Available online at www.sciencedirect.com

SCIENCE DIRECT®

Carbon 43 (2005) 1550–1555

CARBON

www.elsevier.com/locate/carbon

A novel hybrid of carbon nanotubes/iron nanoparticles: iron-filled nodule-containing carbon nanotubes

Suwen Liu, Rudolf J. Wehmschulte *

Department of Chemistry and Biochemistry, Room 208, University of Oklahoma, 620 Parrington Oval, Norman, OK 73019, USA

Received 17 May 2004; accepted 2 February 2005
Available online 5 March 2005

Abstract

A straightforward, one-step method for the preparation of novel carbon nanotube/iron nanoparticle hybrids with some degree of shape control is reported herein. These carbon nanostructures differ from those reported previously: the nanoparticles were not attached to or coated onto the surface of carbon nanotubes but embedded inside the carbon wall. They were synthesized in good yield by thermolysis of ferrocene and thiophene mixtures in a closed steel vessel. The shapes and compositions of these nanostructures can be simply controlled by adjusting the reaction temperature and relative amounts of the precursors. Iron-filled T-junction carbon nanotubes were also obtained easily by this procedure. These iron-filled nodule-containing carbon nanotubes (INCNTs) are either empty or filled with iron or iron carbide (Fe(C)) nanowires. The outer diameters of these nanotubes range from 70 to 150 nm and the lengths reach up to several micrometers. The average size of the Fe(C) nanoparticles (or empty cores) inside the nodules is about 50 nm in diameter. The carbon in the INCNTs is amorphous. Sulfur was found being responsible for the disordered structure and playing a unique role in promoting the growth of INCNTs as well as the formation of T- or Y-junctions.

Keywords: Carbon nanotubes; Annealing; Electron microscopy; X-ray diffraction; Microstructure

1. Introduction

Metal-filled carbon nanotubes or nanoparticles have been attracting intense attention in recent years owing to their unique electronic, magnetic and nonlinear optical properties [1]. It has been suggested that these materials might find important applications in diverse areas such as magnetic data storage, xerography and magnetic resonance imaging [2]. The metal particles show quantum effects as their dimensions decrease to the nanoscale, and the carbon shells isolate the metal particles from each other as well as from the outside environment [1].

Metallocenes are important catalysts for the chemical synthesis of carbon nanotubes via various gas-phase deposition procedures [3]. Single-walled carbon nanotubes (SWNT) and well-aligned multi-walled carbon nanotubes (MWNT) have been synthesized with ferrocene as a catalyst [4–6]. Nanotubes filled with iron nanowires or nanoparticles have also been prepared using the same catalyst [7,8]. For this type of synthesis, additional carbon sources such as acetylene or benzene were necessary [4,5,8–12]. Furthermore, thiophene (sulfur) seems to play a crucial role in the formation, filling and structural control of carbon nanotubes. For example, it was demonstrated that a sulfur impurity (of approximately 0.25%) was the cause for the filling of nanotubes with various materials [13]. Rao's group prepared Y-junction nanotubes in large quantities by pyrolysis of a mixture of a metallocene with thiophene [14]. A small amount of thiophene was also used as a promoter to grow SWNTs and to increase the yield of either SWNTs or MWNTs under different growth conditions [4,15].

* Corresponding author. Tel.: +1 405 325 2388; fax: +1 405 325 6111.
E-mail address: rjwehmschulte@ou.edu (R.J. Wehmschulte).

0008-6223/$ - see front matter
doi:10.1016/j.carbon.2005.02.002

Hybrid materials consisting of CNTs and nanocrystals are expected to be useful for a variety of applications [16]. One method to obtain such materials involves coating of nanotube sidewalls with inorganic nanoparticles [17]. For example, CNTs have been coated with various metal nanoparticles [18,19]. However, many metals (e.g. Au, Al, Pd, and Fe) interact only weakly with the sidewalls of carbon nanotubes, and the nature of the interaction is presumably van der Waals [17]. All procedures reported to date for carbon nanotubes coated with nanoparticles have applied at least two steps, namely, preparation of CNTs followed by modification of the CNT sidewalls.

Here, we report the straightforward, one-step preparation of novel carbon nanotube/Fe nanoparticle hybrids with some additional degree of shape control. These hybrids are called iron-filled nodule-containing carbon nanotubes (INCNTs). These carbon nanostructures differ from those reported previously; the nanoparticles were not attached to or coated onto the surface of the CNTs but embedded inside the carbon wall of the CNTs. They consist of thick-walled carbon nanotubes whose cores are either empty or contain iron nanowires. The thick carbon walls, which are amorphous, support nodules, most of which are filled with iron nanoparticles. Finally, iron-filled T-junction carbon nanotubes were also easily obtained in the products by simply changing the reaction conditions.

2. Experimental

2.1. Synthesis of INCNTs

The synthesis was carried out in a 2 mL closed vessel cell, which was assembled from stainless steel Swagelok parts. A 3/8 in. (0.95 cm) union part was capped from one side by a standard plug. Precursors were filled into an inner quartz tubule to avoid contact with the steel wall of the vessel. Reaction conditions are listed in Table 1. In a typical synthesis, 75 mg of ferrocene powder was placed into the quartz tubule inside the cell at room temperature, 20 mg thiophene was added, and the vessel was tightly closed. The reactor was heated at 27 K/min to the desired temperature (1000 °C or 1150 °C) and was kept at this temperature for 3.0 h. The reaction took place under the autogeneous pressure of the precursors. After allowing it to cool naturally to ambient temperature, the vessel was found to be unpressurized. About 60 mg black powder-like solid was obtained from inside the quartz tubule.

2.2. Instrumentation

Transmission electron microscopy (TEM) was performed at 200 kV. Specimens for TEM observations were sonicated in isopropyl alcohol for 15 min and then loaded onto copper grids (200 mesh) that were covered with holey carbon. Scanning electron microscopy (SEM) was performed and X-ray diffraction (XRD) patterns were taken with an X-ray diffractometer (CuK_α radiation, 45 kV and 40 mA). Based on SEM and TEM observations, the yield of nodule-containing carbon nanotubes was estimated at over 60%.

3. Results and discussion

Thermolysis of ferrocene, ferrocene/benzene or ferrocene/benzene/thiophene mixtures in a simple ''makeshift'' autoclave at 1000–1150 °C for 3 h resulted in complete carbonization of the organic precursors. As detailed below, the reaction outcome could be controlled by variation of the reactants as well as the reaction temperature. While this work was written up some reports were published describing the synthesis of MWNTs via thermolysis of organometallic precursors in sealed containers [20,21]. However, none of these procedures afforded materials similar to those reported herein. The products were analyzed with powder XRD, TEM, SEM and EDX.

Table 1
Reaction conditions for INCNTs

Samples	S-164	S-257-1	S-257-2	S-257-3	S-264-2	S-228
Reaction temp. (°C)	1000	1000	1000	1000	1150	1000
Reaction time (h)	3	3	3	3	6	3
Ferrocene (mg)	100	75	75	75	75	0
Thiophene (mg)	0	20	7	7	20	0
Benzene (mg)	0	0	0	28	0	0
Thiophenol (mg)	0	0	0	0	0	75
C peaks in XRD[a]	Yes	no	no	no	no	no
Major feature	No INCNTs	INCNTs	INCNTs T-tubes	INCNTs Fe-filled	CNS[b] CNTs	No INCNTs

[a] C peaks: obvious graphitic phase in X-ray diffraction patterns.
[b] CNS: carbon nanoshells.

3.1. TEM and SEM observations

Fig. 1 shows a low-magnification TEM image of a typical sample of INCNTs. The outer diameters of these nanotubes range from 70 to 150 nm, the inner diameters from 15 to 50 nm, and the lengths from hundreds of nanometers to several micrometers. Nodules, which were either empty or filled with Fe and Fe_3C (referred to as Fe(C) hereafter) nanoparticles, grew along the nanotubes within the walls. The average size of the Fe(C) nanoparticles (or empty cores) is about 50 nm in diameter. Fig. 2a shows an HRTEM image for a typical INCNT. The Fe(C) nanoparticles are isolated and covered by carbon within the wall of the nanotube. However, the hollow cylindrical cores of the nanotubes do not seem to be affected by the nodules growing on them. Their shape and diameter remain unchanged. The walls of the nanotubes consist of disordered carbon structures, unlike conventional carbon nanotubes, which give well-ordered graphitic layers. The coverage of the nanotubes varies. Some tubes were found to be densely covered with nodules, and the nodules themselves were embedded in the wall of carbon nanotubes (Fig. 2b). In this sample, we also found short tube branches, which could be the beginning of T-junction carbon nanotubes (arrows in Fig. 2b).

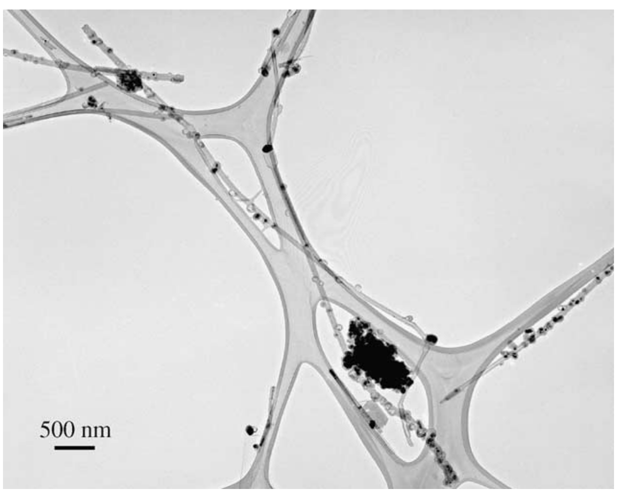

Fig. 1. Low-magnification TEM image of nodule-containing carbon nanotubes, prepared at 1000 °C (Sample 257-1).

The yield of nodule-containing carbon nanotubes is dependent on the ferrocene:thiophene ratio of the precursors. Increasing this ratio from 75:20 to 75:7 (Sample 257-2) led to an increase in the formation of long iron-nanowire filled tubes and a concomitant decrease of the amount of nodule-containing tubes. T-junction carbon nanotubes also appeared. Fig. 3a shows a T-shaped carbon nanotube that is a combination of a hollow nodule-containing tube and a Fe(C) nanowire-filled carbon nanotube. Clearly, there is a thin wall between the nanowire and the hollow cylindrical core of the nodule-containing carbon nanotube. Fig. 3b shows an individual tube with two T-junctions. The branching tube at the right is partially filled with a Fe(C) nanowire. The left-hand junction, however, shows a branching tube with a thin wall (8.6 nm) and a large inner diameter (96 nm) containing a Fe nanoparticle (50 nm). After the sample was tilted 37° in the direction marked in Fig. 3b, the diameter only showed a slight difference indicating that the tube is not a flattened carbon nanotube [22]. Usually, the branch tubes contain no or very few nodules. Fig. 3c shows an SEM image for such nodule-containing

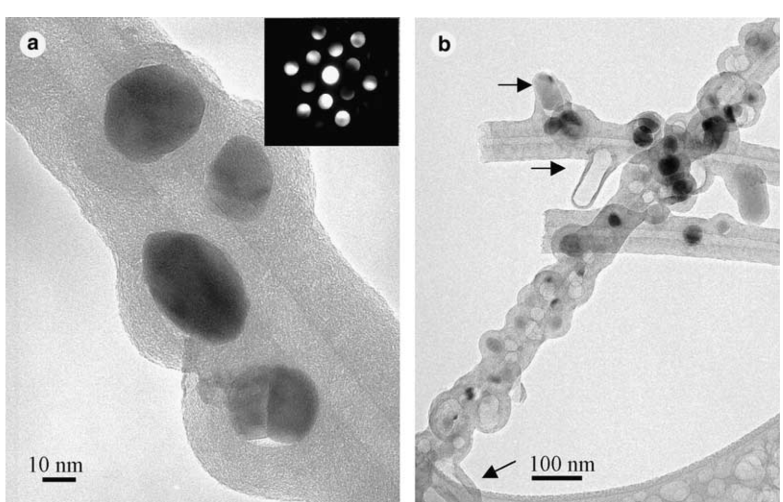

Fig. 2. (a) HRTEM image of an individual nodule-containing carbon nanotube. Inset is a selected area electron diffraction (SAED) pattern of the nodules consistent with Fe(bcc). (b) A nanotube densely covered with nodules. Arrows point to short tube branches. Both images were taken from Sample 257-1.

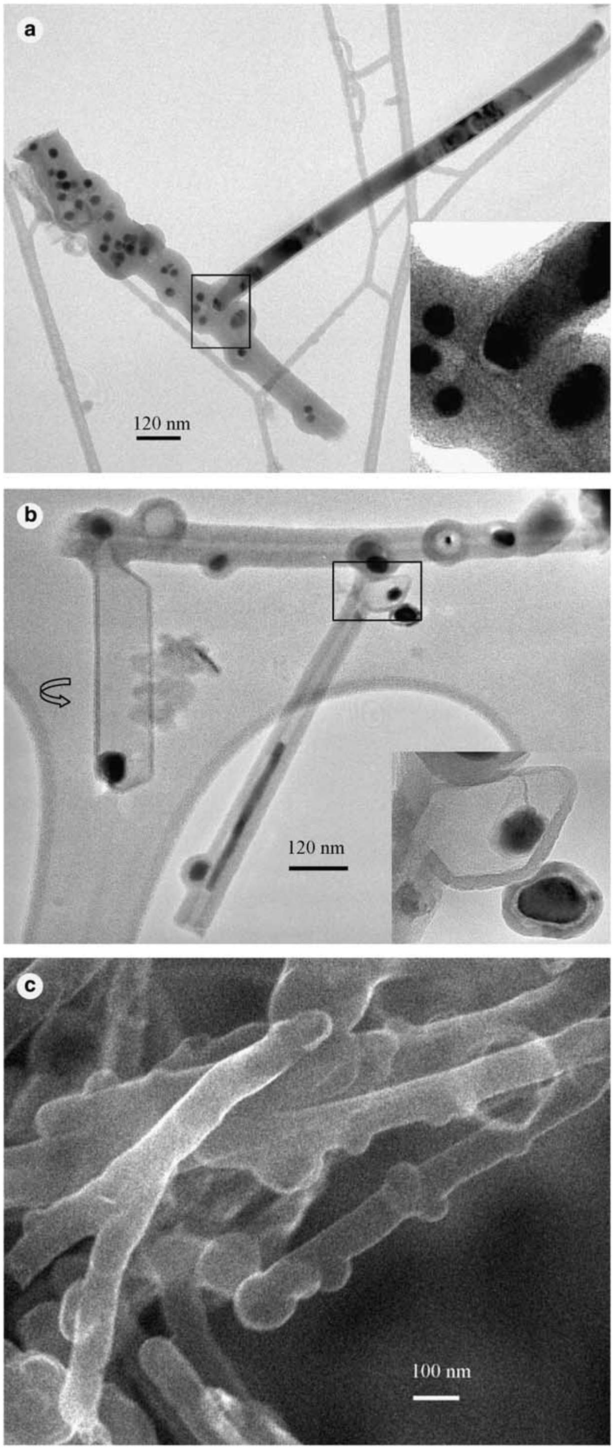

Fig. 3. (a) TEM image of an individual nodule-containing T-junction carbon nanotube. Inset is a close-up of the junction. (b) TEM image of a tube with two junctions. Inset is an HRTEM image for the right junction. (c) SEM image showing exteriors of nodule-containing and T- (or Y-) junction carbon nanotubes. All images were taken from Sample 257-3.

carbon nanotubes, which supplies an exterior view of the nodule-containing carbon nanotubes.

Addition of an extra carbon source (benzene, 20 mg) to the precursors (ferrocene, 75 mg and thiophene,

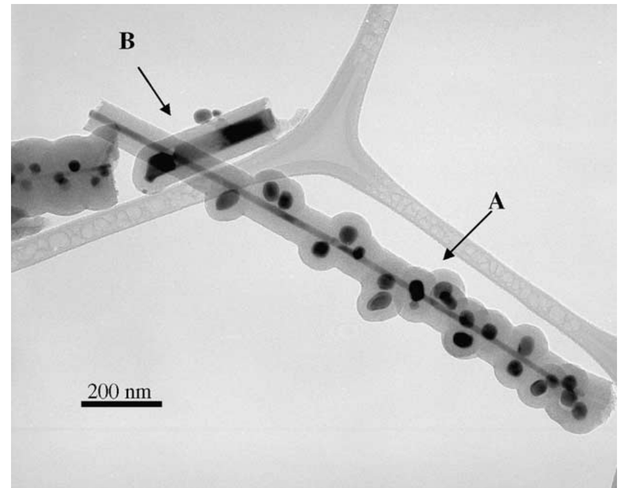

Fig. 4. TEM image of nodule-containing carbon nanotubes filled with nanowires (Sample 257-3).

7 mg), led to the formation of a mixture of nodule-containing carbon nanotubes and multiwalled carbon nanotubes, both kinds filled with Fe(C) nanowires (Fig. 4). The former (arrow A) were usually quite long (2 μm), had thicker walls (44 nm) and contained thinner Fe(C) nanowires (25 nm). The latter (arrow B), which comprised the majority, were variable in length (200 nm to several micrometers), had thinner walls (34 nm), and the enclosed thicker Fe(C) nanowires averaged 65 nm in diameter. Both kinds of nanotubes usually possessed one open and one closed end. So far, it is common to all samples that only the thick-walled nanotubes are covered with nodules. An increase of the thermolysis temperature (1150 °C) and reaction time (6 h) resulted in a dramatic decrease in the amount of nodule-containing carbon nanotubes. Only a few carbon nanotubes covered very densely with nodules were detected. HRTEM images of this sample (Fig. 5a and b) reveal that the carbon layers are still not well-ordered. The major products are aggregated fullerene-like structures of hollow carbon nanoparticles and Fe-filled carbon nanotubes. Some of the carbon nanoparticles are iron-filled (Fig. 5c).

3.2. Powder XRD analysis

The powder XRD patterns of the samples are in agreement with the TEM data, and the peaks can be indexed to bcc Fe (JCDPS 6-696) and iron carbide Fe_3C (orthorhombic, JCDPS 76-1877). Although the HRTEM images show the presence of graphite lattice fringes in some of the nodule walls, there is no long-range order, and the graphite XRD peaks are very weak (see Fig. 6). The main peaks for the ferrocene-only reaction at 1000 °C can be indexed to bcc Fe, some carbide Fe_3C (orthorhombic) and graphite (Fig. 6a). These results are similar to those in a recent report [23]. In

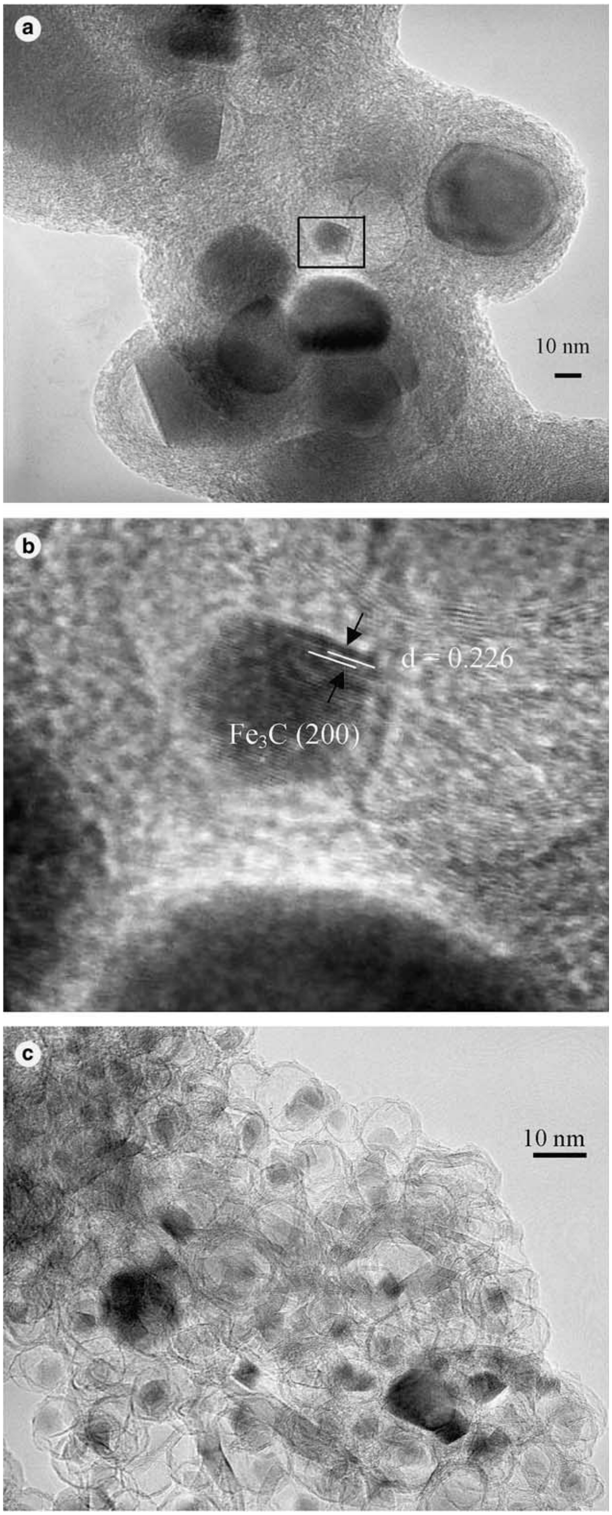

Fig. 5. (a) HRTEM micrograph of the nodule-containing carbon nanotube sample prepared at 1150 °C for 6 h (Sample 264-2). (b) A close-up of the area marked in (a). (c) A close-up of aggregated fullerene-like nanostructures. They are hollow carbon nanoparticles, some of which are partially Fe-filled.

Fig. 6b, however, when thiophene (ferrocene:thiophene ratio of 75:20) was introduced into the reaction at

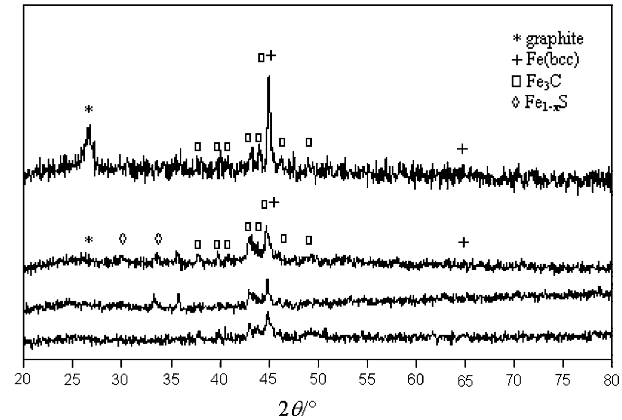

Fig. 6. XRD patterns of selected samples using different precursors. (a) Ferrocene only (Sample 164). (b) Ferrocene:thiophene ratio of 75:20; a small amount of $Fe_{(1-x)}S$ was detected (Sample 257-1). (c) Sample in (b) treated with HCl for 14 h. (d) Ferrocene:thiophene ratio of 75:7 (Sample 257-2). From top to bottom the patterns are a, b, c and d, respectively.

1000 °C, graphite peaks became too weak to be distinguished. Even at the increased temperature of 1150 °C and a prolonged reaction time of 6 h, the XRD data still showed no obvious graphite peaks. Fig. 6c shows the XRD pattern of the sample in Fig. 6b treated by concentrated HCl. Their XRD patterns are similar, with a small amount of $Fe_{1-x}S$ detected in both. Fig. 6d shows the XRD pattern of a sample prepared at 1000 °C with a ferrocene to thiophene ratio of 75:7. No obvious $Fe_{1-x}S$ peak was detected.

3.3. Effects of sulfur

In order to investigate the effects of sulfur, thiophenol was used instead of thiophene (Sample 228). The XRD patterns gave bcc Fe as the main diffraction peaks, but again no obvious graphite peaks were found. However, this reaction did not afford any INCNTs, but gave some iron-filled carbon particles and nanotubes instead. This indicates that sulfur prevents the formation of ordered graphitic structures, which is contrary to the reports that thiophene acts as a "growth promoter" in the formation of single-walled carbon nanotubes [4,15]. On the other hand, thiophene seems to play an important role for the growth of nodule-containing carbon nanotubes and also for T- or Y-junction tubes. Given that HCl treated nodule-containing tubes remain essentially unchanged, it can be concluded that most iron and iron carbides are encapsulated within the carbon shells. Sulfur has been found as FeS and Fe_3S_4 in the products of carbon nanotubes with 5 wt.% of thiophene added [4]. Interestingly, we only detected small amounts of $Fe_{1-x}S$ in the reaction with a high thiophene content (Fig. 6b). The presence of sulfur in the sample was confirmed further by EDX. In the other reactions no obvious $Fe_{1-x}S$ peaks were found in XRD pattern (Fig. 6d). It has been reported that sulfur plays a key role in the formation of metal-filled carbon nanotubes [13]. Our results demonstrate that thiophene is an important precursor for growing Fe(C) nanowire-filled and nodule-containing carbon nanotubes, and also for T-junction carbon nanotubes. Based on these results, we propose that (i) the presence of sulfur inhibits the formation of ordered graphitic structures, and that (ii) thiophene plays a unique role promoting the growth of INCNTs as well as the formation of T- or Y-junctions.

In summary, we have found a very simple procedure for the preparation of INCNTs in high yield using ferrocene and thiophene as precursors. The shape and composition of these nanotubes can be controlled by adjusting the reaction temperature and the relative amounts of the precursors. Furthermore, the simplicity of this method should allow for easy scale-up to gram quantities or more. Metal-filled T- or Y-junction nanotubes have been proposed as suitable building blocks for the development of nanoelectronics [24], and our results may help pave the way for the high-yield construction and assembly of predefined ratios of metal-containing nanoparticles, nanotubes and nanowires.

Acknowledgment

We are grateful to the donors of the American Chemical Society Petroleum Research Fund, the Oklahoma Network for Nanostructured Materials (NSF EPSCoR) and the National Science Foundation of China (No. 50072027). We also thank G. Strout, Dr. G. Lian and B. Chissoe for assistance with TEM and SEM and C. Burba for help with XRD.

References

[1] Harris PJF. Carbon nanotubes and related structures: new materials for the twenty-first century. Cambridge: Cambridge University Press; 1999.

[2] Majetich SA, Artman JO, McHenry ME, Nuhfer NT, Staley SW. Preparation and properties of carbon-coated magnetic nanocrystallites. Phys Rev B 1993;48:16845–8.

[3] Sen R, Govindaraj RA, Rao CNR. Carbon nanotubes by the metallocene route. Chem Phys Lett 1997;267:276–80.

[4] Cheng HM, Li F, Su G, Pan HY, He LL, Sun X, et al. Large-scale and low-cost synthesis of single-walled carbon nanotubes by the catalytic pyrolysis of hydrocarbons. Appl Phys Lett 1998;72:3282–4.

[5] Hou H, Schaper AK, Weller F, Greiner A. Carbon nanotubes and spheres produced by modified ferrocene pyrolysis. Chem Mater 2002;14:3990–4.

[6] Huczko A, Lange H, Sioda M, Zhu YQ, Hsu WK, Kroto HW, et al. Hollow cathode plasma synthesis of carbon nanofiber arrays at low temperature. J Phys Chem B 2002;106:1534–6.

[7] Cao A, Zhang X, Wei J, Li Y, Xu C, Liang J, et al. Macroscopic three-dimensional arrays of Fe nanoparticles supported in aligned carbon nanotubes. J Phys Chem B 2001;105:11937–40.

[8] Grobert N, Hsu WK, Zhu YQ, Hare JP, Kroto HW, Walton DRW, et al. Enhanced magnetic coercivities in Fe nanowires. Appl Phys Lett 1999;75:3363–5.

[9] Andrews R, Jacques D, Rao AM, Derbyshire F, Qian D, Fan X, et al. Continuous production of aligned carbon nanotubes: a step closer to commercial realization. Chem Phys Lett 1999;303:467–74.

[10] Cao A, Ci L, Li D, Wei B, Xu C, Liang J, et al. Vertical aligned carbon nanotubes grown on Au film and reduction of threshold field in field emission. Chem Phys Lett 2001;335:150–4.

[11] Cao A, Zhu H, Zhang X, Li X, Ruan D, Xu C, et al. Hydrogen storage of dense-aligned carbon nanotubes. Chem Phys Lett 2001;342:510–4.

[12] Satishkumar BC, Govindaraj A, Rao CNR. Bundles of aligned carbon nanotubes obtained by the pyrolysis of ferrocene–hydrocarbon mixtures: role of the metal nanoparticles produced in situ. Chem Phys Lett 1999;307:158–62.

[13] Demoncy N, Stephan O, Brun N, Colliex C, Loiseau A, Pascard H. Filling carbon nanotubes with metals by the arc-discharge method: the key role of sulfur. Eur Phys J B 1998;4:147–57.

[14] Satishkumar BC, Thomas PJ, Govindaraj A, Rao CNR. Y-junction carbon nanotubes. Appl Phys Lett 2000;77:2530–2.

[15] Ago H, Ohshima S, Uchida K, Yumura M. Gas-phase synthesis of single-wall carbon nanotubes from colloidal solution of metal nanoparticles. J Phys Chem B 2001;105:10453–6.

[16] Jiang K, Eitan A, Schadler LS, Ajayan PM, Siegel RW, Grobert N, et al. Selective attachment of gold nanoparticles to nitrogen-doped carbon nanotubes. Nano Lett 2003;3:275–7.

[17] Kong J, Chapline MG, Dai H. Functionalized carbon nanotubes for molecular hydrogen sensors. Adv Mater 2001;13:1384–6.

[18] Choi HC, Shim M, Bangsaruntip S, Dai H. Spontaneous reduction of metal ions on the sidewalls of carbon nanotubes. J Am Chem Soc 2002;124:9058–9.

[19] Xue B, Chen P, Hong Q, Lin J, Tan KL. Growth of Pd, Pt, Ag and Au nanoparticles on carbon nanotubes. J Mater Chem 2001;11:2378–81.

[20] Iyer VS, Vollhardt KPC, Wilhelm R. Near-quantitative solid-state synthesis of carbon nanotubes from homogeneous diphenylethynecobalt- and nickel complexes. Angew Chem Int Ed 2003;42:4379–83.

[21] Keller TM, Qadri SB. Ferrocenylethynylbenzenes as precursors to in situ synthesis of carbon nanotube and Fe nanoparticle compositions. Chem Mater 2004;16:1091–7.

[22] Liu S, Yue J, Wehmschulte RJ. Large thick flattened carbon nanotubes. Nano Lett 2002;2:1439–42.

[23] Sun XC, Nava N. Microstructure and magnetic properties of Fe(C) and Fe(O) nanoparticles. Nano Lett 2002;2:765–9.

[24] Li J, Papadopoulos C, Xu J. Nanoelectronics: growing Y-junction carbon nanotubes. Nature 1999;402:253–4.