles and nanofibers is given in Fig. 8a.

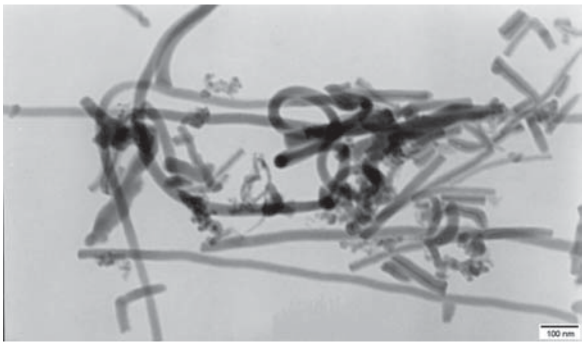


Fig. 8. TEM image of filled CNT and nanofibers from calcined sucrose and graphite sample heated 60 min without catalyst.

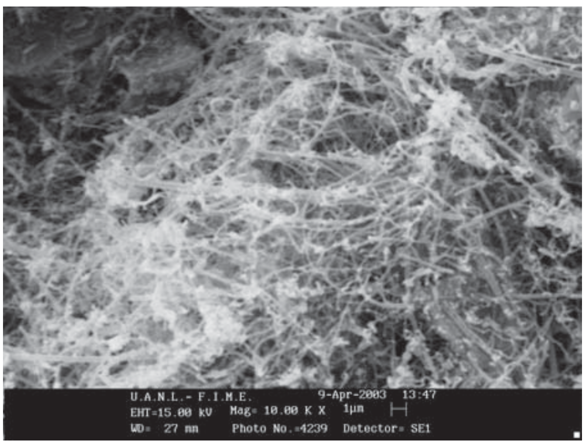


Fig. 9. SEM image of a sample Boric acid and graphite, and heated produced by mixing 180 min in a microwave oven.

Samples produced by mixing boric acid with graphite were analyzed by SEM and TEM. In the SEM study, we detected a great number of nanotubes and nanofibers (Fig.9). The size of these nanotubes was smaller than that of the nanotubes obtained in graphite sample. The presence of a multi-walled bamboo-like structures was detected by TEM; their size were the largest one obtained in all samples studied (Fig. 10).

4. CONCLUSIONS

We have produced nanotubes by vaporization using microwave heating. The optimal process time

Fig. 10. TEM image of a CNT and a multi-walled bamboo-like structure in Boric Acid graphite heated 180 min without catalyst.

was 60 min. The presence of calcined sucrose decrease the quantity and size of nanotubes, but increase nanofibers and filled nanotubes. In the presence of boric acid, samples contain a great number of nanotube and multi-walled bamboo-like structures. In addition, the aligned multi-layer carbon nanotubes were obtained. Their diameters are from 50 to 400 nm and their lengths are from 1 mm to 10 mm. Layer size is about 117 Å.

Small CNT's have bamboo-like structure with empty closed compartments inside. When we use boric acid or calcined sucrose, carbon nanotubes contains a nanotube or nanofiber inside, and both samples contain fibers with diameters from of 5 to 12 μm.

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