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Carbon nanotube synthesis using ferrocene and ferrocenyl sulfide. The effect of sulfur

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Multiwalled carbon nanotubes (MWCNTs) have been synthesized by the floating catalyst method using toluene as the carbon source and mixtures of ferrocene and ferrocenyl sulfide as the catalyst. Products were characterized by both low-resolution and high-resolution (HR) TEM analysis. It was found that the presence of large amounts of sulfur in the reactant mixture generated only amorphous carbon while lower amounts of sulfur led to mixtures of MWCNTs and carbon fibres. The product distribution, yield and the tube diameters varied with the sulfur content. HRTEM analysis revealed that the MWCNTs were poorly graphitized. Comparison with data using other sulfur sources (S_8, thiophene) suggested that the proximity of the sulfur to the Fe catalyst in the gas phase did play a role in the CNT formation and provides a method of 'carrying' elements to a catalytic site. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: carbon nanotubes; ferrocene; sulfur; catalysis

INTRODUCTION

Research in the area of carbon nanotubes (CNTs) has grown enormously since the pivotal publication by Iijima in 1991.[1] Since then the development of CNTs has been spurred by the potential applications of these novel materials in molecular electronics, energy storage, biomedicine and others.[2–4]

To achieve these applications, synthetic strategies have been devised to produce the CNTs both cheaply and in high yield, and indeed today CNTs are produced commercially (http://www.personal.rdg.ac.uk/~scsharip/tubes.htm; http://www.fibrils.com/hyperion). CNTs come in a wide range of lengths, shapes and types [single wall (SW), double wall (DW) and multiple wall (MW)] and their properties are also affected by the tube chirality. Furthermore, other forms of filamentous carbon (e.g. fibres with herringbone structures) can also have nanometer length scales and their study and use have paralleled those of the CNTs.[5,6]

Many synthetic strategies have been employed to make CNTs and fibres, one of the most facile being the catalytic CVD (chemical vapour deposition) method—using either a classical catalyst/support or a 'floating catalyst' procedure.[5–8] In the floating catalyst method, which readily permits synthesis scale-up, volatile organometallic complexes are used as catalyst sources to convert organic precursors into CNTs. A limitation of the CVD method over other procedures (e.g. arc discharge) is that the CNTs produced have many defects and, while the defects may be useful, control over the defects has as yet not been successfully achieved.

Early work on the synthesis of carbon fibres revealed that the addition of sulfur enhanced the yield of carbon fibres.[9,10] The addition of sulfur to a catalyst anode in the arc discharge CNT process was also found to enhance both the yield and the quality of the CNTs produced.[11–13] Not long afterwards, the sulfur addition approach was used in CVD CNT synthesis[14] and many studies have since been reported on the effect of sulfur on CNT production. While the addition of a low percentage addition of sulfur to a 'floating catalyst' has been

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shown to increase the yield of the CNTs, large amounts of sulfur reduce the CNT yield.[15,16] Thiophene[17–23] and sulfur powder[8,12,23–26] have been widely used as the sulfur sources. Thiophene has been found to influence the number of CNT walls and provide a means of controlling the formation of SWCNTs[7,22,27] relative to MWCNTs. Indeed sulfur can also influence the number of internal tubes produced (SWCNT vs DWCNT)[7,13,14,27–29] and sulfur powder was found to be essential in the formation of DWCNTs.[28,30,31] In some cases, the addition of sulfur compounds can also affect the shape of the CNTs.[32] Thiophene is also considered to play a key role in forming SWCNT bundles[33] and super long SWCNTs strands.[34,35]

To date a number of mechanisms have been proposed to explain the effect of the sulfur on the reaction. Thus, sulfur is proposed to exert its influence by (i) blocking active sites on the catalyst,[36,37] (ii) lowering the melting point of the catalyst (a eutectic effect)[6,38,39] or (iii) interacting with the growing tube/fibre.[40,41] However, there is no consensus yet on the mechanism of sulfur or other so called 'impurities' in influencing CNT formation.

In an attempt to evaluate the effect of sulfur on the catalytic growth of CNTs using the 'floating catalyst' approach, we have carried out a study using ferrocene as a catalyst and sulfur-ring substituted ferrocene as the sulfur source for the reaction. In particular we have used $Fe(C_5H_4SMe)_2$ as our sulfur source since the material (i) can be readily synthesized,[42] (ii) is volatile and (iii) is soluble in many CNT carbon sources. Further, it has been suggested that the weak effect of sulfur on CNT production in the floating catalyst method relative to the arc discharge method could be due to 'time for the benzene and thiophene to meet iron particles, and the contact time between reactants' and iron particles is an important factor in fibre formation.[43] This methodology using $Fe(C_5H_4SMe)_2$ should overcome the contact time issue. Herein we report on the use of $Fe(C_5H_4SMe)_2$–ferrocene mixtures for the catalytic synthesis of CNTs (and fibres) from toluene as carbon source. This is a continuation of our attempt[44–47] and those of other authors[48,49] to systematically explore the use of organometallic complexes in the synthesis of CNT and other tubular, spherical and fibre-like materials. In particular we wish to exploit the use of organometallic complexes as 'carriers' of elements to catalyst sites in carbon nanotube synthesis.

EXPERIMENTAL

Ferrocene (Fc) was purchased from Strem Chemicals and used as received. The preparation of ferrocenyl sulfide catalyst was carried out as described elsewhere.[42] A quartz tube reactor (800 × 28 mm i.d.) was inserted horizontally into an electrical furnace with the outlet of the tube connected to a gas bubbler similar to studies reported by other workers.[50] The temperature inside the quartz tube was determined by means of a thermocouple placed in the middle of the furnace. As previously reported, a second moveable thermocouple was used to establish the profile of the temperature in the reactor.

Synthesis of CNTs was carried out in the temperature range 800–1000 °C, in 5% H_2 in argon (v/v) (AFROX) at atmospheric pressure. The flow rate of H_2 in argon was kept constant at 100 ml/min. Mixtures of ferrocene and ferrocenyl sulfide with different weight ratios were dissolved in toluene (Merck Chemicals). The catalyst solutions were placed in a 10 ml syringe and injected into the heated tube by means of a SAGE syringe pump (at 0.8 and 0.2 ml/min injection rate). The solutions were injected into the tube reactor via a specially designed quartz tube (2 mm i.d., 200 mm in length), cooled by water, similar to that described in the literature.[44–47] This specially designed tube enabled the solution to be injected directly into the high temperature region of the large quartz tube reactor.

The carbon deposited materials formed were scraped from the walls of the quartz tube in both the high-temperature and low-temperature regions (temperature <300 °C) in the tube. Carbon products were also collected at the rear end of the quartz tube; these products were carried away from the hot zone by the gas stream. The carbon materials were characterized by scanning electron microscopy (SEM; Jeol JSM-840), low-resolution transmission electron microscopy (TEM; Jeol JEM-100S), high-resolution transmission electron microscopy (HRTEM; Phillips CM200), XRD (Philips PW187020/00) and Raman spectroscopy (J-Y T64000). The number and size of the carbon materials were obtained from the SEM/TEM micrographs by counting procedures and represent average values. The nanotube yield was calculated from the wt% of the products obtained relative to the mass of solvent injected into the system.

RESULTS AND DISCUSSION

Reference reactions

The reaction performed with ferrocene, Fc (no S source) gave results consistent with data reported previously for the same system,[45] indicating that Fc–toluene mixtures produced CNTs and amorphous carbon in the temperature regime 800–1000 °C.

Products obtained with toluene and no Fc gave only amorphous carbon and carbon spheres.[46] Reactions were also attempted with only 1,1′-bis(methylthio)ferrocene, FcS_2Me_2 (1–5 wt%), and in every instance no CNTs were produced. This result is consistent with the poisoning of the iron catalyst by excess sulfur.[51]

Effect of temperature

In a typical reaction, the carbon source (toluene) and the catalysts (Fc and FcS_2Me_2) were injected into the hot quartz tube reactor, where both carbon source and catalysts are decomposed immediately. The iron atoms are derived from thermal decomposition of ferrocene and

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1,1′-bis(methylthio)ferrocene that form catalyst particles by collision and coalescence. After that the precipitation of carbon begins and carbon nanotubes are formed.

A temperature study was undertaken on the reaction for a given set of reaction conditions (at constant flow rate; constant Fc:FcS_2Me_2 molar ratio). The data indicated that both the quality and quantity of CNTs produced followed expected trends[7,8,22,28,29,30]—the highest yields of CNTs were found at $T = 1000\,°C$ and this temperature was used in the later studies.

Effect of Fc : FcS_2Me_2 molar ratio

The effect of Fc:FcS_2Me_2 molar ratio (6 : 1 up to 148 : 1) was investigated (1000 °C) at two different flow rates (Table 1). In general four types of carbonaceous products were obtained, namely fibres, amorphous C, MWCNTs and spheres. In contrast with other literature procedures used in studying sulfur effects, no SWCNTs or DWCNTs were formed in the reaction.

In the yield analysis (Table 1), the CNT and fibre yields have been combined. At the lower flow rate (0.2 ml/min) the total amount of carbonaceous material produced generally increased with the Fc:FcS_2Me_2 ratio (Fig. 1). At the higher flow rate the total yield of material was less affected by the ratio.

More significant is the finding that the yield of fibres and MWCNTs is affected by the catalyst : S ratio (Fig. 1). In general, at the lower flow rate (0.2 ml/min) the CNT formation remained constant, the amorphous C content decreased and the yield of carbon fibres increased as the Fc:FcS_2Me_2 molar ratio increased. The optimal ratio appears to be about a 73 : 1 ratio of Fc:FcS_2Me_2 (Table 1), suggesting that the two effects, catalyst poisoning and catalyst activation, are in competition with each other. This is entirely consistent with published literature reports for related systems when S is used as an additive. To further explore this issue an analysis of the carbon materials was undertaken by TEM analysis (Table 1).

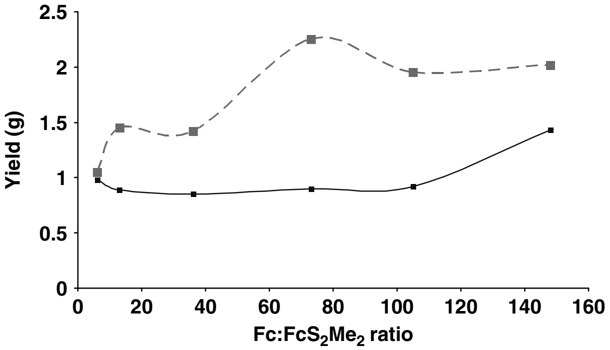

Figure 1. CNT yield vs Fc:FcS_2Me_2 (6 : 1–148 : 1) metal ratio, at 1000 °C and injection rate of 0.2 ml/min (- - - -) and 0.8 ml/min (———).

The TEM analysis visually reveals that the Fc:FcS_2Me_2 molar ratios (and flow rates) influence the width of the CNTs. Some examples are shown in Fig. 2. The mean outer diameters and inner diameters of the CNTs were measured as a function of Fc:FcS_2Me_2 molar ratio (and flow rate). The data at the lower flow rate reveal that the diameters of the tubes increase to a maximum and then decrease with Fc:FcS_2Me_2 molar ratio (Fig. 3). The CNT wall thickness is also influenced by the Fc:FcS_2Me_2 molar ratio and follows the same trend as

Table 1. Effect of Fc:FcS_2Me_2 mixture on the formation of CNTs

Metal	Injection rate (ml/min)	Notes	Mean diameter (nm)
Fc:FcS_2Me_2	0.8	Tubes (60%), spheres (30%) and a-C (10%)	68T (outer), 16 (inner), 14 (particle), 120S
(6 : 1) 5 wt%	0.2	Tubes (40%) and a-C (60%)	44 (outer), 15 (inner)
Fc:FcS_2Me_2	0.8	Tubes (15%), spheres (5%) and a-C (80%)	47T (outer), 12 (inner), 200S
(13 : 1) 5.0 wt%	0.2	Tubes (30%) and a-C (70%)	38 (outer), 13 (inner)
Fc:FcS_2Me_2	0.8	Tubes (20%), a-C (80%)	70T (outer), 30 (inner)
(36 : 1) 5.0 wt%	0.2	Tubes-fibres (80%), a-C (20%)	61T (outer), 22(inner), 110F
Fc:FcS_2Me_2	0.8	Tubes (35%) and a-C (65%)	57 (outer), 30 (inner)
(73 : 1) 5.0 wt%	0.2	Tubes (40%) and a-C (60%)	79 (outer), 34(inner)
Fc:FcS_2Me_2	0.8	Tubes-fibres (70%), a-C (30%)	80T (outer), 30(inner), 120F
(105 : 1) 5.0 wt%	0.2	Tubes-fibres (80%), a-C (20%)	65T (outer), 22 (inner), 120F
Fc:FcS_2Me_2	0.8	Tubes-fibres (60%),, a-C (20%), spheres (20%)	76T (outer), 32 (inner), 187F, 280S
(148 : 1) 5.0 wt%	0.2	Tubes-fibres (80%), a-C (20%)	30T (outer), 22(inner), 100F
Fc : thiophene	0.8	Tubes-fibres (70%), a-C (30%)	54T (outer), 20 (inner), 130F
(4 : 1) 5.0 wt%	0.2	Tubes-fibres (80%), a-C (20%)	44T (outer), 20(inner), 100F
Fc : sulfur	0.8	Tubes-fibres (90%), a-C (10%)	74T (outer), 20(inner), 110F
(2 : 1) 5.0 wt%	0.2	Tubes-fibres (80%), a-C (20%)	42T (outer), 22(inner), 100F

T = tubes, S = spheres, F = fibres, a-C = amorphous carbon; temperature = 1000 °C; H_2 flow rate = 100 ml/ min.

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for the CNT diameters (Fig. 4). The solid fibres have a larger diameter than the CNTs (100–130 nm) and have no hollow core typical of CNTs.

The data further reveal that the CNT inner channel, which reflects the size of the catalyst particle, also increases and then decreases in size as the Fc:FcS_2Me_2 molar ratio varies.

EDX analysis of the particles only revealed the presence of Fe but not S, showing that the S content of the particles was low (XRD analysis confirmed only the presence of graphitic carbon but not the presence of S or Fe). Fibre formation occurs at the expense of the amorphous carbon, suggesting that the S content reduces the fibre content.

HRTEM analysis of a typical CNT is shown in Fig. 5. The metal particles were observed at the tip of the tube (and/or in the middle of the tube). Most of the tubes were closed. It can be seen that the material is not well graphitized. The metal particle is surrounded by graphitic material, but the outer layers show the well-known 'wavy' behaviour seen in many CNTs.

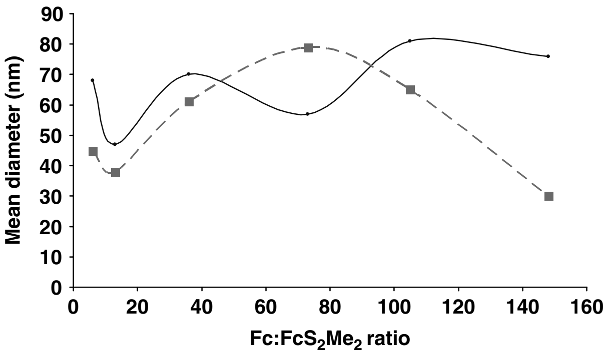

Figure 3. Mean diameter of the CNTs vs Fc:FcS_2Me_2 metal ratio (6 : 1–148 : 1), at 1000 °C and injection rate of 0.2 ml/min (- - - -) and 0.8 ml/min (———).

Comparison of different sulfur sources

A comparison of data obtained with different sulfur sources (sulfur source = FcS_2Me_2, S_8, thiophene) at different Fc : S ratios was made (see Table 1). The data reveal that, when the S source = thiophene (Fc:S = 4 : 1) or S_8 (Fc:S = 2 : 1), the carbon products produced are similar (mixture of fibres, amorphous C and MWCNTs). Furthermore, the iron particles that produce the CNTs are both about 20 nm (average) in diameter.

In contrast, when FcS_2Me_2 is used as the S source at about the same Fc : S ratio (Fc : S = 6 : 1 and 13 : 1), the yield of tubes is much lower and no fibrous material is produced. A similar product distribution to that achieved with S = S_8 or thiophene was also obtained *at a lower Fc : S ratio*. Thus, the data for Fc : S ratios of 105 : 1 and 148 : 1 (for S = FcS_2Me_2)

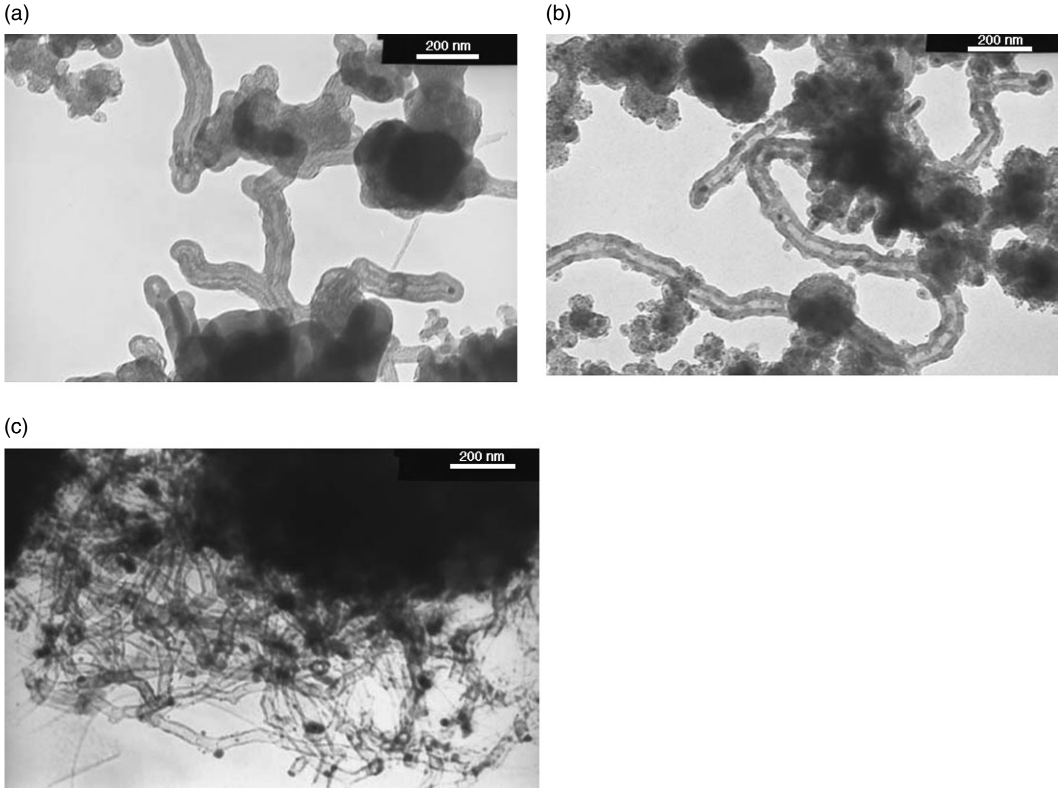

Figure 2. (a) TEM image of CNTs [1000 °C; Fc:FcS_2Me_2: (36 : 1); 0.8 ml/min; 5 wt%]; (b) TEM image of CNTs [1000 °C; Fc:FcS_2Me_2: (36 : 1); 0.2 ml/min; 5 wt%]; (c) TEM image of CNTs [1000 °C; Fc:FcS_2Me_2: (73 : 1); 0.8 ml/min; 5 wt%].

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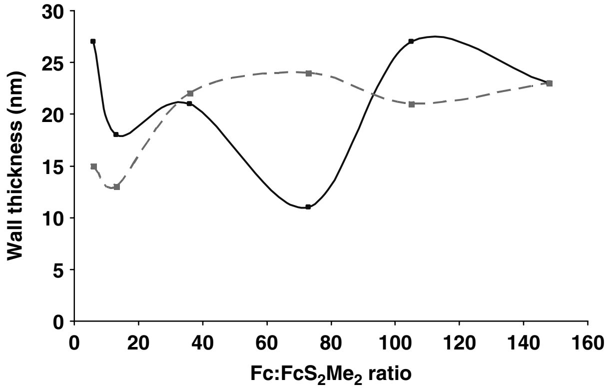

Figure 4. Wall thickness of the CNTs vs Fc:FcS$_2$Me$_2$ (6 : 1–148 : 1) metal ratio, at 1000 °C and injection rate of 0.2 ml/min (- - - -) and 0.8 ml/min (———).

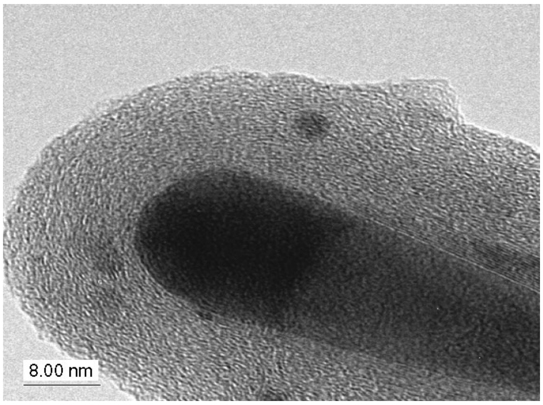

Figure 5. HRTEM image of an MWCNT [1000 °C; Fc:FcS$_2$Me$_2$: (73 : 1); 0.8 ml/min; 5 wt%].

give carbon deposits similar to that with the 2 : 1 and 4 : 1 ratio when the S source is thiophene or sulfur. Further, TEM analysis showed that the size of iron particle is similar for the three different S sources at these differing Fc : S ratios. This confirms that the proximity of the Fe and S in the FcS$_2$Me$_2$ modifies the catalyst behaviour. The proximity leads to a better interaction between the Fe and S and thus *much less sulfur is needed to produce the enhanced effects of S on the CNT synthesis.*

CONCLUSIONS

The synthesis of ferrocene moieties that covalently are bound to elements that can influence the synthesis of CNTs provides a route to the control of CNT morphology. In this instance sulfur has been incorporated into a catalyst for CNT synthesis. The sulfur as expected did modify both the tube diameter and the product yield of the CNTs. In our studies, the presence of sulfur gave MWCNTs instead of DWCNTs or SWCNTs.[7,8,22,27,28,30] It has also been shown from the literature that the presence of sulfur additive increases the diameter of the fibres or carbon nanotubes[7,8,13,27–29] and this agrees with our data. It is believed that sulfur enhances the growth of graphitic carbon and thus assists in the synthesis of wide (many layered) CNTs. More importantly, it was observed that *less* sulfur was required to induce the changes when compared with using sulfur added from an external source (S$_8$, thiophene). This would suggest that the proposal of using organometallics to 'carry' elements to the active metal catalytic site is feasible.

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