

# Floating catalyst CVD synthesis of carbon nanotubes from $\text{CpFe}(\text{CO})_2\text{X}$ ( $\text{X} = \text{Me}, \text{I}$ ): Poisoning effects of I

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## Abstract

Multiwalled carbon nanotubes (MWCNTs), carbon fibers (CFs) and carbon spheres (CSs) were synthesized by an injection chemical vapour deposition (CVD) method using toluene solutions of  $\text{CpFe}(\text{CO})_2\text{Me}$  as catalyst. The effect of pyrolysis temperature (800–1000 °C), catalyst concentration (5 and 10 wt% in toluene) and solution injection rate (0.2 and 0.8 ml/min) on the type and yield of carbonaceous product synthesized was investigated. The carbonaceous materials were characterized by transmission electron microscopy (TEM), thermal gravimetric analysis (TGA) and Raman spectroscopy. The use of  $\text{CpFe}(\text{CO})_2\text{I}$  as catalyst generated only carbon fibres and balls (wide range of conditions). Studies involving the addition of  $\text{I}_2$  to catalyst solutions confirmed the poisoning effect of I on CNT production.

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## 1. Introduction

Carbon nanostructured materials, including carbon nanotubes (CNTs), have been synthesized in the presence of a metal using different techniques such as arc discharge [1], laser ablation [2] and chemical vapour deposition (CVD) [3]. A facile method for producing CNTs is through the floating catalyst CVD method in which the catalyst is introduced into a hot reaction zone by: (i) a syringe process using the catalyst dissolved in a carbon source [4]; (ii) by sublimation of the catalyst at elevated temperatures (solid to gas phase) [5] or (iii) using a gaseous catalyst source e.g.,  $\text{Fe}(\text{CO})_5$  [6]. These methods do not require a support for the catalyst; the catalyst and the carbon source are directly reacted in the gas phase where the carbon source decomposes to form the carbon nanostructures. The catalysts that are commonly used are organometallic compounds such as metallocenes, typically  $\text{Fe}(\text{C}_5\text{H}_5)_2$  [5],

and  $\text{Fe}(\text{CO})_5$  [7]. Indeed, a review of the literature reveals that of the many hundreds of publications written on the catalyzed synthesis of CNTs, mostly entail the use of ferrocene [8].

Very few studies have been reported in which other organometallic complexes of Fe have been used to make structured carbon materials [4c,4d,9]. The key factors in the choice of using organometallic catalysts to produce CNTs must include cost, volatility/solubility, metal oxidation state and carbon content of the ligand.

In our studies we have explored the effect of modifying the ligand set around a metal, in particular, by varying substituents attached to the Cp ring in ferrocene in synthetic procedures [4c,4d]. To further explore organometallic catalyst-ligand effects on CNT synthesis we have widened the range of our studies.

Herein we present our study on the synthesis of MW (multi walled) CNT growth using  $\text{CpFe}(\text{CO})_2\text{Me}$  and  $\text{CpFe}(\text{CO})_2\text{I}$  complexes as iron catalysts. These reagents were chosen as they combine the ligand types most commonly used in CNT synthesis studies to date, and have

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the appropriate physical properties for study. The study also permits an investigation of the effect of halide (I) on the reaction.

A literature search reveals only one earlier report related to the use of these types of complexes in CNT synthesis. In this study MWCNTs were prepared by an injection CVD method using either  $[\text{CpFe}(\text{CO})_2]_2$  or  $(\text{C}_8\text{H}_8)\text{Fe}(\text{CO})_3$  as a catalyst source, toluene as carbon source and  $\text{H}_2$  in a  $\text{Ar}/\text{N}_2$  mixture as carrier gas [9f].

## 2. Experimental

Ferrocene and  $[\text{CpFe}(\text{CO})_2]_2$  were purchased from Strem Chemicals. The complexes,  $\text{CpFe}(\text{CO})_2\text{I}$  [10] and  $\text{CpFe}(\text{CO})_2\text{Me}$  [11] were synthesized as described elsewhere. A quartz tube reactor ( $800 \times 28$  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 in the literature [12]. The temperature inside the quartz tube was determined by means of a thermocouple placed in the middle of the furnace. As previously described, a second moveable thermocouple was used to establish the profile of the temperature in the reactor.

The synthesis of CNTs was carried out in the temperature range  $800$ – $1000$  °C, under 5%  $\text{H}_2$  in argon (v/v) (AFROX) at atmospheric pressure. The flow rate of  $\text{H}_2$  in argon was kept constant at 100 ml/min.  $\text{CpFe}(\text{CO})_2\text{Me}$  and  $\text{CpFe}(\text{CO})_2\text{I}$  with different weight ratios were dissolved in toluene (Merck chemicals). The catalyst solutions were placed in a 10 ml syringe driven by a SAGE syringe pump at rates of  $\sim 0.8$  and  $\sim 0.2$  ml/min. The solutions were injected into the quartz tube reactor via a specially designed quartz tube (2 mm i.d., 200 mm in length), cooled by water [4b]. Similar procedures were used when ferrocene,  $[\text{CpFe}(\text{CO})_2]_2$  and iodine containing solutions were used.

The carbon deposited materials formed were scraped from the walls of the quartz tube. The carbon materials were characterized by low resolution transmission electron microscopy (TEM) (Joel JEM 100S) and Raman spectroscopy (J-Y T64000). Thermal gravimetric analysis (TGA) measurements were performed in air on a Perkin–Elmer TGA 7 to determine the characteristics of the nanotubes and the iron residue content. The number and size of the carbon tubes and spheres formed were obtained from the TEM photographs by counting procedures and represent average values.

## 3. Results and discussion

### 3.1. General results

Synthesis of various carbon nanostructures were carried out using toluene solutions of  $\text{CpFe}(\text{CO})_2\text{Me}$  and  $\text{CpFe}(\text{CO})_2\text{I}$  complexes as catalysts. Using the preparation conditions described in Table 1, carbon products such as carbon fibers (CFs), carbon spheres (CSs) and carbon

nanotubes (CNTs) were obtained (Figs. 1–3, Suppl. Figs. S1–S3) in varying amounts. When  $\text{CpFe}(\text{CO})_2\text{Me}$  was employed as a catalyst, high yields of MWCNTs were obtained using various reaction conditions (Table 1). The  $\text{CpFe}(\text{CO})_2\text{I}$  catalyzed reactions *only* produced amorphous carbon, fibers and spheres.

Figs. 1 and 2 show low magnification TEM images of CFs and CSs produced from  $\text{CpFe}(\text{CO})_2\text{Me}$  as catalyst. The average diameter of the fibers ranged from 70 to 200 nm while the mean diameter of spheres ranged between 220 and 440 nm. Fig. 3 show TEM images of as-synthesized CNTs. The outer diameter of the nanotubes ranged from 19 to 41 nm with the inner diameter ranging from 11 to 15 nm. Metal particles were observed inside the tubes by TEM analysis (shown by the arrow in Fig. 3). The presence of an iron particle inside the tube is consistent with iron acting as a catalyst for CNT formation [13]. Indeed it has been shown in the literature that no CNTs are prepared by the CVD method in the absence of a catalyst [4b].

The injection rate (0.2–0.8%) was observed to have no effect on the morphology and size of the CNTs formed [4b,9f,12], but did affect the amount of carbonaceous material formed at the lower injection (0.2 ml/min) rate, generating more carbonaceous material.

$\text{CpFe}(\text{CO})_2\text{Me}$  catalyzed reactions were studied at  $800$ – $1000$  °C. Table 1 shows that the products formed at various reaction temperatures had different morphologies as identified from TEM images. When a lower temperature ( $800$  °C) was used the  $\text{CpFe}(\text{CO})_2\text{Me}$  catalyst formed more CNTs than amorphous carbon and carbon fibers, than at higher temperatures ( $1000$  °C). The outer diameter of the nanotubes generally increased with the reaction temperature (Table 1).

A low catalyst concentration of catalyst in toluene (5 wt%) yielded more CNTs relative to a high catalyst concentration (10 wt%) (Table 1). These results are consistent with previous literature reports i.e. low catalyst concentrations are required for optimal deposition of CNTs [4b,9f].

Harris et al. have shown that MWCNTs could be grown by pyrolysis of toluene solutions of  $[\text{CpFe}(\text{CO})_2]_2$  in a two-stage furnace [9f]. It was reported from this study that low concentrations of the dimer were effective in the formation of aligned MWCNTs. Reactions were attempted with  $[\text{CpFe}(\text{CO})_2]_2$  as a catalyst in this study using a *single-stage furnace* at  $800$  °C and results were similar to those observed with  $\text{CpFe}(\text{CO})_2\text{Me}$  (see Suppl. Material, Fig. S2; more MWCNTs were formed at  $800$  °C than at higher temperatures with diameters in the 20–80 nm range). The outer diameters of the grown CNTs were also comparable to the diameters of CNTs synthesized by Harris et al. [9f].

It was noted from these results that similar tube yields were obtained when either  $\text{CpFe}(\text{CO})_2\text{Me}$  (10 wt%) or  $[\text{CpFe}(\text{CO})_2]_2$  (5 wt%) catalysts were used but the  $\text{CpFe}(\text{CO})_2\text{Me}$  catalyst formed CNTs with a slightly

Table 1  
Effect of CpFe(CO)<sub>2</sub>Me and CpFe(CO)<sub>2</sub>I on CNTs growth

Metal content <sup>a</sup>	Temperature (°C)	Injection rate (ml/min)	Yield (g)	Notes <sup>b</sup>	Mean diameter <sup>c</sup> (nm)
CpFe(CO) <sub>2</sub> I 5.0 wt%	800	0.8	0.002	a-C (90%), fibers (10%)	144 F
CpFe(CO) <sub>2</sub> I 5.0 wt%	900	0.8	0.012	a-C (20%), spheres (80%)	439 S
CpFe(CO) <sub>2</sub> I 5.0 wt%	1000	0.8	0.829	a-C (5%), spheres (95%)	276 S
CpFe(CO) <sub>2</sub> I 10.0 wt%	800	0.8	0.009	a-C (95%), fibers (5%)	150 F
CpFe(CO) <sub>2</sub> I 10.0 wt%	900	0.8	0.011	a-C (10%), spheres (90%)	631 S
CpFe(CO) <sub>2</sub> I 10.0 wt%	1000	0.8	0.905	a-C (5%), spheres (95%)	223 S
CpFe(CO) <sub>2</sub> Me 5.0 wt%	800	0.8	0.124	Tubes (70%), fibers (10%), a-C (20%)	25 T (10 inn), 120 F
CpFe(CO) <sub>2</sub> Me 5.0 wt%	900	0.8	0.198	Tubes (10%), fibers (20%), a-C (70%)	25 T (10 inn), 100 F
CpFe(CO) <sub>2</sub> Me 5.0 wt%	1000	0.8	0.295	Tubes (5%), fibers (30%), a-C (60%), spheres (5%)	30 T (14 inn), 115 F
CpFe(CO) <sub>2</sub> Me 5.0 wt%	800	0.2	0.109	Tubes (70%), fibers (20%), a-C (10%)	27 T (15 inn); 200 F
CpFe(CO) <sub>2</sub> Me 5.0 wt%	900	0.2	0.228	Tubes (10%), fibers (60%), a-C (30%)	32 T (14 inn), 150 F
CpFe(CO) <sub>2</sub> Me 5.0 wt%	1000	0.2	0.345	Tubes (10%), fibers (70%), a-C (20%)	33 T (12 inn), 140 F
CpFe(CO) <sub>2</sub> Me 10.0 wt%	800	0.8	0.157	Tubes (30%), a-C (70%)	19 T (15 inn)
CpFe(CO) <sub>2</sub> Me 10.0 wt%	900	0.8	0.250	Tubes (5%), fibers (25%), a-C (70%)	37 T (11 inn), 70 F
CpFe(CO) <sub>2</sub> Me 10.0 wt%	1000	0.8	1.395	Tubes (10%), fibers (10%), a-C (80%)	30 T (13 inn), 100 F
CpFe(CO) <sub>2</sub> Me 10.0 wt%	800	0.2	0.198	Tubes (40%), a-C (60%)	20 T (12 inn)
CpFe(CO) <sub>2</sub> Me 10.0 wt%	900	0.2	0.394	Tubes (5%), fibers (10%), a-C (85%)	41 T (11 inn), 80 F
CpFe(CO) <sub>2</sub> Me 10.0 wt%	1000	0.2	1.536	Tubes (10%), fibers (20%), a-C (70%)	35 T (14 inn), 120 F
[CpFe(CO) <sub>2</sub> ] <sub>2</sub> 10.0 wt%	800	0.8	0.023	Tubes (70%), a-C (30%)	37 (12 inn)
Fc:I (50:1) 5.0 wt%	800	0.8	0.280	Tubes (80%), a-C (20%)	36 (12 inn)
Fc:I (50:1) 5.0 wt%	900	0.8	0.314	Tubes (60%), fibers (20%), a-C (20%)	34 T (11 inn), 120 F
Fc:I (1:1) 5.0 wt%	800	0.8	0.003	Tubes (20%), a-C (80%)	33 (15 inn)
[CpFe(CO) <sub>2</sub> ] <sub>2</sub> :I (10:1) 5.0 wt%	800	0.8	0.006	Tubes (40%), a-C (60%)	34 (19 inn)
[CpFe(CO) <sub>2</sub> ] <sub>2</sub> :I (1:1) 5.0 wt%	800	0.8	0.005	Tubes (15%), a-C (75%)	33 (17 inn)

<sup>a</sup> CpFe(CO)<sub>2</sub>Me, cyclopentadienyl dicarbonyl methyl iron; CpFe(CO)<sub>2</sub>I, cyclopentadienyl dicarbonyl iodine iron; Fc, ferrocene; [CpFe(CO)<sub>2</sub>]<sub>2</sub>, cyclopentadienyliron dicarbonyl dimer.

<sup>b</sup> a-C, amorphous carbon.

<sup>c</sup> F, fibers; T, tubes; S, spheres; inn, inner diameter.

smaller diameter (see Table 1). It is thus clear that the presence of the Me group in CpFe(CO)<sub>2</sub>Me does not affect the nature of the CNTs produced in any significant way.

This is consistent with the ability of generating CpFe(CO)<sub>2</sub> radicals at high temperatures which then decompose to generate Fe and carbon species used to synthesize the CNTs.

### 3.2. Effect of iodine atoms

It is well known that addition of heteroatoms affects the synthesis of CNTs. Thus addition O and S atoms give cleaner CNTs [14] while N and B atoms are incorporated into the CNTs [15]. The effect of halide heteroatoms on CNT synthesis has to our knowledge not been commented on previously.

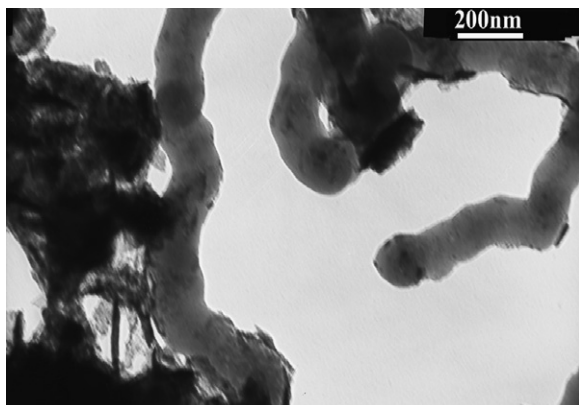


Fig. 1. TEM image of CFs (800 °C; CpFe(CO)<sub>2</sub>I: 5 wt% in toluene; 0.8 ml/min injection rate).

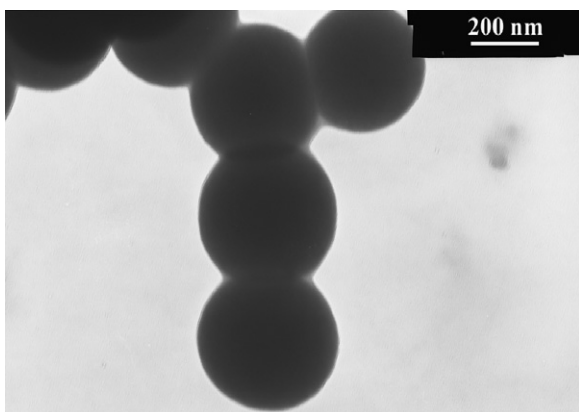


Fig. 2. TEM image of CSs (800 °C; CpFe(CO)<sub>2</sub>I: 10 wt% in toluene; 0.8 ml/min).

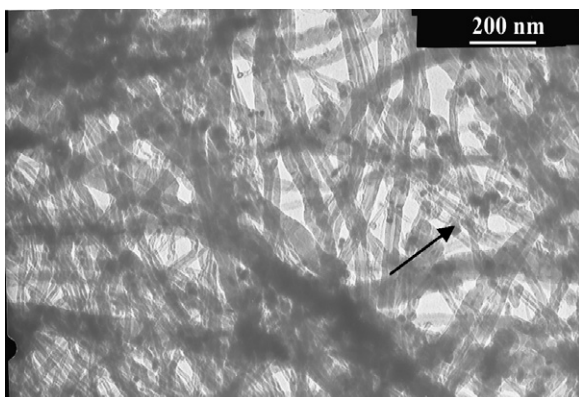


Fig. 3. TEM image of CNTs (800 °C; CpFe(CO)<sub>2</sub>Me: 5 wt% in toluene; 0.8 ml/min injection rate) (arrow = metal particle).

Pyrolysis of CpFe(CO)<sub>2</sub>I–toluene solution produced only CFs and CSs with no formation of CNTs (Figs. 1 and 2). Reaction conditions were varied but *no CNTs were ever formed*.

This finding was confirmed by performing a reaction of ferrocene with varying amounts of I<sub>2</sub>. For example, when I<sub>2</sub> was added to a solution of ferrocene (Fc) in toluene

(Fc:I = 50:1 molar ratio) MWCNTs were obtained (Fig. S5). The outer diameter of these CNTs were found to be similar to the diameter of the tubes grown from ferrocene (5 wt%, 800 °C) as reported in the literature [4b]. However, when a higher ratio of iodine Fc:I (1:1) was used, very low yields of products were noted and more amorphous carbon (80%) was formed with poor formation of CNTs (20%) (see Table 1).

Iodine was also added to [CpFe(CO)<sub>2</sub>]<sub>2</sub> in ratios of 10:1 and 1:1 (5 wt%, [CpFe(CO)<sub>2</sub>]<sub>2</sub>). The reaction performed in the absence of iodine gave 70% CNTs and 30% amorphous carbon but when I<sub>2</sub> was added (1:1 ratio), only 15% CNTs were formed (85% amorphous carbon).

The poisoning effect is attributed to the high concentration of iodine (radicals or ions) which are formed by decomposition of the Fe–I bond at high temperature. The I species either react with the Fe or alternatively react with growing carbon polymers to inhibit CNT growth.

### 3.3. Analysis of CNTs

The as-synthesized MWCNTs were also characterized by TGA in air and an example is shown in Fig. 4. The weight loss is due to the combustion of carbon with oxygen and therefore, corresponds to the carbon content in the sample. The major mass loss observed (67%) in the temperature range of 420–584 °C is due to the oxidation of carbon nanotubes, consistent with other studies reported in the literature [16].

The residue after complete carbon oxidation was 18.8 wt% of the original mass which corresponds to iron oxide content in the original sample. Similar results were obtained by Harris et al. where they observed 17.6 wt% for the iron oxide content after complete oxidation when low concentrations of catalyst were applied [9f].

Fig. 5 shows the first order Raman spectra of CNTs obtained using CpFe(CO)<sub>2</sub>Me and ferrocene as catalysts, prepared under similar conditions (5 wt%, at 800 °C, 0.8 ml/min injection rate). In Fig. 5a broad peaks at 1358

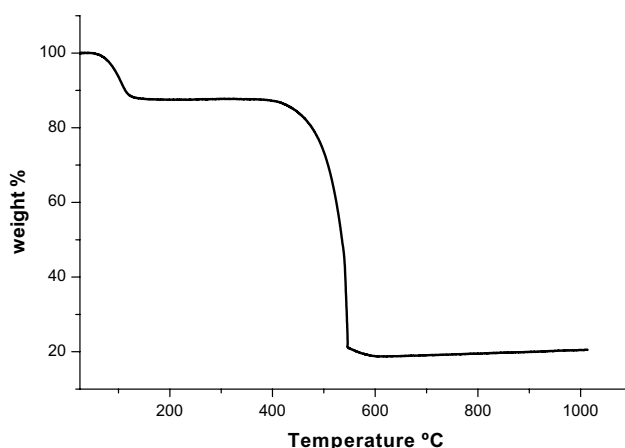


Fig. 4. TGA of CNTs grown using CpFe(CO)<sub>2</sub>Me (5 wt%, at 800 °C, 0.8 ml/min injection rate).



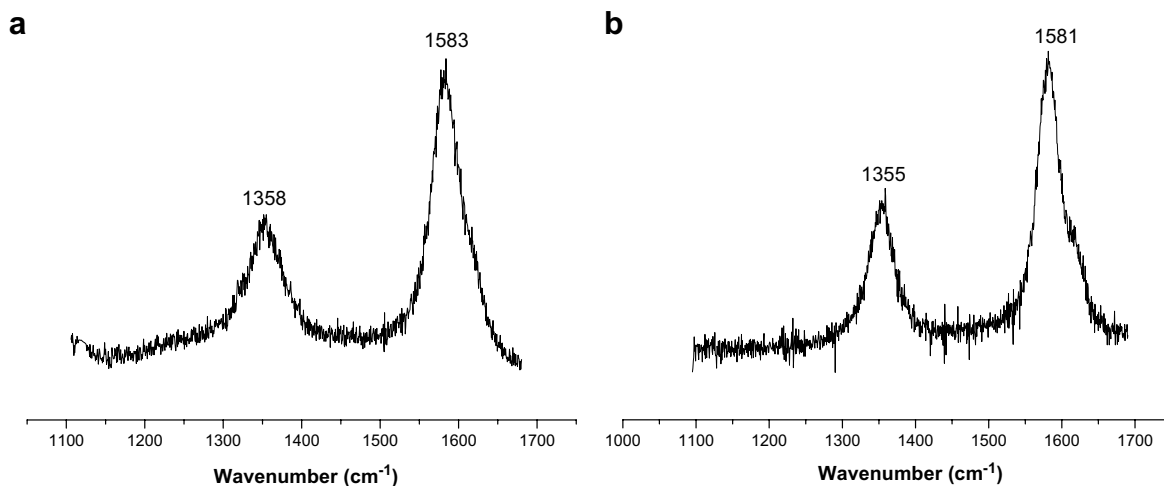


Fig. 5. Raman spectra of MWCNTs grown from: (a) CpFe(CO)<sub>2</sub>Me (5 wt%, at 800 °C, 0.8 ml/min injection rate) and (b) ferrocene (5 wt%, at 800 °C, 0.8 ml/min injection rate).

and 1583 cm<sup>-1</sup> correspond to D and G-bands, respectively, as reported in the literature [17]. These Raman lines fall within the expected range as reported by others [18]. CNTs synthesized from ferrocene show a weak D' band at 1615 cm<sup>-1</sup> which is normally positioned next to the G-band, while CNTs formed by CpFe(CO)<sub>2</sub>Me have a less pronounced D' band. This D' band is due to the presence of defects. The ratio of the intensity of the D and the G peaks ( $I_D/I_G$ ) is used to measure the disorder in the CNTs [19]. The  $I_D/I_G$  ratio of CNTs formed using CpFe(CO)<sub>2</sub>Me was found to be 0.4 while the  $I_D/I_G$  ratio of tubes formed by ferrocene was 0.5. This indicates that CNTs formed from ferrocene are slightly more disordered when compared to the tubes formed using CpFe(CO)<sub>2</sub>Me.

#### 4. Conclusions

MWCNTs with outer diameters in the range of 19–41 nm have been synthesized by an injection CVD method using solutions of CpFe(CO)<sub>2</sub>Me dissolved in toluene in a single-stage furnace. CpFe(CO)<sub>2</sub>Me gave the best yield of CNTs at low temperature (800 °C), high flow rates (0.8 ml min<sup>-1</sup>) and low concentrations (5%). Injection rates were observed to have little effect on the morphology or size distribution of the CNTs.

CpFe(CO)<sub>2</sub>I in toluene was shown to be inactive for CNT growth under a wide range of reaction conditions. Addition of a large amount of iodine to ferrocene or [CpFe(CO)<sub>2</sub>]<sub>2</sub> gave low yields of CNTs indicating the negative effect of iodine on CNT growth. This finding suggests a method for controlling CNT growth by addition of reagent poisons and further investigations to pursue this proposal are underway.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.03.013.

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