

Obtaining bamboo-structured, multiwalled carbon nanotubes using the spray pyrolysis method

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In this paper we have investigated the synthesis of multiwalled carbon nanotubes by spray pyrolysis, which is a type of catalyzed chemical vapour deposition method. As carbon sources we have used pyridine (C₅H₅N) and benzene (C₆H₆) and a mixture of these. As catalyst precursor ferrocene Fe(C₅H₅)₂ was added to the liquid carbon source. The thermal decomposition of ferrocene/benzene/pyridine solution was realized in an argon or nitrogen atmosphere. The obtained nanotubes were investigated by TEM and HRTEM. The TEM images indicate that most of the samples obtained, using pyridine, contain "bamboo-like" carbon nanotubes.

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1. Introduction

Carbon nanotubes (CNTs) are an allotrope of carbon besides graphite and diamond. CNTs are marvellous materials, which have attracted much research interest. They were discovered in 1991 by Iijima [1] and could be especially useful, for example, in electronic devices, due to their unique properties [2]. It is possible to influence the electronic, vibrational, chemical and mechanical properties of CNTs by replacing some carbon atoms by either boron or nitrogen atoms [3]. Thus, if boron replaces some C atoms in the graphene sheet (sp² carbon system), this results in p-type states in the valence band, whereas when N atoms substitute for C atoms, electrons are injected into the conduction band, an n-type material arises. Boron-doped CNTs were found to be uniformly metallic using theoretical calculations [4]. The nitrogen-doped CNTs were found to be either metallic or narrow energy gap semiconductors [5].

For the synthesis of doped CNTs it is possible to use similar methods with those used for pure CNTs, changing one or some of the experimental parameters. Generally, the CNTs are synthesized by three techniques: by electric arc discharge [1], by laser ablation [6] and by chemical vapour deposition [7]. The arc discharge technique consists of an electric arc between two graphite electrodes, one of which contains a catalyst as a metal powder (Fe, Ni, Co) in an inert atmosphere (Ar, He). The laser ablation technique uses a laser to evaporate a graphite target which contains the catalyst metal powder. In the chemical vapour deposition (CVD) method, the metal catalyst is used in the form of nanoparticles which react with hydrocarbon gas (or vapour) at temperatures of 500–900 °C. The CNTs can be extracted from the final product by a purification

process, before being used for specific applications. Spray pyrolysis is a type of CVD method, where the carbon source and the catalyst are introduced simultaneously into the reactor [8].

N containing carbon sources have been used with the arc discharge, laser ablation and CVD techniques, to synthesize carbon nanotubes with varying success [10]. So far synthesis experiments with CVD have been the most successful in producing bamboo structured and N doped MWCNTs [11–13].

We characterized our samples using TEM, HRTEM.

2. Experimental

In our experiments, for the synthesis of CNTs, we have used the spray pyrolysis method. The essence of the method is that the carbon source (a liquid hydrocarbon) and the catalyst precursor (e.g. ferrocene) is sprayed into the reaction chamber (quartz tube), in the form of a solution having a temperature of 875 °C using a sprayer and argon or nitrogen (Ar, N₂) as carrier gas.

In our experiments we used benzene (C₆H₆), pyridine (C₅H₅N), or their mixture as carbon source and ferrocene Fe(C₅H₅)₂ as catalyst precursor. Argon (Ar) and nitrogen (N₂) gases were used as carrier gas. We investigated the influence of the nature of the carrier gas and that of the composition of the benzene–pyridine mixture on the quantity and quality of the obtained MWCNTs.

TEM and HRTEM were used for the characterization of the final product. TEM investigations give important data referring to the characteristics of CNTs, their inner and outer diameters, as well as an estimate of the graphitization level of the multiwall nanotube walls.

The final product was purified by refluxing in diluted HNO_3 (40 vol. %) at 100 °C.

The experimental apparatus and the procedure used by us, as well as the purification procedure are described in detail in our earlier papers [8, 9].

3. Results and discussion

We have studied the effect of the quantity of pyridine in the pyridine–benzene mixture, used as carbon source

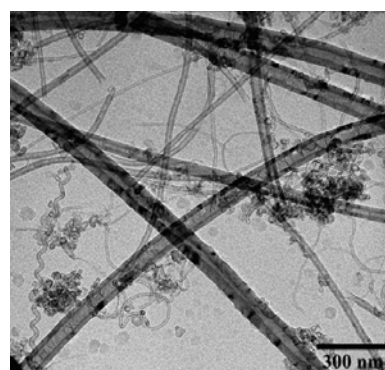
and the effect of carrier gas nature on the quantity and quality of so obtained CNTs. During the synthesis, the values of characteristic experimental parameters were: the flow-rate of the carrier gas 500 l/h, the temperature of the reactor 875 °C, the flow-rate of the solution 1 ml/ min., and the catalyst concentration 3.5 g ferrocene in 50 ml liquid carbon source. The experimental results are summarized in Table 1.

Table 1. Experimental results.

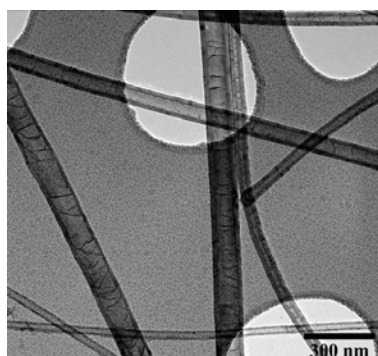
Sample	Carbon source	Carrier gas	Percentage of pyridine in the mixture	Quantity of final product (from 50 ml carbon source)	Ratio of CNT soot after and before purification
			vol. %	g	%
S105	pyridine	Ar	100	2.4154	70
S130	pyridine–benzene mixture	Ar	75	2.1515	80
S87	pyridine–benzene mixture	Ar	50	1.410	85
S129	pyridine–benzene mixture	Ar	25	1.024	75
S133	benzene	Ar	0	1.2367	80
S106	pyridine	N_2	100	0.570	65



a



c



b

Fig. 1. TEM images of the CNTs obtained from pyridine as carbon source. a) TEM image of sample S105 (using Ar as carrier gas) showing a spiral nanotube; b) sample S105 after purification; c) sample S106 (using N_2 as carrier gas) after purification.

On the basis of the data included in Table 1, we can conclude that the quantity of the final product dramatically increases when pyrolyzing 100 % pyridine instead of benzene. The quantity of the produced CNT soot is smaller when we used N_2 instead of Ar carrier gas. This result can be attributed partly to the fact that the N_2 gas could contain traces of O_2 which consumes a part of the carbon source.

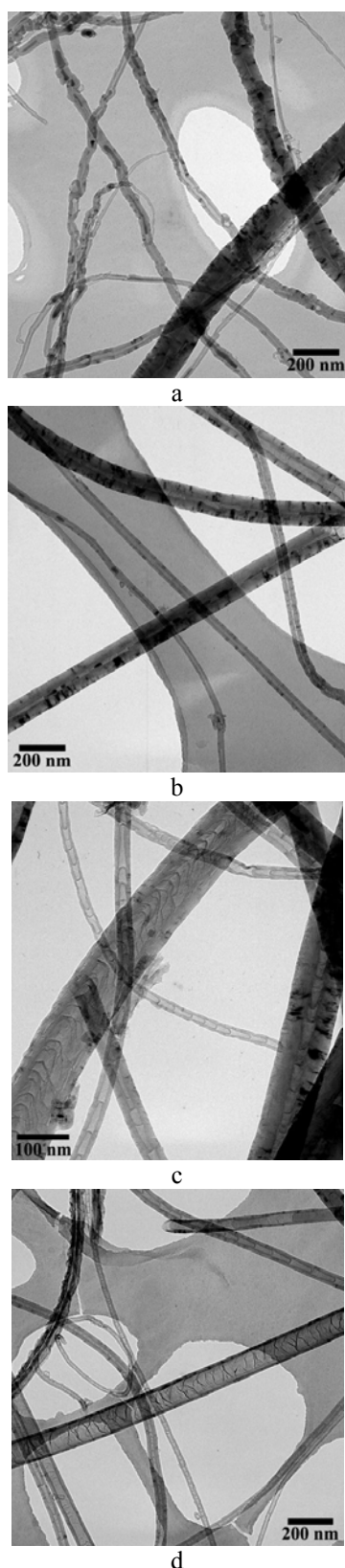


Fig. 2. Characteristic TEM images of the CNTs obtained from a) benzene (sample S133); b) pyridine–benzene mixture (sample S129, pyridine concentration 25 vol. %); c) pyridine–benzene mixture (sample S87, pyridine concentration 50 vol. %); d) pyridine–benzene mixture (sample S130, pyridine concentration 75 vol. %). Images were made after purification of the samples.

The quality of obtained N-doped CNTs was investigated by TEM and HRTEM. The TEM images of CNTs are shown in Figs. 1 and 2. The ratio of bamboo structured multiwalled nanotubes increases with increasing the pyridine content of the carbon source. Sometimes spiral-like CNTs were observed.

After TEM analysis we can conclude, that at high pyridine concentrations, along with the increasing ratio of bamboo-like tubes, nanotubes displaying defective inner graphitic walls are produced (see Fig. 2d, Fig. 1b). On the basis of the TEM images we have plotted the diameter distribution of CNTs in our samples. These distributions show that the mean outer nanotube diameters are larger, in samples produced using higher pyridine concentrations. These distributions are plotted in Fig. 3 for 0, 50 and 100 vol. % pyridine concentration in carbon sources of the obtained samples. HRTEM images of the bamboo-like structures are shown in Fig. 4.

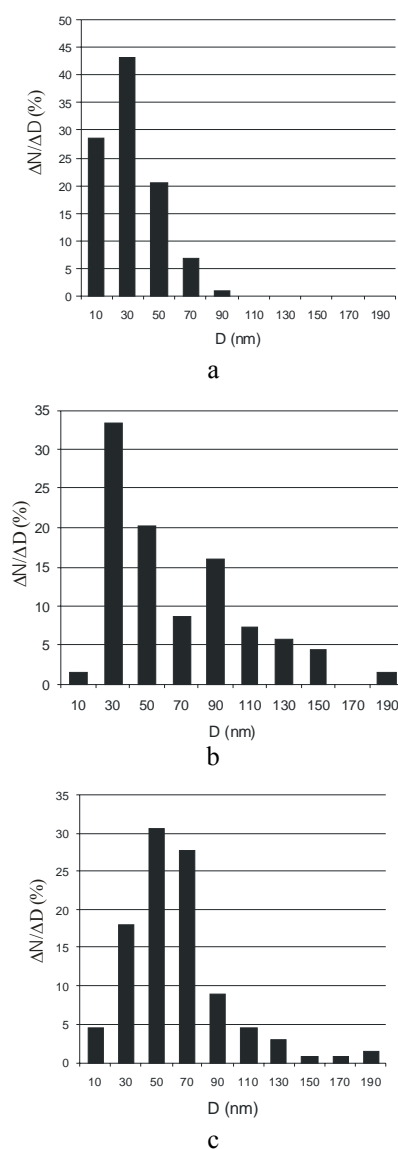
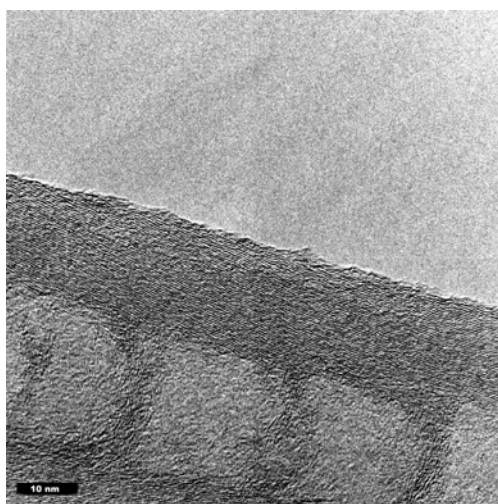


Fig. 3. The distribution of outer diameters (D) for CNTs obtained using a) benzene; b) pyridine–benzene mixture 50 vol. %; c) pyridine as carbon source.



a



b

Fig. 4. HRTEM images of bamboo-like CNTs, sample S105. Bar length 10 nm.

4. Conclusions

The spray-pyrolysis method, as a procedure for the synthesis of CNTs can be used for the production of “bamboo-like” CNTs, which are possibly N doped. Further investigation is necessary to estimate the level of N doping in the MWCNTs obtained.

The quantity of the final product, the ratio of “bamboo-like” CNTs and their mean diameter increase if the quantity of pyridine increases in the carbon source.

Using pyridine or a mixture of pyridine–benzene, the as produced samples contain traces of CNTs of spiral form.

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