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Synthesis of bamboo–structured multiwalled carbon nanotubes by spray pyrolysis method, using a mixture of benzene and pyridine

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Spray pyrolysis is one of the most widely used methods for carbon nanotube synthesis. This is mainly because of its scalability and the low cost of the carbon nanotubes produced. In our synthesis experiments, multiwalled carbon nanotubes (MWCNT) are formed by spraying a solution of ferrocene-liquid hydrocarbon into a quartz reactor, heated to a temperature of around 800^{o}C, with the aid of Ar gas. The most suitable carbon sources are found to be benzene and its derivatives (toluene, xylene). In our current paper we report, how this simple method can be used, to produce MWCNTs with bamboo structure, as evidenced by TEM and HRTEM measurements. Bamboo-structured MWCNTs are obtained by adding pyridine to the ferrocene-benzene solution. We have studied the effect of pyridine concentration on the ratio and morphology of the bamboo MWCNTs in the obtained samples. Such bamboo-shaped nanotubes are known to contain nitrogen incorporated into their structure. The nitrogen doping has an important effect on the physical properties of carbon nanotubes. Potential applications of doped nanotubes include gas sensors, nanoscale emitters and nanoelectronic devices.

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1. Introduction

Since the discovery of multiwalled carbon nanotubes (MWCNT) [1], various methods have been developed to obtain this new form of carbon [2-5]. Their synthesis methods and characterisation has been studied extensively. A great deal of research effort is focused on exploiting the exciting physical properties of carbon nanotubes with the goal of producing novel nanoscale devices, sensors, etc. Practical applications of carbon nanotubes require the synthesis of carbon nanotubes with certain well defined properties (diameter distribution, alignment, filling with various materials, etc.). The most promising method, by which such properties can be influenced, is Chemical Vapour Deposition (CVD) [6, 7]. One of the great advantages of CVD is the possibility of selective CNT growth on different surfaces [8], or on pre-patterned catalyst [9], making it an effective tool in nano-engineering.

Scientific interest has also been focused on CNTs exhibiting exotic structures, like Y or T junctions [10,11], bamboo and fish-bone structures [12-14]. The graphene shells of bamboo MWCNTs have a "stacked cone" morphology. It is believed that these MWCNTs possess a higher degree of structural defects, than hollow MWCNTs. These structural defects are attributed to either pyridinic or substitutional N incorporation into the graphene lattice [17]. Experimental evidence points to the fact that active N, in the reaction zone, plays a key role in the growth mechanism of such bamboo MWCNTs [14-17]. M. Jung et al. have also shown that the presence of active N can be beneficial for CNT growth [25]. Since the mechanical and electronic properties of CNTs strongly depend on their chirality, diameter, defect structure, etc., such nanotubes have entered the spotlight of nano-science [18].

Using the spray pyrolysis (or injection CVD) method our team has successfully obtained high purity, aligned MWCNT bundles, using various aromatic and aliphatic hydrocarbons [19, 20] and ferrocene as catalyst precursor. The major advantage of spray pyrolysis over other CVD methods is that the catalyst precursor and liquid hydrocarbon can be introduced continuously into the reaction zone, thus making possible the cheap, semi continuous synthesis of MWCNTs [21]. Moreover it provides an easy way of the controlled insertion of liquid additives into the reactor. We have investigated the effect of pyridine addition to the hydrocarbon feedstock on the morphology of the obtained MWCNTs by TEM and HRTEM. The presence of N, in some cases, has drastic effects on the MWCNTs obtained. At high pyridine

concentrations, the samples contain bamboo structured nanotubes.

2. Experimental

The MWCNT samples were prepared in a quartz glass reactor, heated by an electrical furnace to the desired temperature. The electrical furnace has an effective heating length of 20 cm, the quartz reactor an inner diameter of 18 mm. Ferrocene (Aldrich, 98%) acting as the catalyst precursor was dissolved in a benzene-pyridine mixture (pyridine: Fluka 99.8%) and fed into the reactor by means of a sprayer, using Ar gas. The synthesis apparatus is described in detail in our previous paper [22].

To examine the effect of pyridine addition to the carbon feedstock, we mixed benzene and pyridine in concentrations of 0, 5, 25, 50, 75, 100 vol% of pyridine in solution. For each synthesis experiment, we used 50 ml of pyridine-benzene mixture, in this we dissolved 3.5 g of ferrocene. Before each experiment, the quartz tube was cleaned with hydrofluoric acid. The electric furnace was gradually heated to a temperature of 875°C, during this time the reactor was flushed with Ar gas flowing at about 50 l/h. After the reactor had reached the desired temperature, the Ar flow rate was stepped up to 500 l/h and the solution of ferrocene in benzene-pyridine was fed into the reactor through the sprayer. The solution flow rate was kept at a constant value of 1 ml/min. After 50 ml of solution was injected, the solution flow was stopped and the reactor gradually cooled to room temperature, Ar flow rate was kept at 50 l/h during this time. MWCNT deposition occurred in the hot zone of the quartz tube reactor. This material can easily be removed from the inner surface of the quartz tube, by scratching with a sharp metal tool. An amount of 0.2 g of each sample was purified by a treatment in nitric acid (40 wt%) [22]. This treatment effectively removes catalyst particles and amorphous carbon from the as prepared samples. TEM images presented in this paper have been obtained on purified samples, unless stated otherwise.

TEM measurements were performed on a Philips CM20 microscope, operating at 200 kV. HRTEM characterization of the samples was realized using a JEOL 3010 (300 kV) microscope. For the TEM measurements, the samples were dispersed in ethanol and ultrasonicated. Droplets of the suspension were dried on holey amorphous carbon film suspended on a copper grid.

3. Results and discussion

Table 1. shows a list of the samples prepared by a varying addition of pyridine to the benzene carbon source. By using only benzene as carbon source, MWCNTs are obtained having a diameter of 10 nm to 80 nm, with a mean diameter of around 20 nm [23]. These samples also contain a small percentage of very thick nanotubes (diameter more than 100 nm). The tubes often contain encapsulated catalyst material (Fe, Fe_3C) in the form of nanowires, which can be as long as a few hundred nanometers (see Fig. 1a). These MWCNTs often have a non uniform outer and inner diameter along their length.

Table 1.

Sample	Pyridine concentration (vol%)	Molar ratio of nitrogen to carbon in the solution (N/C)	Quantity of the sample (g)	Weight loss of sample after purification treatment
P100	100%	18.83%	2.4154	31%
P75	75%	13.85%	2.1515	20%
P50	50%	7.61%	1.4100	14%
P25	25%	4.52%	1.0241	24%
P5	5%	0.79%	1.5029	20%
P0	0%	0%	1.3475	18%

With the addition of 25 vol% of pyridine to the benzene-ferrocene solution, the uniformity of the tube diameter noticeably increases. Also the bending, buckling of the tubes diminishes, with respect to the tubes prepared using only benzene (Fig. 1c). This tendency gets stronger with higher pyridine concentration. In the sample prepared using 5 vol% pyridine, the nanotube morphology does not change drastically. It is worth mentioning that in this sample, MWCNTs with Y branchings have been evidenced by TEM. In sample P25 a small percentage of nanotubes contain periodic bamboo like compartments (Fig. 1b). Increasing the pyridine concentration to 75 vol%, the percentage of bamboo structured nanotubes goes up to about 10-15%. Above 50 vol% concentration, three types of MWCNTs can be identified. The first type is the class of bamboo-nanotubes with periodic enclosures these usually have a small inner diameter. The second are the MWCNTs with larger inner diameters they tend to have defective inner walls, which show up as crinkles of graphite on the TEM images (Fig. 1d). The third class of MWCNTs have smooth inner graphitic shells. The last two classes of nanotubes show a larger inner diameter. As the pyridine concentration increases, the increase of mean inner and outer diameters of the nanotubes can be observed. The large inner diameter (30-50 nm) tubes are not encountered in the sample synthesised using pure benzene as carbon source. This leads us to the conclusion that the growth mechanism of such nanotubes differs somewhat from the mechanism responsible for nanotube growth in the case of benzene.

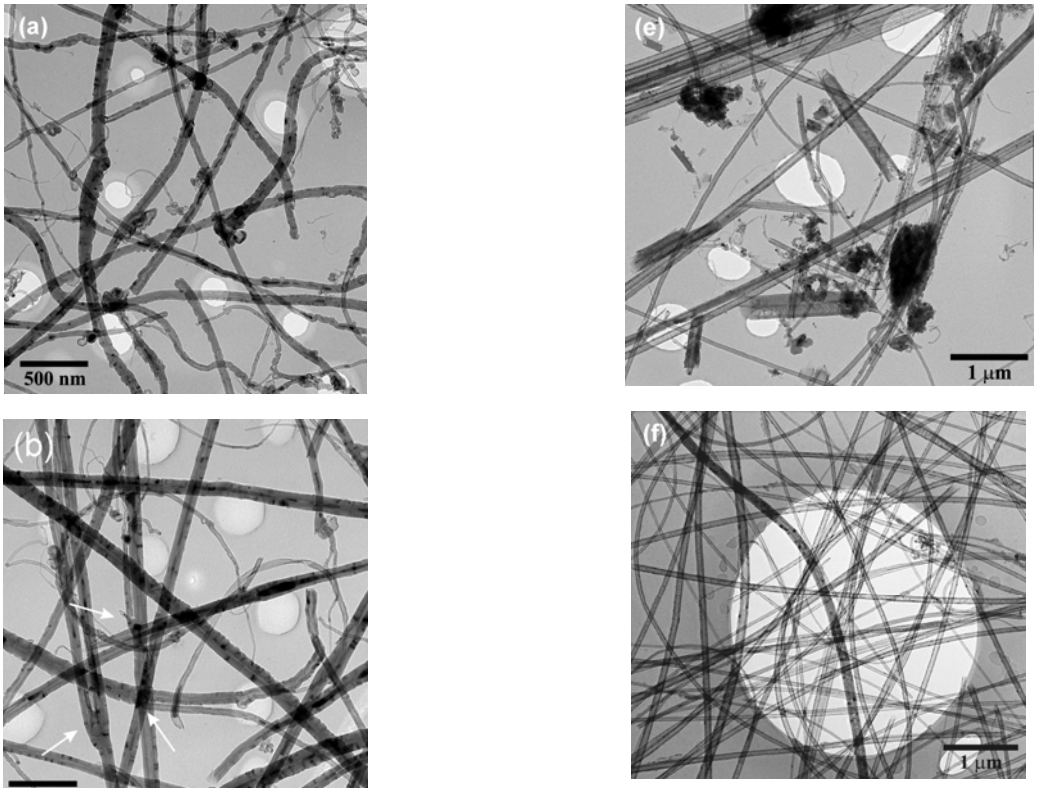

Fig. 1. (a) MWCNTs obtained by the spray pyrolysis of benzene-ferrocene solution (P0); (b) 5 vol% pyridine addition, Y junctions denoted to by arrows (P5); (c) sample obtained with 25 vol% pyridine addition (P25); (d) pyridine:benzene ratio 1:1 (P50); (e) TEM image of unpurified sample (P100) synthesised using only pyridine as carbon source; (f) P100 purified sample, the short tubes have been removed by the purification treatment.

HRTEM investigations were carried out on the nanotubes in sample P100. Fig. 2a shows the HRTEM image of a tube wall close to an enclosure of the inner graphitic walls. The curved walls of the bamboo compartment adhere perfectly to the nanotube walls. The walls themselves show a good crystallinity. The tube walls are at an angle of about 8^{o} to the tube axis. The termination of the graphene shells can be seen all along the outer edge of the tube wall. Based upon the HRTEM measurements, we can conclude that the bamboo shaped MWCNTs have a so called "stacked cone" structure. This architecture of the nanotubes is also reflected in the tube endings, they are almost always cone shaped, either concave or convex, like in sample P100 (see inset in Fig. 2b). Fig. 2b shows a HRTEM image of a nanotube, having a large inner diameter. These tubes also have a stacked cone structure, similar to the bamboo nanotubes. This is also indicated by the cone-like endings of these nanotubes (see for egz. the nanotube in the middle of Fig. 1d). Some of the inner walls of the tube are bent and crinkled. Fig. 2c shows the HRTEM image of a CNT with a high degree of crystallinity.

Using only pyridine for nanotube synthesis, the

majority of tubes show a large inner diameter and defective inner graphene walls. The percentage of bamboo nanotubes has also increased, in comparison with the sample prepared utilizing 75 vol% pyridine. In this case a few long uniform strands of MWCNTs were found too (Fig. 1e, 1f). Figure 1e shows a bundle of parallel nanotubes. It is highly likely that these tubes were formed as a part of vertically aligned bundles [23], that grow perpendicular to the quartz surface and were not separated by the ultrasonic treatment. Alongside the long strands of nanotubes, some very short tubes are also present in the samples (Fig. 1e).

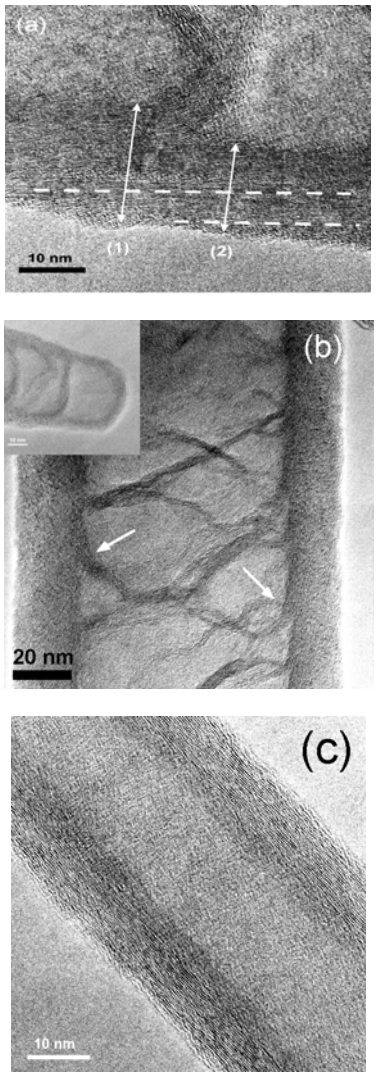

Fig. 2. a. HRTEM image of a MWCNT from sample S105. Dashed lines show the direction of the graphitic walls, they make an angle of about 8° with the tube axis. Wall thickness at point 1 is 23.3 nm, while at point 2 is 16.5 nm; ***b****. HRTEM image of a CNT from sample P100. The inner walls of the nanotubes show buckling and bending. Inset: HRTEM image of a convex cone shaped tube ending (white bar: 10 nm);* **c***. CNT from sample P100 showing no defects in the tube interior. The tube walls show a high degree of crystallinity.*

By increasing pyridine concen–tration, the encapsulation of catalyst material diminishes, and almost completely disappears in the case of sample P100. This may be attributed to smaller capillary forces acting on the catalyst particle during growth, due to the larger inner diameters of nanotubes. Encapsulation sometimes occurs in the bamboo structured nanotubes, at the enclosures of the graphitic walls (see Fig. 1c), although this is not the case with the wast majority of our bamboo tubes.

In Table 1. we summarize some experimental data regarding our synthesis experiments at various pyridine concentrations. With high N content of the solution, the quantity of obtained material increases. At the same time, the weight loss of the sample after purification by nitric acid is the greatest at 100 vol% pyridine concentration. This weight loss may be attributed to the removal of short nanotubes by the acidic treatment. These short nanotubes in sample P100 have open ends and defective inner graphene shells (Fig. 1e). The defects in the walls can be carbon pentagons or even heptagons in the curved graphite lattice, or due to nitrogen incorporation [17]. The tubes with large inner diameter and open ends can easily be attacked by nitric acid due to the more reactive defect sites.

4. Conclusions

In addition to regular MWCNTs, tubes having a stacked cone structure can be obtained by the spray pyrolysis of benzene-pyridine mixtures. The active N in the reaction zone acts as a promoter for the growth of long strands of MWCNTs, exhibiting high diameter uniformity along their axis and large inner diameters. The inner walls of these nanotubes are often bent and crinkled. Some nanotubes exhibit periodic, bamboo like enclosures of the inner walls. High pyridine concentrations disfavour the encapsulation of catalyst material in the hollow core of the nanotubes, possibly due to decreased capillary effect. At 5 vol% pyridine addition, MWCNTs having Y branches have been observed by TEM analysis.

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References

[1] S. Iijima, Nature **354**, 56 (1991).
[2] T.W. Ebbesen, P.M. Ajayan, Nature **358**, 220 (1992).
[3] T. Guo, P. Nikolaev, A. Thess, D. T. Colbert, R. E. Smalley, Chem. Phys. Lett. **243**, 49-54 (1995).
[4] M. José-Yacamán, M. Miki-Yoshida, L. Rendón, J. G. Santiesteban, Appl. Phys. Lett. **62**, 202 (1993).

[5] Kin-Tak Lau, David Hui, Composites: Part **B33**, 263 (2002).
[6] Y.C. Choi, Y.M Shin, S. C. Lim, D. J. Bae, Y. H. Lee, B. S. Lee, D. C. Chung, J. Appl. Phys. **88**, 4898 (2000).
[7] R. Kamalakaran, et al., Appl. Phys. Lett. **77**, 3385 (2000).
[8] Y. Chen, J. Yu, Appl. Phys. Lett. **87**, 033103 (2005).
[9] H. Ago, K. Murata, M. Yumura, J. Yotani, S. Uemura, Appl. Phys. Lett. **82**, 811 (2003).
[10] N. Gothard, C. Daraio, J. Gaillard, R. Zidan, S. Jin, A. M. Rao, Nano Letters **4**, 213 (2004).
[11] P. R. Bandaru, C. Daraio , S. Jin, A. M. Rao, Nature Materials **4**, 663 (2005).
[12] X. Wang, W. Hu, Y. Liu, C. Long, Y. Xu, S. Zhou, D. Zhu, L. Dai, Carbon **39**, 1533 (2001).
[13] B. C. Satishkumar, A. Govindaraj, C. P. Vinod, Manashi Nath, C. N. R. Rao, Chem. Phys. Lett. **322**, 333 (2000).
[14] M. Terrones, H. Terrones, N. Grobert, W.K. Hsu, Y. Q. Zhu, J. P. Hare, H. W. Kroto, D. R. M. Walton, Ph. Kohler-Redlich M. Rühle, J. P. Zhang, A. K. Cheetham, Appl. Phys. Lett. **75**, 3932 (1999).
[15] C. H. Lina, H. L. Chang, C. M. Hsu, A. Y. Lo, C. T. Kuo, Diam. and Rel. Mat., **12**, 1851 (2003).
[16] E. J. Lianga, P. Dinga, H.R. Zhanga, X. Y. Guoc, Z. L. Duc, Diam. and Rel. Mat. **13**, 69 (2004).
[17] T. -Y. Kim, K. -R. Lee, K. Y. Eun, K. H. Oh, Chem. Phys. Lett. **372**, 603 (2003).
[18] M. Terrones, A. Jorio, M. Endo, A. M. Rao, Y. A. Kim, T. Hayashi, H. Terrones, J.-C. Charlier, G. Dresselhaus, M. S. Dresselhaus, Materials Today **7**, 30 (2004).
[19] Al. Darabont, P. Nemes–Incze, K. Kertész, L. Tapasztó, A. A. Koós, Z. Osváth, Zs. Sárközi, Z. Vértesy, Z. E. Horváth, L.P. Biró, J. Optoelectron. Adv. Mat. **7**, 631 (2005).
[21] Z. E. Horváth, K. Kertész, L. Petho, A.A. Koós, L. Tapasztó, Z. Vértesy, Z. Osváth , Al. Darabont, P. Nemes-Incze, Zs. Sárközi, L.P. Biró, Current Applied Physics **6**, 135 (2006).
[20] Z. E. Horváth, A. A. Koós, Z. Vértesy, L. Tapasztó, Z. Osváth, P. Nemes–Incze, L. P. Biró, K. Kertész, Zs. Sárközi, Al. Darabont, Proc. of the NATO Advanced Study Institute on Carbon Nanotubes: From Basic Research to Nanotechnology; Sozopol, Bulgaria, 21-31 May 2005, p. 53
[22] L. P. Biró, Z.E. Horváth, A.A. Koós, Z. Osváth, Z. Vértesy, Al. Darabont, K. Kertész, C. Neamtu, Zs. Sárközi, L. Tapasztó, J. Optoelectron. Adv. Mater. **5**, 661 (2003).
[23] L. Tapasztó, K. Kertész, Z. Vértesy, Z. E. Horváth, A. A. Koós, Z. Osváth, Zs. Sárközi, Al. Darabont, L. P. Biró, Carbon **43**, 970 (2005).
[24] C. J. Lee, J. Park, Appl. Phys. Lett. **77**, 3397 (2000).
[25] M. Jung, K.Y. Eun, J.-K. Lee, Y.-J. Baik, K.-R. Lee, J. W. Park, Diam. and Rel. Mat. **10**, 1235 (2001).

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