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Effect of Ferrocene/Carbon Ratio on the Size and Shape of Carbon Nanotubes and Microspheres

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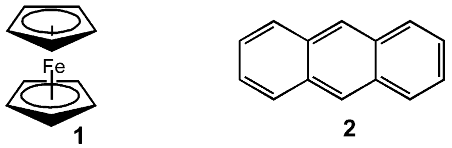
Summary: Carbon nanotubes and microspheres have been synthesized in sealed tubes in the presence of ferrocene and anthracene. Small changes in the Fe/C ratio in the solid-state pyrolysis of ferrocene/anthracene mixtures give rise to different kinds and sizes of shaped carbon materials. The variation of reaction temperature also has an impact on the yields and properties of the products formed.

Introduction

Organometallic complexes have often been used in the synthesis of shaped carbon materials that include carbon nanotubes (CNTs),[1] carbon fibers,[2] and carbon microspheres (CMs).[3] The advantages of using organometallic compounds is that they do not need to have a counterion and they act both as a catalyst and as a carbon source to form the shaped carbon materials. This methodology thus provides a means of simplifying studies in which these catalysts are used to make these shaped carbon materials. Numerous approaches have been used to study the effect of organometallic complexes on the formation of shaped carbon materials such as CNTs. The use of various chemical vapor deposition (CVD) methods, typically at atmospheric pressure, involving organometallic catalysts such as ferrocene,[4] alkylferrocenes,[5] and $Fe(CO)_5$,[6] together with organic solvents, which also act as carbon sources, has been well documented. More recently there has been an upsurge of interest in the synthesis of CNTs by pyrolysis of organometallic complexes in a confined space such as a stainless steel autoclave or sealed glass vessels, at autogenous pressure, especially using Fe and Co metal catalysts.[7] However, minimal research on the role and control of the metal to carbon ratio in the synthesis of CNTs has been documented, even though this is known to impact on the shaped carbon materials formed. This paper demonstrates a simple pyrolysis study involving ferrocene (**1**) and anthracene (**2**) mixtures (Scheme 1), carried out in sealed quartz tubes, and reveals the effect of the Fe/C ratio on CNT and CM formation. Ferrocene provides a means of adding the Fe, together with a carbon source, into a reactor without the addition of a catalyst support. Anthracene was chosen for the study to provide a variable source of carbon and to keep the H content near constant as the Fe/C ratio was varied. It should be noted that studies with anthracene as carbon source have been reported (flow[8] and nonflow CVD systems[9]), while the use of ferrocene in sealed vessels has been explored before in CNT synthesis.[10]

Scheme 1. Structures of Ferrocene (1) and Anthracene (2)



Experimental Section

Ferrocene was purchased from Strem Chemicals, while anthracene was obtained from Aldrich Fine Chemicals; both were used as received. A mixture of ferrocene and anthracene (100 mg) was sealed under vacuum in quartz tubes (10 cm in length and 1.0 cm internal diameter) in different ratios. The tubes were introduced into an electrical furnace that was heated at a rate of 3 °C/min to 500 °C, i.e. above the ferrocene and anthracene decomposition temperatures, and the tubes were held at this temperature for at least 30 min to ensure complete decomposition of reagents. The tubes were then heated at a rate of 2 °C/min to 700, 800, or 900 °C and held at that temperature for 12 h before being gradually cooled to room temperature. The black material obtained was scraped out and characterized by both low-resolution transmission electron microscopy (TEM; JEOL JEM 100 S) and elemental analysis (Oxford Instruments EDS). The samples for TEM analysis

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Table 1. Relative Percent Distribution of Amorphous Carbon, CNTs, and CMs with Changes in the Fe/C Ratio at 800 °C

amt (mg)		Fe/C	amorphous	CNT yield (%)	CM yield (%)
ferrocene	anthracene	ratio	C yield (%)	(mean outer diam (nm))	(mean diam (μm))
0	100	0	50	0	50 (2.5)
5	95	0.016	30	0	70 (1.0)
10	90	0.033	5	5 (60)	90 (0.4)
20	80	0.068	5	95 (65)	0
25	75	0.087	10	90 (70)	0
30	70	0.106	15	85 (71)	0
40	60	0.146	25	75 (75)	0
50	50	0.190	35	65 (77)	0
60	40	0.236	40	60 (80)	0
70	30	0.287	50	50 (81)	0
75	25	0.314	60	40 (81)	0
80	20	0.342	65	35 (85)	0
90	10	0.401	75	25 (86)	0
100	0	0.467	80	20 (88)	0

were prepared by sonication of the carbonaceous materials in methanol or ethanol. A few drops of the resulting suspension were placed onto a holey carbon TEM copper grid for analysis. Raman spectra were measured using the single spectrograph stage of a Jobin-Yvon T64000 Raman spectrometer. The excitation source was 636.4 nm from a tunable Spectra-Physics dye laser. The laser beam was focused onto the sample using the 20× objective of an Olympus microscope. The backscattered light was dispersed using a 600 line/mm grating and detected using a liquid nitrogen cooled CCD detector. Thermogravimetric analysis (TGA) measurements were performed under nitrogen on a Perkin-Elmer TGA 7 to determine the decomposition temperature of ferrocene and anthracene. The number and size of the carbon tubes and spheres formed were obtained from the TEM photographs by counting procedures and represent average values.

Results and Discussion

The reaction of anthracene and ferrocene was attempted under a range of experimental conditions, and eventually a protocol was established that ensured complete decomposition of the reactants. This is described in the Experimental Section. In the reaction, the Fe^{2+} catalyst is reduced by the hydrogen generated from the anthracene and the cyclopentadienyl ligand. As the hydrogen contents produced from either **1** or **2** are the same, the total amount of hydrogen in the sealed vial is not a variable in the reaction. After completion of the reaction (700, 800, or 900 °C, for 12 h), products were collected from the glass vials, and the results obtained are shown in Table 1. In every instance a black product was obtained in yields of >90%. The impure black material was analyzed by TEM. Three types of shaped carbon materials were observed: carbon microspheres (CMs), multiwalled carbon nanotubes (MWCNTs), and amorphous material (Figure 1a−c). The multiwalled nature of the CNTs was readily established by TEM studies. The relative ratio of these three materials is given in Table 1. A plot of the relative percentage of CNT and CM products as a function of Fe/C ratio is provided in Figure 2.

It is clear from Figure 2 that the Fe/C ratio has a major impact on CNT or CM formation. The data are consistent with experiments performed using the floating catalyst CVD method where low concentrations of catalyst favor CNT production,[11] and when no catalyst is used, only CMs and amorphous material are produced.[1e]

What is remarkable is the small range of Fe/C ratios that results in transformation of product from CMs to CNTs. Thus, the addition of a small amount of ferrocene to anthracene to obtain an Fe/C ratio of 0.016 generates more spheres and less amorphous material than in comparison to the reaction without ferrocene (Table 1). This is even more apparent when a further slight addition of ferrocene to anthracene was used to obtain an Fe/C ratio of 0.033. At this ratio less amorphous material was found. The data strongly reflect the Fe catalyst influence in the system.

Also, a further increase in the ferrocene to anthracene ratio to achieve a value of 0.068 gives a very high yield of CNTs with little amorphous material and no CMs. Figure 2 clearly shows that as the Fe/C ratio increases, the quantity of the CNTs decreases. No spheres are found under these reaction conditions. Interestingly, by increasing the Fe/C ratio from 0 to 0.033, a significant decrease in the sphere's radius was observed. Thus, the Fe/C ratio affects not only the kind of shaped carbon materials formed but also their sizes.

Increasing the Fe/C ratio further leads to an increase in the diameter of the nanotubes. This is believed to be due to the formation of larger particles at a higher metal concentration. The distribution of the diameters of the CNTs also broadened with an increase in iron concentration. At a high concentration of Fe (when only ferrocene is used), shorter tubes with decreased length/diameter ratio were observed that contained Fe particles. When no Fe catalyst was used, the CMs were generally larger than those obtained when a Fe catalyst was used (see Figure 1c,d). It is also interesting to note that defined regular shaped carbon materials (triangles; see Figure 1d) were formed from anthracene when no Fe was present, similar to those observed by Pol et al.[9]

The above observations can be rationalized as follows. When the Fe particles are of the appropriate size, formation of nanotubes will be determined by the reaction temperature and the carbon concentration. An increase in ferrocene concentration results in an increase in the Fe/C ratio such that, at a higher concentration of iron, larger agglomerated iron nanoparticles are formed that do not favor CNT formation. There is also less carbon available to form nanotubes (see the Fe/C ratio; Table 1), and consequently, the amount of nanotubes formed will decrease on both counts. When the Fe content is very low, the carbon will also agglomerate without the intervention of the catalyst but in this instance will form spherical structures or amorphous carbon. It is not clear at this stage as to whether or how the Fe plays any direct role in sphere formation.

The properties of CNTs and CMs were further explored as a function of temperature, and the results are shown in Table 2. The temperature change affects the yield of both CNTs and CMs; maximum yields were obtained at 800 °C. At lower temperatures (700 °C), amorphous material is found, probably due to decomposition of the carbon-containing reagents without interaction with the Fe. At higher temperatures (900 °C) amorphous material is again formed, but this time through decomposition of carbon on the CNTs, as seen from the TEM images. The sizes of the CMs were not strongly affected by the variation in temperature. The change in temperature from 700 to 900 °C also generated CNTs with increased diameters at a particular Fe/C ratio. This is no doubt due to aggregation of the Fe particles at the higher temperature, leading to the formation of larger catalyst particles and hence larger diameters of the CNTs. At 700 °C with a 0.016 Fe/C ratio, most CMs seemed to be fused, while at a 0.033 Fe/C ratio, the mean CNT outer diameter was found to be smaller in comparison to those at 800 or 900 °C.

The Raman spectra of the crude CNTs (Figure 3) showed two well-defined graphite peaks and a shoulder on one peak.[12]

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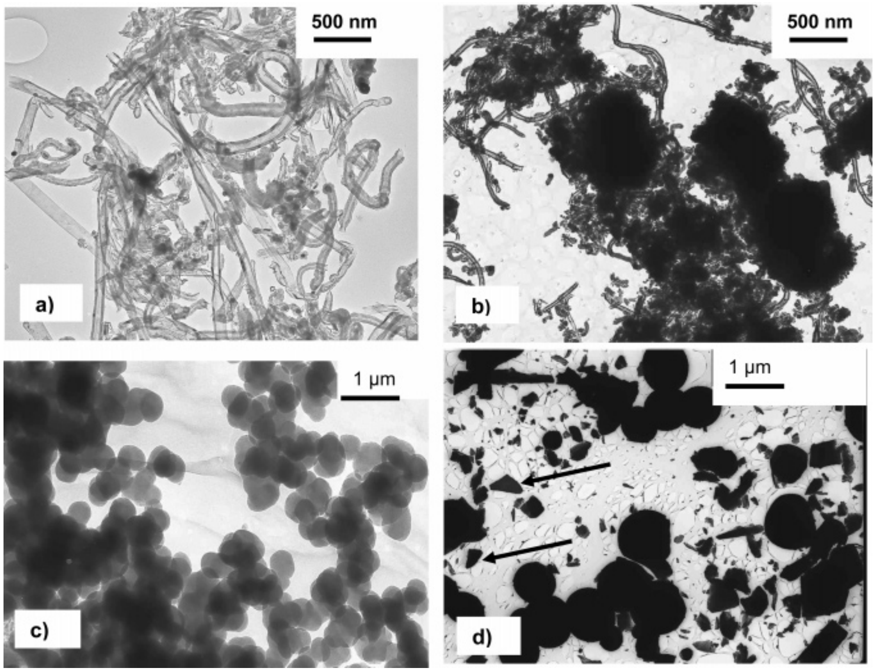

Figure 1. (a−c) TEM images of CNTs formed from reactants with Fe/C ratios of (a) 0.068 at 800 °C, (b) 0.068 at 700 °C, and (c) 0.033 at 800 °C. (d) TEM image of CMs and other SCMs formed in the absence of a catalyst at 800 °C (arrows showing triangles).

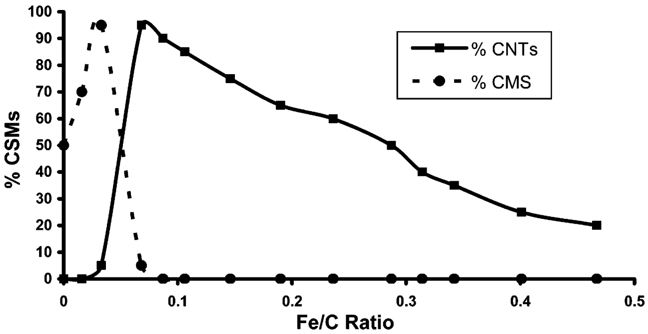

Figure 2. Relative percentage of CNT and CM products produced versus the Fe/C ratio at 800 °C.

Table 2. Percent Distribution of CNTs and CMs on Changes of Temperature

temp (°C)	amt (mg) ferrocene	anthracene	Fe/C ratio	CNT yield (%) (mean outer diam (nm))	CM yield (%) (mean diam (μm))
700	10	90	0.016	0	30 (0.60)
	20	80	0.033	50 (50)	0
800	10	90	0.016	5 (60)	90 (0.40)
	20	80	0.033	95 (65)	0
900	10	90	0.016	0	40 (0.50)
	20	80	0.033	70 (75)	0

The peak at 1580 cm^{-1} (G band) corresponds to the Raman-allowed optical mode, E_{2g}, of two-dimensional graphite and is closely related to the vibration in all sp^2-bonded carbon atoms in a two-dimensional hexagonal lattice. The other peak at 1350 cm^{-1} can be assigned to the vibrations of carbon atoms with dangling-bond in-plane terminations of disordered graphite, while the shoulder at around 1620 cm^{-1} is associated with a disorder mode.[12] The I_D/I_G value obtained was ~1, which implies that the CNTs are not well graphitized.

Conclusion

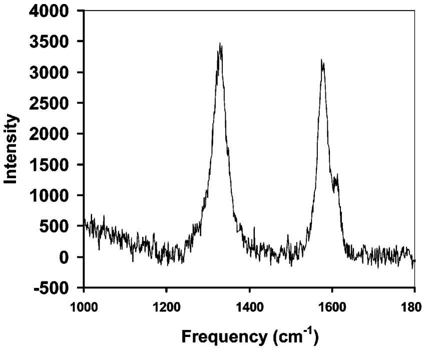

Figure 3. Raman spectrum of the crude CMT sample prepared from an Fe/C reactant ratio of 0.068 at 800 °C.

This method of producing shaped carbon materials not only provides a simple synthesis method but also offers a method of varying the Fe/C ratio and hence the synthesis of either CNTs or CMs under specific reaction conditions. A small change in the Fe/C ratio (from 0.033 to 0.068) yields different shaped carbon materials. The Fe/C ratio affects not only the kinds of shaped carbon materials formed but also their dimensions. The general trend shows that an increase in Fe/C ratio leads to an increase in the outer diameter of the CNTs. A further increase in Fe/C ratio gives products with a decreased length/diameter ratio: i.e., at high concentrations of iron, relatively short CNTs were obtained. On the other hand, a small amount of Fe increased the CM yield and generated spheres smaller than those observed in the absence of catalyst. The study thus reveals the importance of the metal to carbon ratio on the synthesis of shaped carbon materials and suggests that control of this value can be effectively used to control the kind and size of shaped carbon materials formed.

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