

SYNTHESIS OF CARBON NANOTUBES BY SPRAY PYROLYSIS AND THEIR INVESTIGATION BY ELECTRON MICROSCOPY

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The present work is devoted to the synthesis of carbon nanotubes by spray pyrolysis method. This procedure is a version of CCVD method (Catalysed Chemical Vapour Deposition). Using a quartz reactor we have studied the influence of the history of the reactor wall surface, the length of the reactor and different aliphatic, saturated hydrocarbons as carbon sources on the quality and quantity of the final product. In order to study the influence of the reactor length on the quantity of the carbon nanotubes produced, we used two reactors of different lengths. The history of the reactor wall surface was determined by the purification process applied to the quartz reactor, which was realized with a mixture of hydrofluoric acid:nitric acid (1:1). This purification process changes the surface structure of the reactor wall, together with the catalyst, and determines the amount of the final product, which contains the carbon nanotubes. We have observed that part of the obtained carbon nanotubes have open endings. The samples obtained were purified and examined by TEM and STM.

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1. Introduction

The discovery of carbon nanotubes by Iijima [1], has started extensive research in the field, due to their promising physical properties. Much of research is related to the unique mechanical and electrical behaviour of carbon nanotubes [2,3,4], which has lead not only to fundamental scientific studies, but also to a wide range of applications from carbon nanotube reinforced composite materials [5], to nanoscale electronic devices [6]. Investigations are in progress for application of carbon nanotubes as chemical filters [7], storage systems and field emission sources [8].

The most important methods developed to produce single and multiwall carbon nanotubes include electric arc discharge [9], laser ablation [10] and CCVD (Catalysed Chemical Vapour Deposition) [11]. In any industrial application an important issue in the production process of carbon nanotubes is the quality and quantity of the final product, taking into account the cost of the production process. CCVD has been reported to be a low cost method in producing multiwalled carbon nanotubes and nanotube bundles. The CCVD process is based on the decomposition of hydrocarbons in a reaction furnace. The decomposed hydrocarbons reconfigure in the presence of transition metal catalysts to form carbon nanotubes. Spray pyrolysis is a type of CCVD method, in which the carbon source, in the form of liquid hydrocarbons, acts as a solvent for the catalyst and is sprayed into the furnace, which is heated to a temperature of 800 – 1000 °C. Spray pyrolysis is a method of producing large amounts of, well graphitized, multiwall carbon nanotubes at low cost, with the promise of industrial up-scaling.

In this paper we report a systematic study of the preparation of multiwall carbon nanotubes by pyrolysis of liquid, aliphatic, saturated hydrocarbons, as carbon sources at 875 °C, in the presence of ferrocene as catalyst precursor. We mainly investigated the influence of the nature of above

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mentioned different carbon sources on the morphology of the multiwalled carbon nanotubes. The diameter and structure of the carbon nanotubes were characterized by transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM).

For purification of the material *gathered from the furnace* we described a two – steps purification process instead of the three – steps process [12].

In addition we will present the influence of the history of the furnace wall surface on the quality and quantity of the multiwall nanotubes.

2 Experimental

2.1. Experimental setup

The apparatus used for preparation of multiwall carbon nanotubes by catalytic decomposition of hydrocarbons was described in our earlier paper [13]. During our earlier work we have investigated benzene as carbon source in the presence of ferrocene as catalyst. The solution of ferrocene in benzene was introduced into the quartz reactor by Ar as carrier gas. In this case we evaluated the optimal parameters which yield the best experimental results, referring to the final product. These optimal parameters are: 1 ml / min flowrate of ferrocene – benzene solution, 875°C reactor temperature, 3 g ferrocene / 50 ml benzene, 500 l / hour flow rate of Ar gas. In our recent work we used these optimal experimental parameters which were established for the benzene as carbon source.

2.2 Experimental procedure

These parameters were also applied in the case of n – pentane, n – hexane, n – heptane and n – octane used as carbon sources instead of benzene in the present work. These hydrocarbons are good solvents of ferrocene. We were able to prepare good solutions of ferrocene in the above mentioned liquid, aliphatic, saturated hydrocarbons. In spite of this we must remark that in the case of n – pentane and n – octane the concentration of the solutions were smaller than 3 g / 50 ml solvent. This is due to the fact that the solubility of ferrocene in these solvents are smaller. These concentrations were: 2.33 g / 50 ml n – pentane and 2.1 g / 50 ml n – octane.

For the purification of the samples we have used two step purification process. In the first step the crude material was treated six hours in diluted nitric acid. The second step consisted of boiling the material resulting from the first step in distilled water for six hours. The quality of the crude as well as the purified samples were investigated by TEM.

3. Results and discussion

Table 1 shows data on the liquid, aliphatic, saturated hydrocarbons used as carbon sources and the experimental results which were obtained at optimal values of the experimental parameters. These parameters indicate that the best experimental results regarding the quantity of the final product which contains the multiwall carbon nanotubes were obtained in the case of n – heptane. In the following we will analyse in detail, the obtained experimental results referring to each studied solvent.

Table 1.

Sample	Carbon source (ml)	Amount of catalyst (g/50ml)	Crude product (g)	Crude product used for purification (g)	Purified product gained (g)	Quantity of Material ratio after/ before purification
S36	100 ml n – pentane	2.33 g ferrocene	0.803(6)	0.3	0.163(9)	54.6%
S24	100 ml n – hexane	3 g ferrocene	0.996(6)	0.3	0.152(7)	50.9%
S31	100 ml n – heptane	3 g ferrocene	1.440(0)	0.3	0.208(4)	69.4%
S35	100 ml n – oktane	2,1 g ferrocene	0.622(9)	0.3	0.182(8)	60.9%

Fig. 1 shows one of the TEM images of the purified sample prepared by using *n* – pentane as carbon source. On the basis of the TEM images we can conclude that, the majority of the carbon nanotubes present in the sample, have smooth surfaces, only some of them show roughness, thus proving poor graphitization. Along the length of the carbon nanotubes the inner and outer diameter is constant. The carbon nanotubes predominantly do not contain encapsulated catalyst, or other by-products. Nevertheless, there are some nanotubes which contain a small amount of encapsulated catalyst in the tube interior and the tube walls. It is important to note that the proportion of these nanotubes in the sample is smaller than in the case when was used benzene as carbon source. The detailed study of the TEM image indicates that one third of the nanotubes present in the sample have open endings. We also note, that in the case of benzene (as carbon source) nanotubes having open ends were not observed. On the bases of the TEM images of the purified and crude samples we can not affirm that the amount of the nanotubes whith open ends has increased in the purified samples. The outer diameter of these nanotubes varies from 10 nm to 80 nm, (Fig. 3). TEM images show that 70% of the purified sample is constituted of carbon nanotubes.

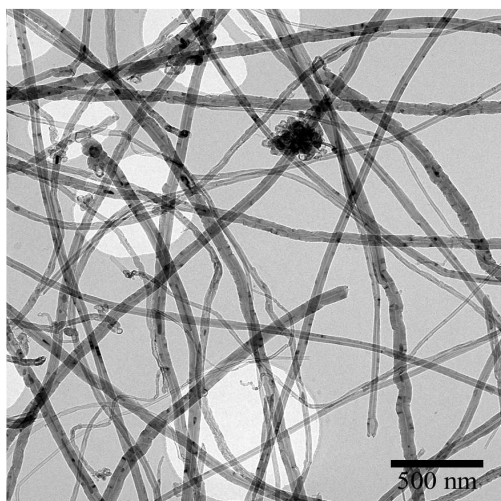


Fig. 1. TEM image of S36 (*n* – pentane) sample.

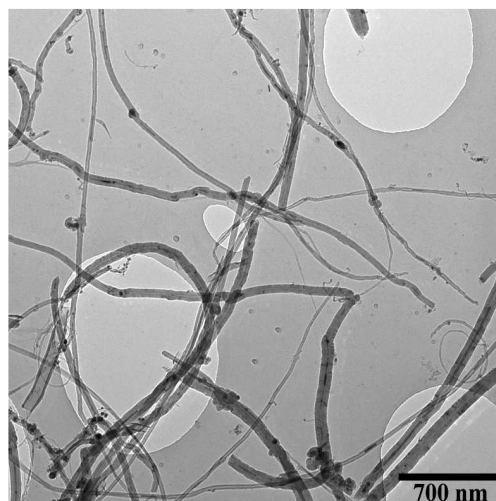


Fig. 2. TEM image of S24 (*n* – hexane).

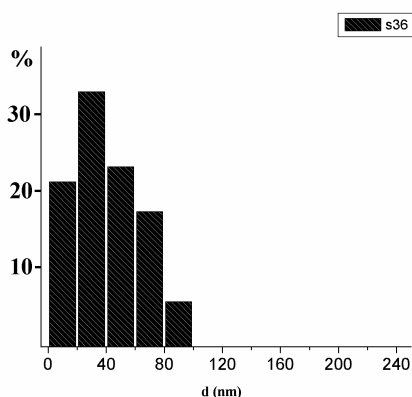


Fig. 3. The diameter distribution of nanotubes in sample S36.

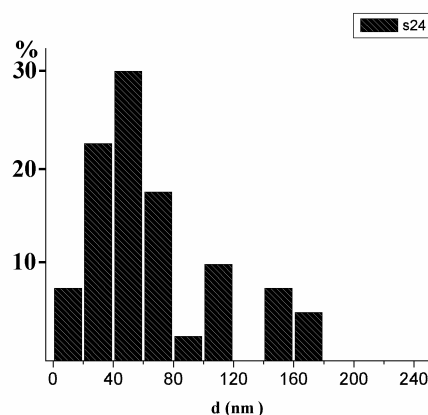


Fig. 4. The diameter distribution of nanotubes in sample S24.

In Fig. 2. the TEM image of S24 (*n* – hexane) sample is illustrated. From TEM images it results that the surface of the nanotubes is smooth and well graphitized, just as in the case of *n* – heptane. The inner and outer diameter along the length of the nanotubes is constant. Part of the

nanotubes contain catalyst in small amount. 80% of the purified sample consists of carbon nanotubes. The diameter distribution of the nanotubes in sample S24 can be seen in Fig. 4.

The TEM image of sample S31 (n – heptane) is visible in Fig. 5. The TEM analysis reveals that the nanotubes of this sample are mostly straight and their surface is smooth. On the surface of some nanotubes we found grains of catalyst which are covered with amorphous carbon. The diameters of the nanotubes are uniform but the nanotubes contain catalyst in greater amount than in the case of S36, S24 samples. The outer diameters change between 30 nm and 150 nm, while the inner diameter varies from 9 nm to 15 nm. The diameter distribution is illustrated in Fig. 7.

In Fig. 6. One of the TEM images of the purified S35 sample (n – octane) is displayed. As we can see in Fig. 6. most of the nanotubes are straight and as well as in the case of the other samples discussed here, the diameter along the length of the nanotubes is uniform. As Fig. 8. indicates the characteristic diameter of the carbon nanotubes in the sample is between 20 nm and 30 nm. The inner diameter of the nanotubes varies from 3 nm to 15 nm, and only a small portion of the nanotubes are filled by catalyst particles. In the case of this sample more nanotubes which open endings are present, than in the case of sample S36 (n – pentane): around 40%.

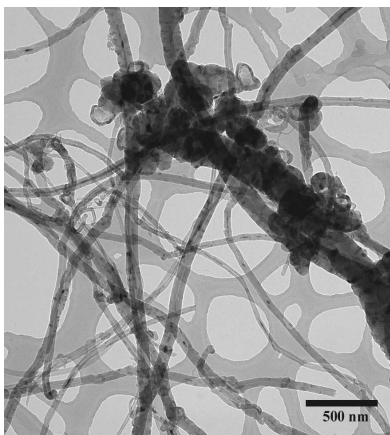


Fig. 5. TEM image of S31 (n – heptane) sample.

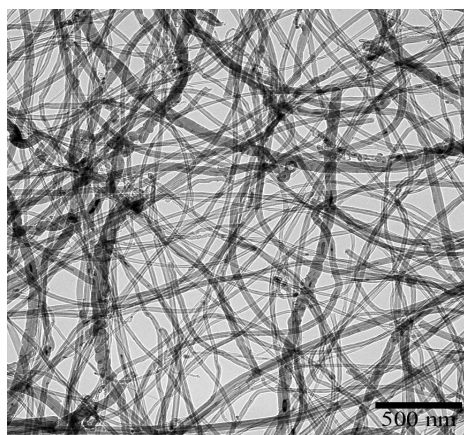


Fig. 6. TEM image of S35 (n – octane).

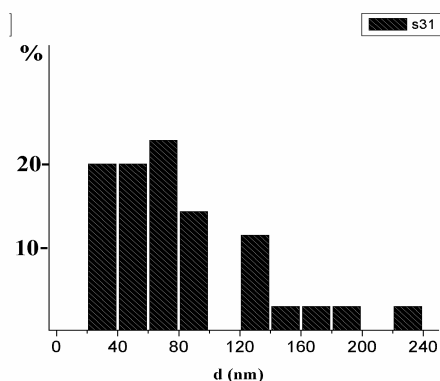


Fig. 7. The diameter distribution of nanotubes in sample S31.

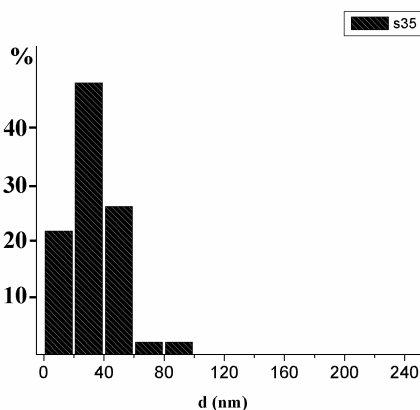


Fig. 8. The diameter distribution of nanotubes in sample S35.

The efficiency of the purification process used by us is demonstrated in Figs. 9 and 10. Fig. 9 displays the crude sample (S35) and Fig. 10 illustrates the same sample after purification. The purification process eliminates the by-product from between the nanotubes but the impurities in the tubes and on the tube walls still remain. This purification process, above all, is meant to eliminate catalyst particles and the compounds which contain Fe. The by-product which contains mainly carbon is less affected (as can be seen in Fig. 5 in the case of n – heptane).

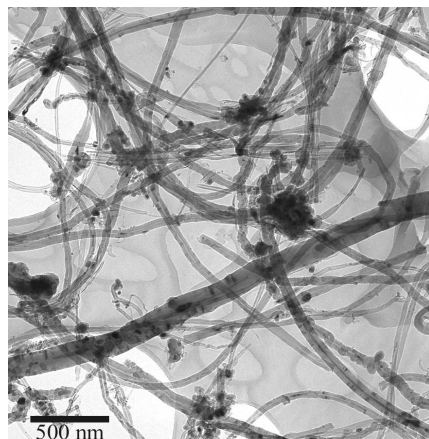


Fig. 9. TEM image of sample S35 before Purification.

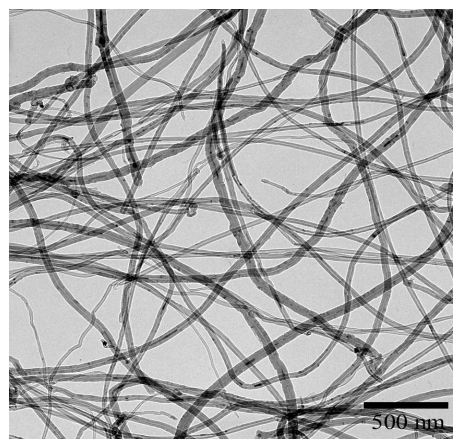


Fig. 10. TEM image of sample S35 after Purification.

After removing most of the crude product from the reactor (quartz tube), some of this product still remains well bonded to the reactor wall. In order to regain this material (or to clean the reactor) we treated the quartz tube with a mixture of concentrated nitric acid and hydrofluoric acid in a proportion of 1:1. The disadvantage of this treatment is that it makes the reactor wall thinner and after 10 – 15 exposures to this treatment becomes unusable. The advantage of this treatment consists in the modification of the surface quality. The surface becomes rough. This roughness together with the catalyst promote the growth of the nanotubes. We believe that the number of nucleation centers for nanotube growth is greater than in the case of a smooth surface. This statement is supported by our experimental results. We performed two experiments using two reactors in the same experimental conditions. In one of the experiments we used a new reactor which had a smooth surface and we have obtained 0.8985 g of final product. In another experiment the quartz tube was treated 5 times. The amount of final product obtained this way was 1.095 g. In addition, in the first case the effective length of the reactor was greater.

We also studied the effect of the reactor length on the quantity of the final product. For this we used two reactors of different lengths each treated 5 times. In the shorter reactor, having 22 cm effective length, we obtained 1.1381 g of crude material, while in the reactor having a longer effective length of 35 cm the amount of crude material was 1.5538 g. The carbon nanotubes can be formed better at the high temperature regions of the reactor surface. The area of this surface is greater in the case of a longer reactor.

Some of the samples were examined also by FESEM. Fig. 11 illustrates a bundle formed by aligned multiwall carbon nanotubes.

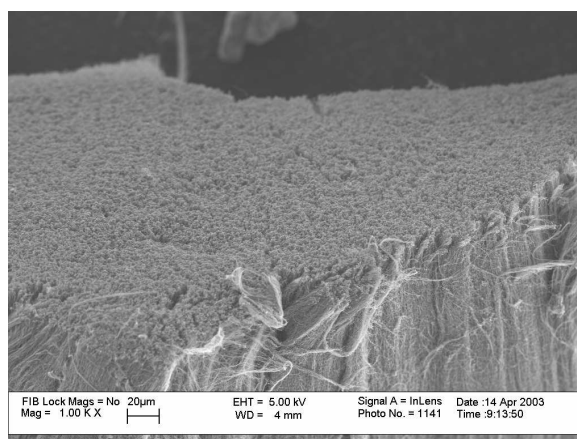


Fig. 11. FESEM image of a bundle of aligned multiwall carbon nanotubes.

4. Conclusions

Using the spray pyrolysis method we produced multiwall carbon nanotubes as well as bundles formed by aligned carbon nanotubes using aliphatic, saturated hydrocarbons as carbon source, with the promise of industrial up – scaling. This method yields mainly multiwall carbon nanotubes at the working temperature of 875 °C. The synthesized carbon nanotubes can be characterised in the following way. The nanotubes are less filled with catalyst than in the case of nanotubes prepared by the pyrolysis of benzene. The use of our two steps purification method eliminates the by-product situated between the carbon nanotubes, but the impurities inside the nanotubes and in the tube walls still remain. The nanotubes prepared by the pyrolysis of n – pentane and n – octane have open ends in a ratio of up to 40%. We cannot affirm that the number of nanotubes with open ends has increased after the purification of the samples.

The best results referring to the quantity of the crude material was obtained in the case of n – heptane. The removal of the residual crude product, from the quartz tube, by the mixture of concentrated nitric acid and hydrofluoric acid alters the quality of the reactor surface. This treatment has two effects. The first effect is the contribution to the thinning of the reactor wall, the second effect is the fact that the roughness, caused by treating contributes to the increase in the amount of the crude material.

As a final conclusion we can say that if we use 3 g ferrocene / 50 ml n – heptane the crude product is 1.44 g, from which after purification approximately 70% remains behind as multiwall carbon nanotubes.

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