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Inexpensive, upscalable nanotube growth methods

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Abstract

Despite of the very promising foreseen applications, the use of carbon nanotubes in wider range is still limited by the high production costs. In this paper, our latest results concerning two inexpensive methods of carbon nanotube growth with the promise of industrial upscaling are presented. In case of the DC "arc in water" method, the effect of the angle of the two electrodes on the product yield was investigated. The highest nanotube yield and lowest amount of impurities were found at 90° electrode angles. We have studied the applicability of several liquid hydrocarbons and other metallocenes different from the most widely used benzene/ferrocene solution in case of the injection CVD or "spay pyrolysis" method. Toluene, xylene, cyclohexane, cyclohexanone, n-hexane, n-heptane, n-octane and n-pentane were used as carbon source and cobaltocene and nickelocene as catalyst source. All these compounds were found to be suitable for nanotube production. The highest yield and the best quality were obtained when a mixture of ferrocene–nickelocene was used as catalyst and xylene as carbon source.
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1. Introduction

Since the discovery of carbon nanotubes [1], intense research has been done to investigate their remarkable properties [2–4], and various production methods have been developed. A wide range of applications is foreseen for these nanoscopic objects, which include nanoelectronics [5,6], chemical sensing [7,8], composite materials with improved properties [9,10], etc. However, the large scale use of carbon nanotubes is still limited by the high production costs. The development of simple production methods, without vacuum equipment, and low living labor demand is therefore highly needed. In this

paper we present two inexpensive methods of carbon nanotube growth with the promise of industrial upscaling.

The "arc in water" method is based on the generation of electric arc plasma between two carbon (graphite) electrodes submerged in water. DC arc in water experiments showed that carbon onions [11] and carbon nanotubes [12] can be produced by this technique. In a previous paper we demonstrated that AC experiments are equally suitable for nanotube production [13]. The benefit of the AC method as compared to DC arc is that there is no deposition on the cathode, the product can be removed from the reaction container by the streaming water if suitable filtration is applied. Computer controlled stepper motors regulated the distance of the electrodes in order to maintain the arc, the voltage between

the electrodes was used as feedback signal. In a typical experiment, bucky onions, carbon nanotubes, soot and graphitic particles can all be found in the final product. Experiments of AC arc plasma between two graphite electrodes were performed using different arc currents and electrode angles. TEM investigations showed that the proportion of multiwall carbon nanotubes and polyhedral nano-onions to the graphite particles and soot was dependent both on the arc current and the angle of electrodes. Nanotubes and polyhedral nano-onions are situated always together in agglomerations, their proportion within these agglomerations is approximately 50%, regardless the production conditions. One way to change the amount of the different constituents in the product (to optimize the experiment for nanotube production) is to vary the shape of the plasma [14]. In DC experiments, the plasma shape can be changed by the modification of the relative diameter of the electrodes. In case of AC, the plasma shape could be controlled by the modification of the angle between the two identical electrodes (electrode angle).

The second method is the injection CVD (or spray-pyrolysis) method, which involves pumping or spraying a metallocene–hydrocarbon solution into a suitable furnace [15,16]. In contrast to the usual CVD, the injection CVD method does not need catalyst synthesis step, since the catalytic particles are generated in situ continuously throughout the entire growth cycle. This gives the possibility to scale up the method for continuous or semi-continuous production. In a previous paper [17], we reported the production of multiwall nanotubes using benzene as carbon source and ferrocene as catalyst source. In certain cases, the growth of large areas of high purity aligned multi-wall carbon nanotube fields was achieved. STM studies showed the presence of single wall nanotubes in some samples together with multi-wall nanotubes. Several articles were published describing the quality of the nanotubes produced by spray-pyrolysis of ferrocene dissolved in xylene, toluene or benzene, but to the best of our knowledge, none of them compared the efficiency of different catalysts or hydro-carbons. In the present paper, we investigated the influence of metallocenes (ferrocene, cobaltocene and nickelocene) and hydrocarbons (benzene, toluene, xylene, cyclohexane, cyclohexanone, n-hexane, n-heptane, n-octane and n-pentane) on the quality and quantity of the nanotubes grown by spray-pyrolysis.

2. Experiments and results

2.1. Underwater AC arc discharge method

The AC arc experiments were performed between two graphite electrodes submerged in deionized water in a glass vessel. The angle between the electrodes was varied between 30° and 180°. The discharge current was set to 40 A with discharge voltage of 25 V, and it was possible to keep the apparatus running for 1–2 h continuously. During this time, the current fluctuation was not more than 10%. The temperature of the water in the vessel was monitored far from the arc. The final product was filtered and dried at 100 °C for an hour. The weight of the dried product and the remained pieces of the electrodes were measured.

The as prepared samples and the material of the graphite electrodes (ground previously in agate mortar) were characterized by TEM using a Philips CM 20 (Twin) microscope operating at 200 kV. For the TEM study, the powders were suspended in ethanol by ultra-sonication and drop-dried on holey carbon film coated copper grids. The investigations showed that the MWCNTs occur always agglomerated with carbon nano-onions, the so-called bucky onions. These agglo-merations of MWCNTs and bucky onions (AMBs) ranging from a few hundred nanometers to several mi-crons are bonded together chemically, presumably due to the presence of extra atomic oxygen and hydrogen in the arc plasma [18] as compared to the conventional arc growth technique. The MWCNTs are well graphi-tized, closed at the ends with typical outer diameter of 10–35 nm and length of a few microns, however, the outer 1–2 walls are often damaged and they are partly covered with thin disordered material. This can also be the consequence of the reactive formation ambient. Most of the bucky onions are nearly spherical with more or less polyhedral character; their typical dimensions are in the 20–50 nm range. Some nanoparticles are elon-gated, showing transitional shape towards MWCNTs. A TEM image of a part of a typical AMB is presented in Fig. 1.

The samples contain also graphite flakes with a wide range of dimensions: from a few ten nanometers to sev-eral ten microns. There are some clusters of amorphous carbon (soot) also present in the samples but their

Fig. 1. TEM image of an agglomeration of MWCNTs and bucky onions from a sample grown using 40 A arc current.

amount is relatively small. While the proportion of MWCNTs and bucky onions was found to be nearly constant (50–50 vol%) by TEM observations in all cases, the graphite flake content of the samples depends on the production conditions. The graphite flakes, found in the nanotube samples, are very similar to the ones observed in the starting graphite electrode material, and very probably they were simply crumbled from the electrodes. Using carbon electrodes instead of graphite ones, no such graphite particles occur in the product. However, smaller and larger pieces of the carbon electrode material consisting of disordered carbon forms as well as polyhedral graphitic carbon nanoparticles (see Fig. 2) appear in significant amount depending on the process parameters. All these lead to the conclusion that a part of the product can be identified as the fragments of the starting material. Nano-onions similar to the ones presented in Fig. 2 were reported in the literature as results of arc growth process. To decide the origin of these objects in a safe way, the starting material has to be satisfactorily characterized.

Fig. 3(a) depicts the dependence of the relative total yield on the electrode angle. Here the relative total yield is the ratio between the mass of product and the electrode loss. The figure shows that the highest yield was obtained at 30°. TEM investigations showed that the proportion of MWCNTs and polyhedral nano-onions to the graphite particles and soot was also dependent on the electrode angle. Based on the TEM images we estimated the nanostructure content (MWCNTs and nano-onions) as well as the graphite content of the samples. These estimations are presented in Fig. 3(b) and (c). One can see in Fig. 3(b) that the nanostructure content is the lowest in the sample obtained at 30° (which gave the highest yield), while the highest nanostructure yield was found in the sample obtained at 90°. Fig. 3(c) also shows that very high amount of graphite can be found in the sample obtained at 30°, demonstrating that the high yield measured in this case is due mostly to the graphite particles. The fewest graphite content is estimated to be in the sample obtained at 90°. Based on the information in Fig. 3(a) and (b), the relative nanostructure yields could be calculated and they are presented in Fig. 3(d). The figure indicates that the optimal electrode angle for nanostructure production is 90°.

2.2. Injection CVD (spray-pyrolysis) method

As described earlier [17], the injection CVD or "spray-pyrolysis" method is based on the simultaneous injection of the carbon source (e.g. benzene) and the catalyst source (e.g. ferrocene dissolved in benzene) through a sprayer into the reaction furnace. The scheme of our experimental spray-pyrolysis set-up used for the synthesis of carbon nanotubes reported in [17] is similar to that reported by Kamalakaran et al. [15]. In order to find the most efficient catalyst material and carbon source, we investigated the quality and quantity of carbon nanotubes, when different metallocenes (ferrocene, cobaltocene and nickelocene) and hydrocarbons (benzene, toluene, xylene, cyclohexane, cyclohexanone, n-hexane, n-heptane, n-octane and n-pentane) are injected into the reaction furnace. We used the reaction parameters at which we have obtained the best samples regarding the quality as well as the quantity of the carbon nanotubes for ferrocene in benzene solution [17]. These values are: 6 g metallocene in 100 ml hydrocarbon catalyst concentration (except the cases when the solubility of the metallocene in the hydrocarbon was too low), 1 ml/min solution flow-rate, 875 °C furnace temperature and 500 l/h Ar (carrier gas) flow-rate. The samples were purified using 45% HNO_3 aqueous solution. This purification method removed efficiently the amorphous carbon, but is not able to remove the catalyst particles encapsulated in the central channel of the carbon nanotubes [19]. The efficiency of ferrocene, cobaltocene and nickelocene in carbon nanotube production was investigated using the same amount of catalyst material. Benzene was the first investigated hydrocarbon. Because the solubility of cobaltocene and nickelocene in benzene is lower than that of the ferrocene, we used the highest reachable concentration (0.1 g/200 ml benzene) for all the three metallocenes, which is about 100 times lower than the optimal catalyst concentration [20]. The obtained samples were analyzed by TEM. Due to the low metallocene concentration, the yield is low and a significant part of the nanotubes contains many defects. In most cases, the thin nanotubes are straight, but the thick ones are full of defects.
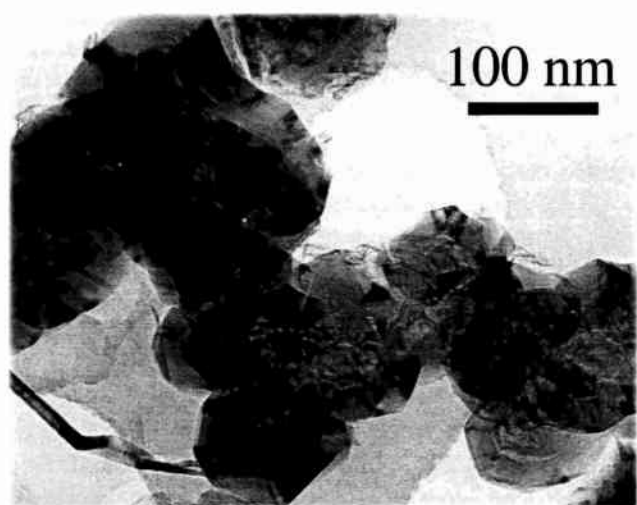

Fig. 2. TEM image of the material of the carbon rod used as electrode in the underwater arc nanotube growth experiment. The samples made of this starting material contain similar forms of carbon including polyhedral carbon nano-onions.
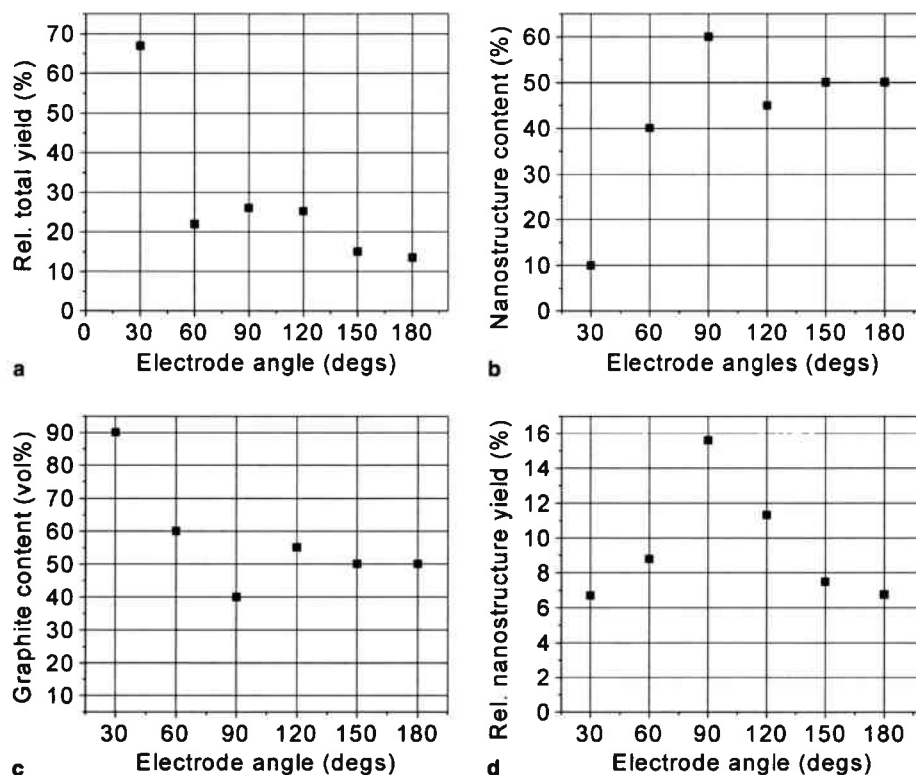
Fig. 3. Electrode angle dependence of the relative total yield (a), nanostructure content (b), graphite content (c) and the relative nanostructure yield (d) of the produced samples.

The efficiency of bimetallic catalyst particles was investigated for ferrocene–cobaltocene, ferrocene–nickelocene and cobaltocene–nickelocene mixtures. We used the optimal ferrocene (6 g in 100 ml benzene), and the highest possible cobaltocene and nickelocene concentration (0.105 g in 100 ml benzene). The ferrocene–cobaltocene and ferrocene–nickelocene mixtures increased the yield of carbon nanotube production compared to ferrocene, and the highest yield was obtained using the ferrocene–nickelocene mixture. These bimetallic catalysts improved the quality and purity of the nanotube samples, too; the samples contain mainly straight nanotubes and negligible amount of amorphous carbon. Representative TEM images of the samples produced with ferrocene–cobaltocene and ferrocene–nickelocene catalysts are presented in Fig. 4. In case of the ferrocene–nickelocene mixture, the average diameter of the nanotubes is lower than in case of ferrocene–cobaltocene catalyst. The quality of the nanotubes is equally good in these two cases. However, both samples contain thick nanotubes with relative high defect concentration. Due to their reduced solubility in benzene, the efficiency of cobaltocene–nickelocene mixture was low. The nanotubes produced in this experiment contain more defects than the previous samples made from catalyst mixtures, and the quality of the nanotubes is similar to those produced using ferrocene catalyst at low concentration, but the yield is much lower.

When other carbon sources were applied, we used the optimal reaction parameters obtained for benzene/ferrocene solution. However, the catalyst concentration was limited by the low solubility of ferrocene in the investigated hydrocarbon (except toluene and xylene). In case of cyclohexane, cyclohexanone, n-hexane, n-heptane, n-octane and n-pentane we dissolved the maximum possible amount of ferrocene (2–5 g in 100 ml carbon source). The highest yield was obtained for xylene. In this case, the weight of purified carbon nanotubes was higher than 50% of the weight of catalyst material. Usually the thin MWCNTs are straight and well graphitized, while the thick ones contain some defects in case of all the investigated carbon source materials.

The diameter of the carbon nanotubes is between 10 and 100 nm for xylene, n-pentane and n-octane; thinner nanotubes were produced from n-octane. The nanotube samples produced from these hydrocarbons contain mainly straight nanotubes; the proportion of lower quality nanotubes is less than one fifth. Representative TEM images of the nanotube samples made from xylene and n-octane are presented on Fig. 5(a) and (b), respectively. The quality of the nanotubes produced from n-pentane and n-octane is similar to the quality of the nanotubes made from xylene (Fig. 5(a)). The samples produced from cyclohexane, n-hexane and n-heptane contain more thick, low quality nanotubes, than the samples produced from xylene, n-pentane and n-octane.
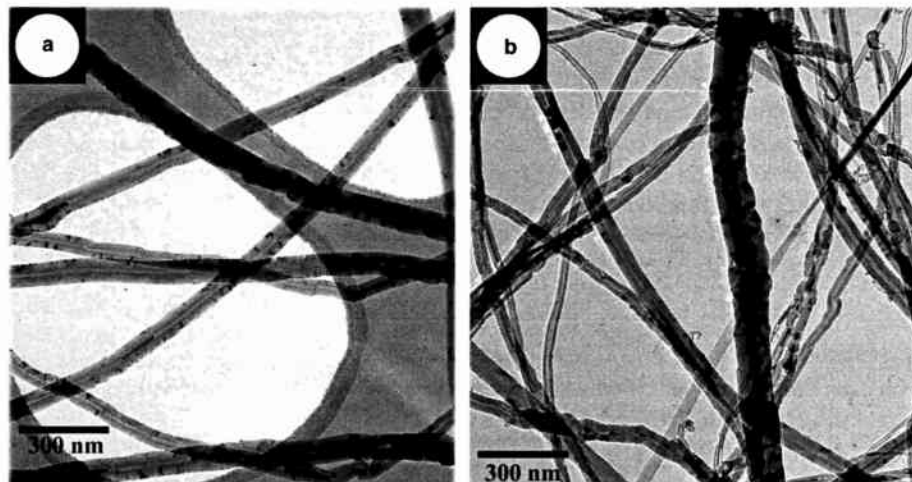
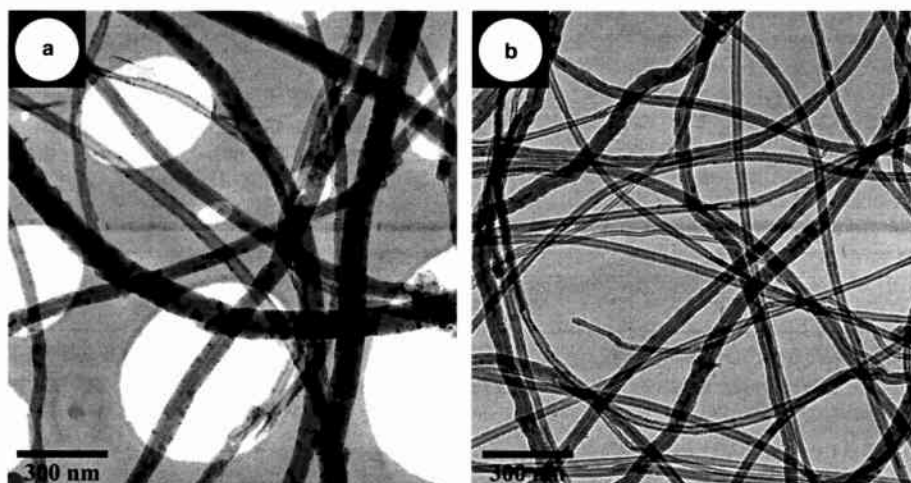Fig. 4. TEM images of nanotubes produced using ferrocene–cobaltocene (a) and ferrocene–nickelocene (b) catalyst.

Fig. 5. TEM images of MWCNTs prepared using xylene (a) and n-octane (b) as carbon source.

In these samples the ratio of irregular nanotubes increased, too.

3. Conclusion

The underwater AC arc discharge was demonstrated to be a cost effective and possibly upscalable method for growth of high quality multi-wall carbon nanotubes. However, side products and impurities like polyhedral carbon nano-onions, amorphous carbon and the material of the starting electrodes occur always in the samples. Nano-onions grow together with the MWCNTs, but the material crumbled from the electrodes can contain other nano-objects. This makes the proper characterization of the starting material necessary for the correct understanding of the processes. The produced nanostructure content is strongly dependent on the electrode geometry. TEM investigations show that the proportion of the MWCNTs and bucky onions is always

the same (50–50 vol%). The highest yield was obtained at electrode angle of 30°, but the sample contained mostly graphite. The optimal geometry for nanostructure production was found to be at electrode angle of 90°. However, much graphite can be found in all the samples, which requires further optimization of the process.

Pure multi-walled carbon nanotubes were grown by the spray-pyrolysis method, injecting a solution of metallocene (ferrocene, nickelocene, cobaltocene and their mixtures) in hydrocarbon (benzene, toluene, xylene, cyclohexane, cyclohexanone, n-hexane, n-heptane, n-octane and n-pentane) into a heated quartz reactor. The limited solubility of the investigated metallocenes in the mentioned hydrocarbons determines the applicability of these materials in similar MWCNT production procedures. MWCNTs were produced with maximum yield when ferrocene–nickelocene catalyst mixture was used and xylene was found to be the most efficient carbon source in our setup despite the process parameters

optimized for benzene. For xylene the weight of purified carbon nanotubes normalized to the weight of catalyst material is higher than 50%. Good quality thin MWCNTs were produced from *n*-octane, but in lower quantity than in case of xylene. Nevertheless, the production of MWCNTs was possible in case of all mentioned hydrocarbons and metallocenes.

Acknowledgements

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