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Synthesis of multi-walled and single-walled nanotubes, aligned-nanotube bundles and nanorods by employing organometallic precursors

Abstract Pyrolysis of organometallic precursors such as metallocenes and iron pentacarbonyl as well as of their mixtures with hydrocarbons such as acetylene or benzene has been carried out under a variety of conditions to synthesize nanotubes. While the use of benzene as a hydrocarbon source generally yields multi-walled nanotubes, it has been possible to obtain single-walled nanotubes (~1 nm diameter) by pyrolyzing a metallocene or a mixture of metallocenes along with acetylene under a high flow rate of Ar. These experiments show that the organometallic precursor produces small nanoparticles of ~1 nm diameter which then catalyze the formation of the single-walled nanotubes. Copious quantities of aligned-nanotube bundles have been obtained by the pyrolysis of acetylene in the presence of high concentrations of ferrocene. Nanorods have been produced by the pyrolysis of ferrocene under vacuum. Single walled nanotubes can be filled or decorated by metals.

Key words Carbon nanotubes · Single-walled nanotubes · Aligned nanotube bundles · Nanorods
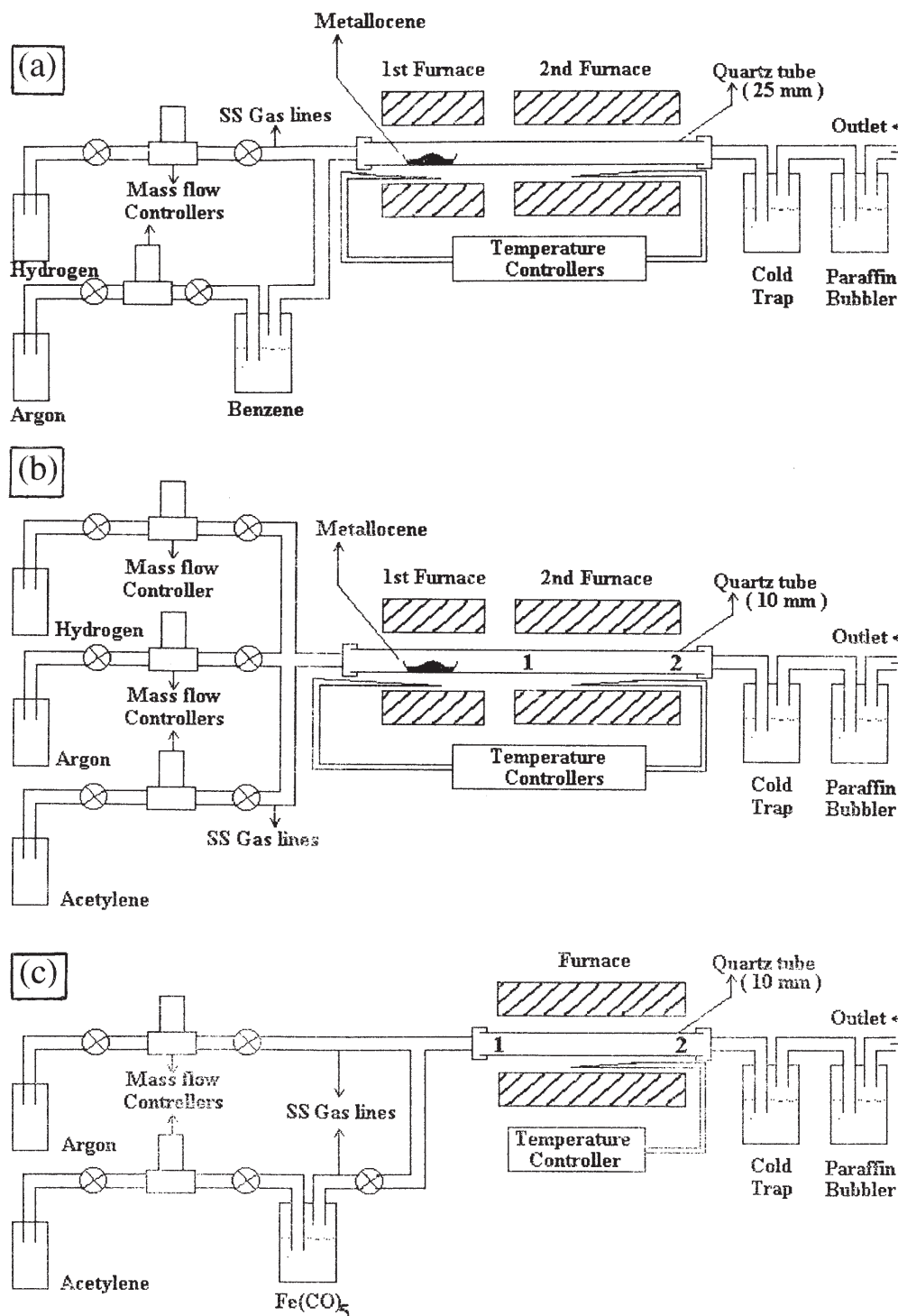
Introduction

Since the discovery of carbon nanotubes, there has been considerable effort to prepare them by different methods. Traditionally, carbon nanotubes have been prepared by arc-evaporation of graphite electrodes [1]. The nanotubes collected at the cathode are generally multi-walled, comprising several graphite layers around the central tubule. Multi-walled nanotubes (MWNTs) can also be prepared by the decomposition of hydrocarbons such as acetylene

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or benzene over small metal particles [2–5]. The metal particles are found to be essential for the formation of nanotubes by the decomposition of hydrocarbons. The size of the metal particles plays a crucial role in determining the nature of the nanotubes obtained. Thus, very small metal nanoparticles (≤5 nm) can yield single-walled nanotubes (SWNTs) [6]. Large metal particles do not yield nanotubes, but instead give rise to metal carbides or metal particles covered by graphene sheets. Since the metal particles play such a crucial role in the formation of nanotubes by the pyrolysis of hydrocarbons, it was our view that there may be considerable advantage in making use of organometallic precursor molecules which on decomposition not only act as a source of carbon but also give rise to small metal clusters or particles which act as catalysts to form the nanotubes. We have therefore made use of organometallic precursors such as metallocenes and iron pentacarbonyl to explore this idea [7]. Furthermore, we have investigated whether SWNTs can be prepared by a careful control of the preparative conditions as well as the relative proportions of the organometallic precursor and the hydrocarbon source. SWNTs are usually prepared by metal catalyzed arc evaporation of graphite electrodes [8] or laser vaporization of transition metal containing graphite targets [9, 10].

An aspect of interest to us investigate whether by the decomposition of organometallic precursors along with hydrocarbons, one could obtain aligned nanotube bundles. Aligned nanotube bundles have hitherto been obtained by very complex procedures. One of the procedures employed is to pass a dispersion of arc-produced carbon nanotubes in ethanol through an alumina micropore filter and then press the nanotube-covered filter onto a polymer sheet [11]. Under pressure, the nanotubes are printed onto the polymer sheet in an aligned manner. Aligned nanotubes have also been obtained by the chemical vapour deposition of acetylene catalyzed by iron nanoparticles embedded in mesoporous silica [12], the pores of the silica controlling the growth direction of the nanotubes. Aligned-nanotube bundles have been prepared

Fig. 1a–c Pyrolysis apparatus employed for the synthesis of carbon nanotubes by pyrolysis of mixtures of (**a**) metallocene + benzene (**b**) metallocene + acetylene and (**c**) $Fe(CO)_5$ + acetylene

recently by the pyrolysis of 2-amino-4,6-dichloro-s-triazine over thin films of a cobalt catalyst, patterned on a silica substrate by laser etching [13]. A salient feature of the precursor strategy employed by us is the ease of control of the relative concentrations or partial pressures of the organometallic precursor and hydrocarbon in the vapour phase, achieved by manipulating the flow rates of the different gaseous species through mass flow controllers. By this means, we expected to prepare SWNTs at one end and aligned nanotube bundles at the other. In this article we report the successful results we have obtained with this relatively simple chemical strategy.

Experimental

In order to prepare MWNTs by metallocene pyrolysis, the set-up shown in Fig. 1(a) was employed. The pyrolysis set-up consists of stainless steel gas flow lines and a two-stage furnace system fitted
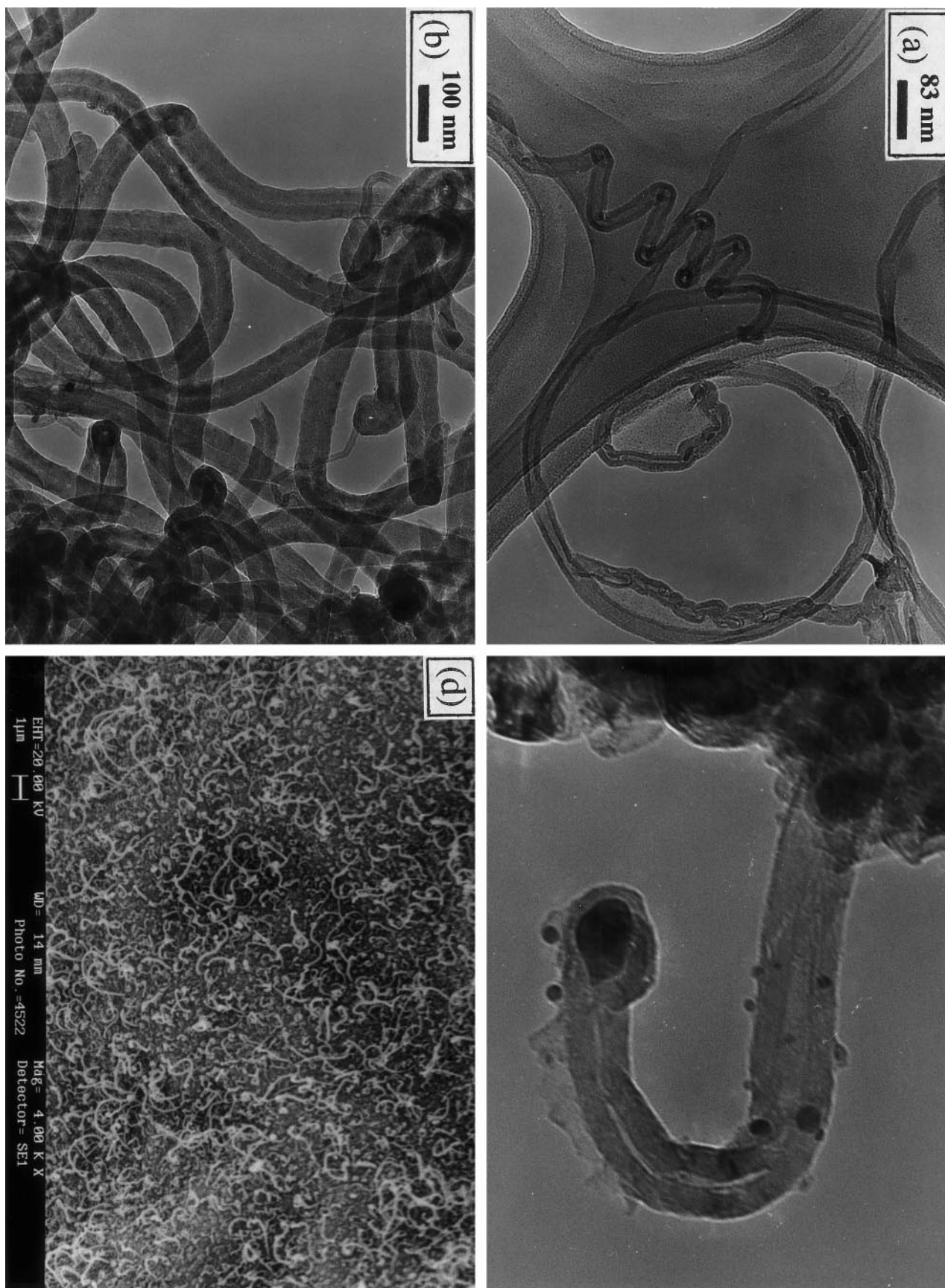
Fig. 2a–d TEM images of carbon nanotubes obtained by the pyrolysis of a mixture of ferrocene and benzene (**a**), a mixture of nickelocene and benzene at 1173 K in 85% Ar 15% H_2 mixture at a flow rate of 1000 sccm (**b**) and a mixture of cobaltocene and benzene at 1173 K in a stream of 75% Ar and 25% H_2 at a flow rate of 50 sccm (**c**). SEM image of carbon nanotubes obtained by the pyrolysis of a mixtures of cobaltocene and acetylene (50 sccm) at 1373 K, in Ar+H_2 flow (total flow rate=1000 sccm) (**d**)
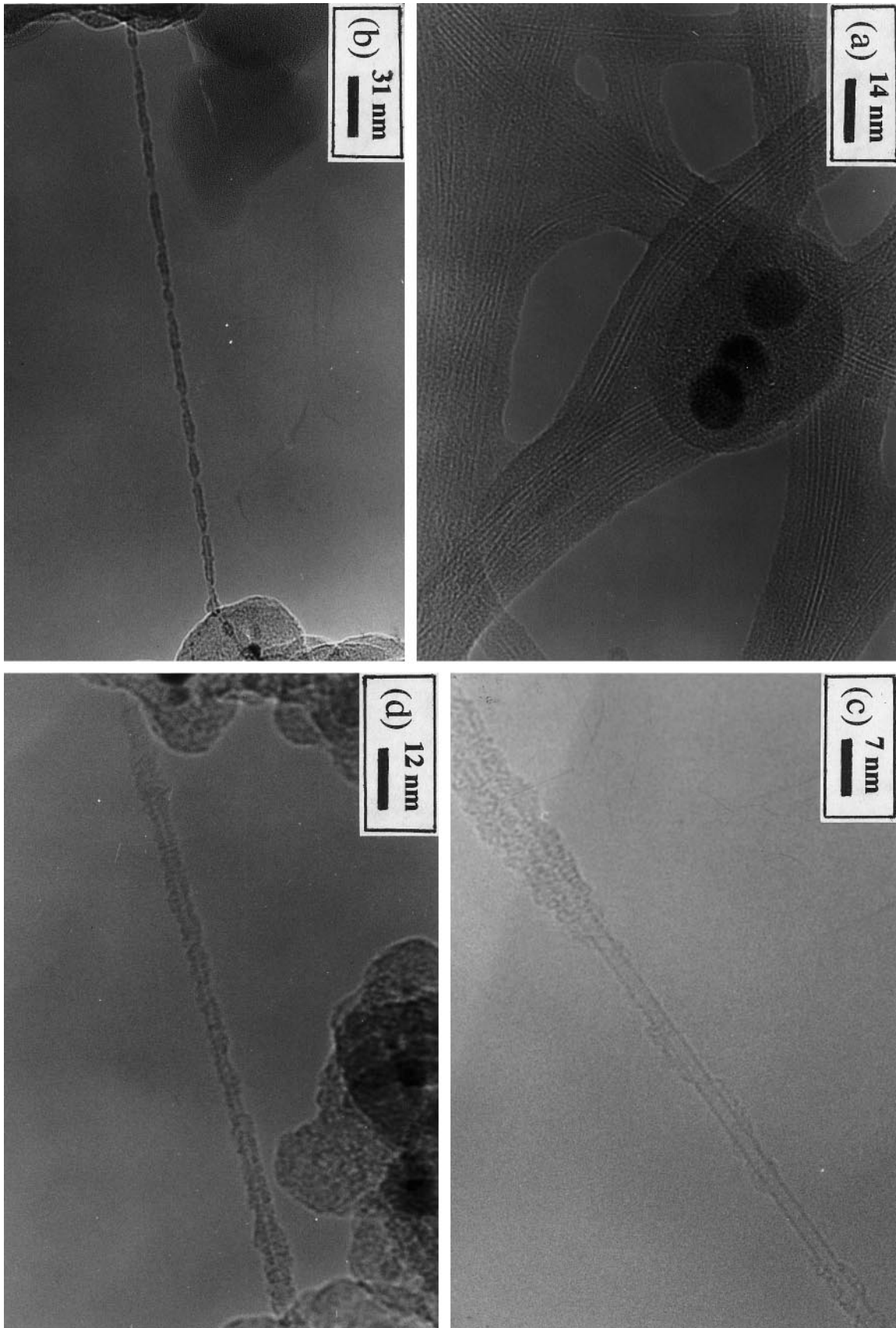
Fig. 3a–d HREM images of SWNTs obtained by arcing graphite rods filled with Ni and Y_2O_3 in He (660 Torr) (**a**), and SWNTs obtained by the pyrolysis of a mixture of nickelocene and acetylene (50 sccm) at 1373 K in Ar flow (1000 sccm) (**b**) (**c**) and a SWNT obtained by the pyrolysis of a mixture of nickelocene and acetylene (25 sccm) at 1373 K in Ar (975 sccm) and H_2 (25 sccm) flow (**d**)

with a quartz tube (25 mm inner diameter, i.d.). The flow rate of the gases was controlled using UNIT mass flow controllers. A known quantity (~100 mg) of the metallocene (of 99% purity) was taken in a quartz boat and placed inside the first furnace. The metallocene was sublimed by raising the temperature of this furnace to 623 K at a controlled heating rate. Argon gas, bubbled at a desired flow rate through a known quantity of benzene (~5 ml) was mixed with hydrogen gas and passed through the quartz tube. The Ar/H_2 gas ratio was maintained at 75%/25% or 85%/15% and the total gas flow rate was kept at 50 sccm or 1000 sccm (sccm=standard cubic centimeter per minute). The metallocene vapour was carried by this gas mixture into the second furnace maintained at 1173 K. The pyrolysis yielded copious quantities of carbon deposits inside the second furnace.

In order to prepare SWNTs by metallocene pyrolysis, the set-up shown in Fig. 1(b) was employed. The pyrolysis set-up consists of a two-stage furnace system fitted with a quartz tube (10 mm i.d). The metallocene placed in the first furnace was sublimed by raising the temperature of this furnace to 623 K at a heating rate of 100 deg min^{-1} Argon and acetylene were passed through the quartz tube at flow rates of 1000 sccm and 50 sccm respectively. The metallocene vapour was carried by this gas mixture into the second furnace maintained at 1373 K. The pyrolysis yielded copious quantities of carbon deposits inside the second furnace. SWNTs were mainly found at the outlet end of the second furnace marked 2 in Fig. 1(b), while MWNTs were present at the inlet end, marked 1.

$Fe(CO)_5$ was pyrolyzed along with acetylene by using the set-up shown in Fig. 1(c). Acetylene (flow rate=50 sccm) was bubbled through a known quantity of $Fe(CO)_5$ (1 ml) and the mixture carried by argon gas (flow rate=1000 sccm) into the furnace, maintained at 1373 K. The argon gas acts as a dilution agent. SWNTs were found at the outlet end of the furnace marked 2 in the Fig. 1(c), MWNTs being present at the inlet end, marked 1. For purpose of comparison, we also synthesized SWNTs by the arc-evaporation of graphite electrodes filled with Y_2O_3 and Ni powder (1 at.% Y and 4.2 at.% Ni) in a He atmosphere of 660 Torr. The graphite rods (6 cm long, 6 mm dia. with a 4 mm dia. hole drilled in the centre) filled with Y_2O_3, Ni and graphite powder were treated with hydrogen at 973 K for 3 h, prior to arcing.

For the preparation of aligned nanotube bundles, pyrolysis of ferrocene was carried out as follows. A known quantity (100 mg) of ferrocene (presublimed 99.99% purity) was taken in a quartz boat located at one end of a narrow quartz tube (10 mm i.d.), which in turn was placed in a dual furnace system (see Fig. 1(b)). The part of the quartz tube containing the ferrocene was in the first furnace and the ferrocene was sublimed by raising the temperature of this furnace to 623 K at a controlled heating rate. Argon gas was passed through the quartz tube at a desired flow rate. The ferrocene vapour was carried by the Ar gas into the second furnace, maintained at 1373 K, where pyrolysis occurred. The main variables in the experiments were the heating rate of ferrocene, flow rate of the argon gas and pyrolysis temperature. Large quantities of deposits accumulated at the inlet of the second furnace.

The carbon products were sonicated in carbon tetrachloride and loaded onto holey carbon copper grids. Transmission electron microscopy (TEM) was performed with a JEOL JEM-3010 microscope operating at 300 kV. The microscope is equipped with a Gatan fiber optically coupled TV system, model 622SC for high resolution imaging. Scanning electron microscopy (SEM) was performed on the as-prepared samples using a LEICA S440i instrument.

Results and discussion

Our first experiments were directed towards establishing the viability of the synthetic strategy, by carrying out the pyrolysis of hydrocarbons such as benzene in mixture with metallocene. We indeed found that in the presence
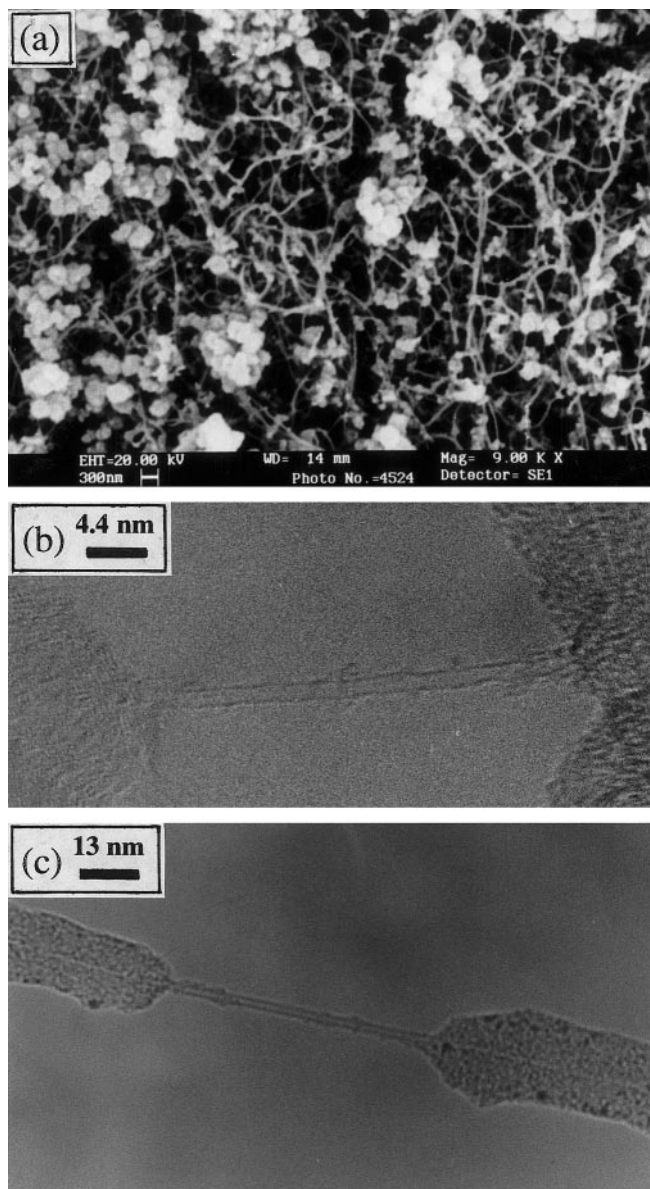

Fig. 4a–c SEM image of SWNTs obtained by the pyrolysis of a mixture of cobaltocene and acetylene (50 sccm) at 1373 K in Ar (975 sccm) and H_2 (25 sccm) flow (**a**). HREM images of the SWNTs (**b** and **c**). The image in (**c**) shows extensive coating of amorphous carbon on the nanotube

of a small proportion of metallocene, pyrolysis of benzene, employing the apparatus in Fig. 1(a), yields large quantities of carbon nanotubes. In Fig. 2(a) we show the TEM image of nanotubes obtained by the pyrolysis of benzene in the presence of ferrocene at 1273 K in 85% Ar - 15% H_2 at a total gas flow rate of 1000 sccm. Pyrolysis of benzene and nickelocene under similar conditions also yields large quantities of nanotubes, as seen in Fig. 2(b). In Fig. 2(c) we show the TEM image of a thick nanotube obtained by the pyrolysis of benzene along with cobaltocene at 1273 K in a stream of 75% Ar and 25% H_2 (total gas flow rate=50 sccm). The metal particle can be clearly seen at the tip of this nanotube indicating
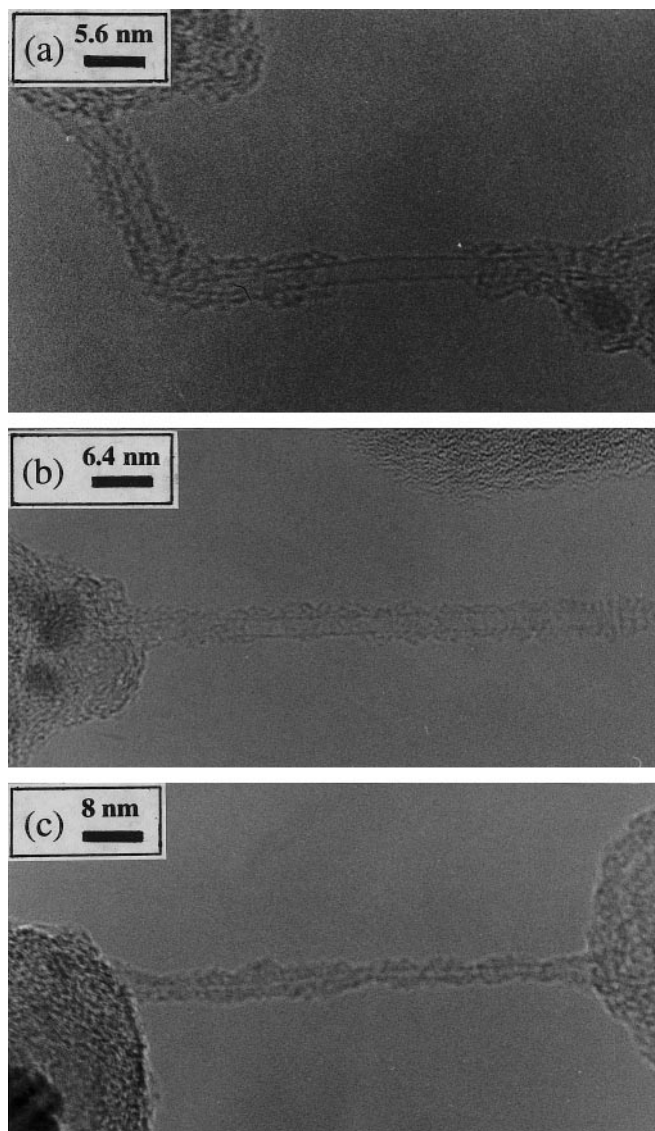
Fig. 5a–c HREM images of SWNTs obtained by the pyrolysis of a mixture of acetylene (50 sccm) with cobaltocene + ferrocene (1:1) (**a**), nickelocene + cobaltocene (1:1) (**b**) and ferrocene + nickelocene (1:1) at 1373 K in Ar (975 sccm) and H_2 (25 sccm) flow (**c**)

Fig. 6a, b HREM images of SWNTs obtained by the pyrolysis of a mixture of $Fe(CO)_5$ and C_2H_2 (50 sccm) at 1373 K in Ar (1000 sccm) flow (**a**), (**b**)

that the metal particle catalyses the nanotube formation. The microscopic images in Fig. 2 clearly show that the nanotubes are multi-walled. The wall thickness can however be controlled by adjusting the relative concentration of the metallocene and benzene in the vapour phase. In Fig. 2(d) we show a SEM image of carbon nanotubes obtained by the pyrolysis of cobaltocene and acetylene (50 sccm) at 1373 K, in Ar (975 sccm) and H_2 (25 sccm) flow, by employing the apparatus in Fig. 1(b). These nanotubes are also multi-walled. These initial experiments on the pyrolysis of a mixture of benzene or acetylene with a metallocene established that MWNTs can readily be prepared by this method.

Having successfully obtained MWNTs by the pyrolysis of a mixture of a metallocene and hydrocarbon, we
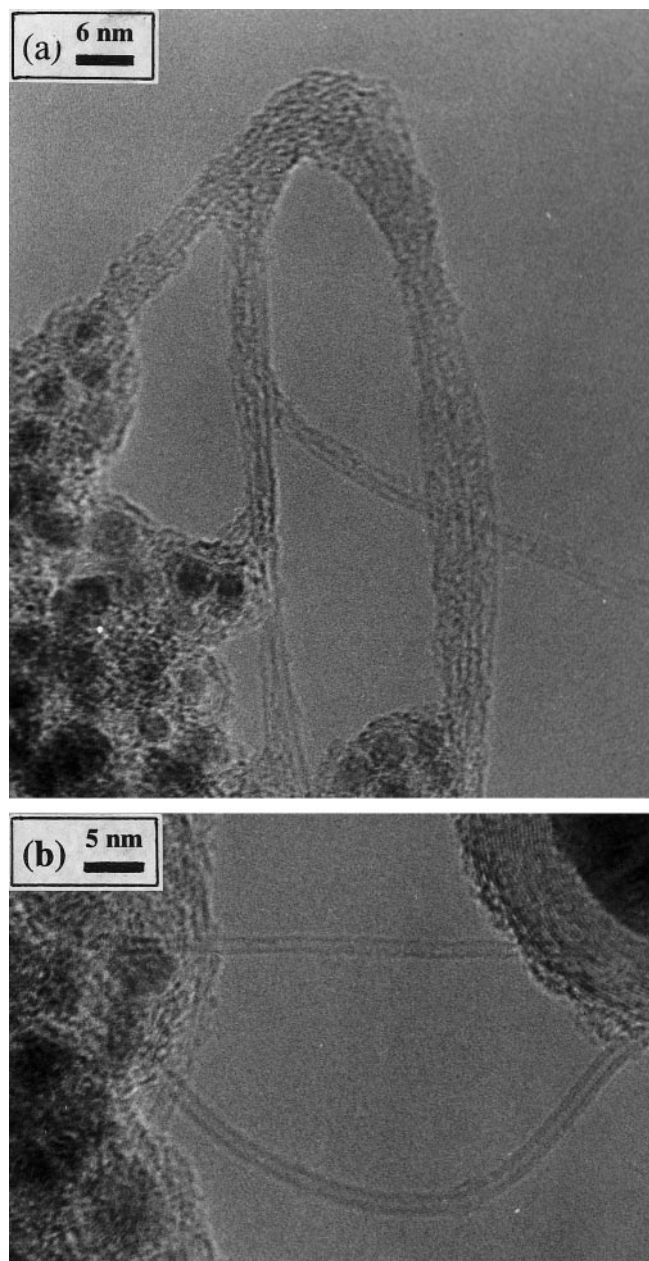
thought it should be possible to control the relative proportions of the metallocene and the hydrocarbon (which acts as an additional carbon source), to obtain SWNTs. We expected the formation of SWNTs at low concentration of carbon in the vapour phase. For purpose of comparision, we first prepared SWNTs by the arc-evaporation of graphite rods filled with Ni and Y_2O_3 in a He atmosphere (660 Torr). This procedure was similar to the one reported by Journet et al. [14], except that we have used Y_2O_3 instead of yttrium metal. The web-like deposit on the chamber walls near the cathode consists of SWNT bundles. The high resolution transmission elec-

Table 1 Nature of the carbon nanotubes obtained by the pyrolysis of acetylene along with different organometallic precursors

Organometallic precursor	Hydrocarbon source	Nature of carbon nanotubes	
		Inlet	Outlet
Ferrocene	Acetylene	Alligned MWNTs	Metal encapsulated graphite nanoparticles
Nickelocene	Acetylene	MWNTs	SWNTs
Cobaltocene	Acetylene	MWNTs	SWNTs
Ferrocene + Nickelocene	Acetylene	Aligned MWNTs	SWNTs
Ferrocene + Cobaltocene	Acetylene	Aligned MWNTs	SWNTs
Nickelocene + Cobaltocene	Acetylene	MWNTs	SWNTs
$Fe(CO)_5$	Acetylene	MWNTs	SWNTs (bundles)

Table 2 Nature of nanotubes and other products obtained by the pyrolysis of mixtures of organometallic precursors with hydrocarbons

Precursor	Hydrocarbon source	Nature of carbon nanotubes and other products
Ferrocene[a]	nil	Mostly metal-filled MWNTs
	acetylene	Inlet: aligned nanotube bundles (MWNTs) Outlet: metal encapsulated graphite nanoparticles
Nickelocene[a]	nil	Inlet: metal-filled MWNTs Outlet: metal encapsulated graphite nanoparticles
	acetylene	Inlet: MWNTs Outlet: SWNTs
Coblatocene[a]	nil	Inlet: metal-filled MWNTs Outlet: metal encapsulated graphite nanoparticles
	acetylene	Inlet: MWNTs Outlet: SWNTs
$Fe(CO)_5$	nil	metal encapsulated graphite nanoparticles
	carbon monoxide	Inlet: uniformed sized (1 m) spherical particles Outlet: nanosized spherical particles
	methane	Inlet: interconnected spherical particles Outlet: spherical particles
	acetylene	Inlet: MWNTs Outlet: SWNTs (bundles)
	benzene	Inlet: rod-like structures (metallic nanorods) Outlet: non-uniformed sized particles

[a] with benzene, only MWNTs are obtained when the quartz pyrolysis tube was of 25 mm diameter. Experiments were not carried out with the narrower quartz tube employed with acetylene

tron microscopic image (HREM) of SWNTs so prepared is shown in Fig. 3(a). The image shows bundles consisting of 10–20 SWNTs forming some kind of high-way junctions. The diameter of the SWNTs is in the range of 1–2 nm and the length extended up to several microns. Figure 3(b) and (c) show the TEM images of isolated SWNTs obtained by the pyrolysis of nickelocene and acetylene (flow rate=50 sccm) at 1373 K in Ar (flow rate=1000 sccm). The diameter of SWNT in Fig. 3(b) is 1.4 nm. It is noteworthy that pyrolysis of nickelocene in admixture with benzene under similar conditions primarily yields MWNTs. Acetylene appears to be a better carbon source for the preparation of SWNTs, since it contains a smaller number of carbon atoms; it is possible that benzene favors the formation of MWNTs since it is more carbon-rich. The bottom portion of the SWNT in Fig. 3(b) shows an amorphous carbon coating around the tube. Indeed, a majority of the SWNTs show the presence of such amorphous carbon coating. This can be avoided by reducing the proportion of the hydrocarbon (C_2H_2) and mixing hydrogen into the Ar stream. The SWNTs obtained with Ar-H_2 as the flow gas show less amorphous carbon deposition around the tubes, as revealed by the HREM image in Fig. 3(d). Pyrolysis of cobaltocene and acetylene under similar conditions also yields isolated SWNTs. The yield of SWNTs is considerably better with cobaltocene than with nickelocene. The SEM image in Fig. 4(a) demonstrates the high yield of SWNTs, present along with other carbonaceous deposits. In Fig. 4(b) and (c), we show the HREM images of SWNTs, with diameters of 1 nm and 1.5 nm respectively. Some of the nanotubes have an excessive coating of amorphous carbon as indicated by Fig. 4(c), where the coating is ~7 nm thick.

Having succeeded in synthesizing SWNTs by the pyrolysis of metallocenes in admixture with acetylene, we carried out the pyrolysis of binary mixtures (1:1 by weight) of metallocenes along with acetylene. This is because, binary metal alloys have been reported to give good yields of SWNTs by arc vaporization [15]. In Fig. 5(a) we show a HREM image of an isolated SWNT obtained on pyrolysis of acetylene (flow rate=50 sccm)
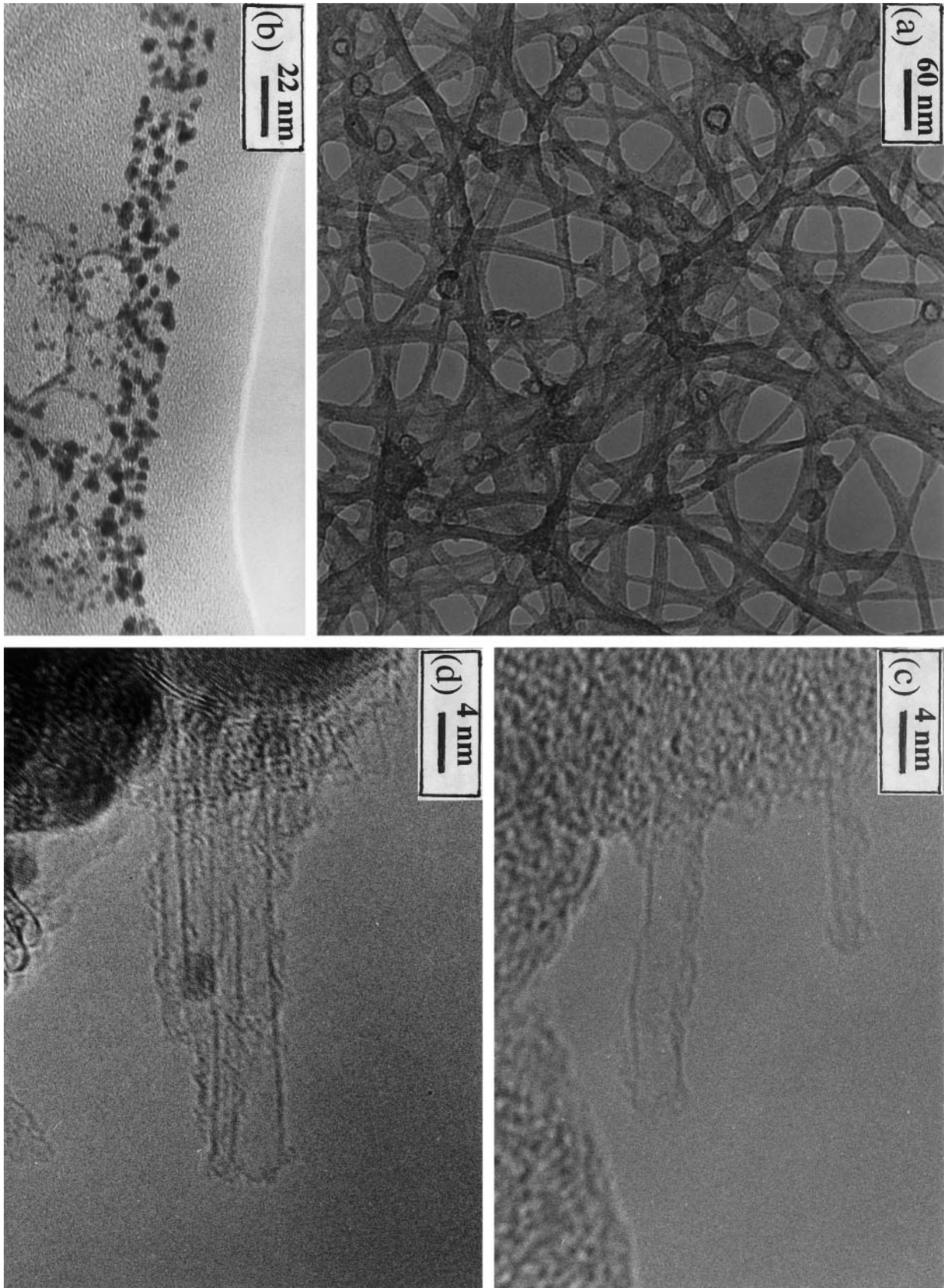
Fig. 7a–d HREM images of SWNTs cleaned by refluxing in nitric acid (**a**), a SWNT decorated by gold nanoparticles (**b**), SWNT opened by stirring with HCl for 5 h at room temperature (**c**) and a SWNT filled with a Pd particle (**d**)
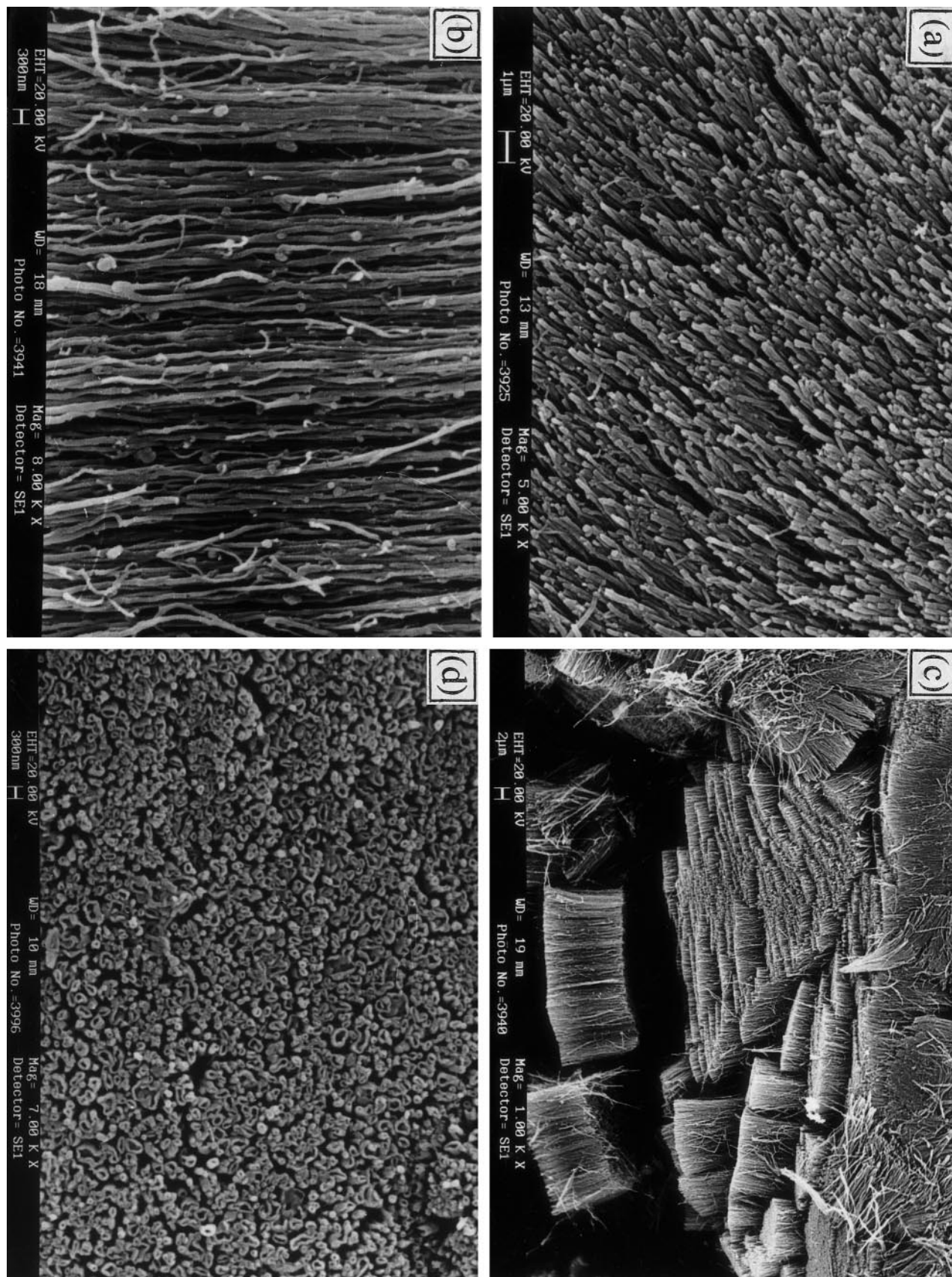
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Fig. 8a–d SEM images of aligned-nanotube obtained by ferrocene pyrolysis. shows the view along the axis (**a**) and perpendicular to the axis of nanotubes (**b**). shows bundles of aligned-nanotube (**c**). shows the top-view of aligned-nanotube bundles obtained by the pyrolysis of ferrocene under vacuum (10^{-5} Torr) at a slow heating rate of 1 deg min^{-1}(**d**)
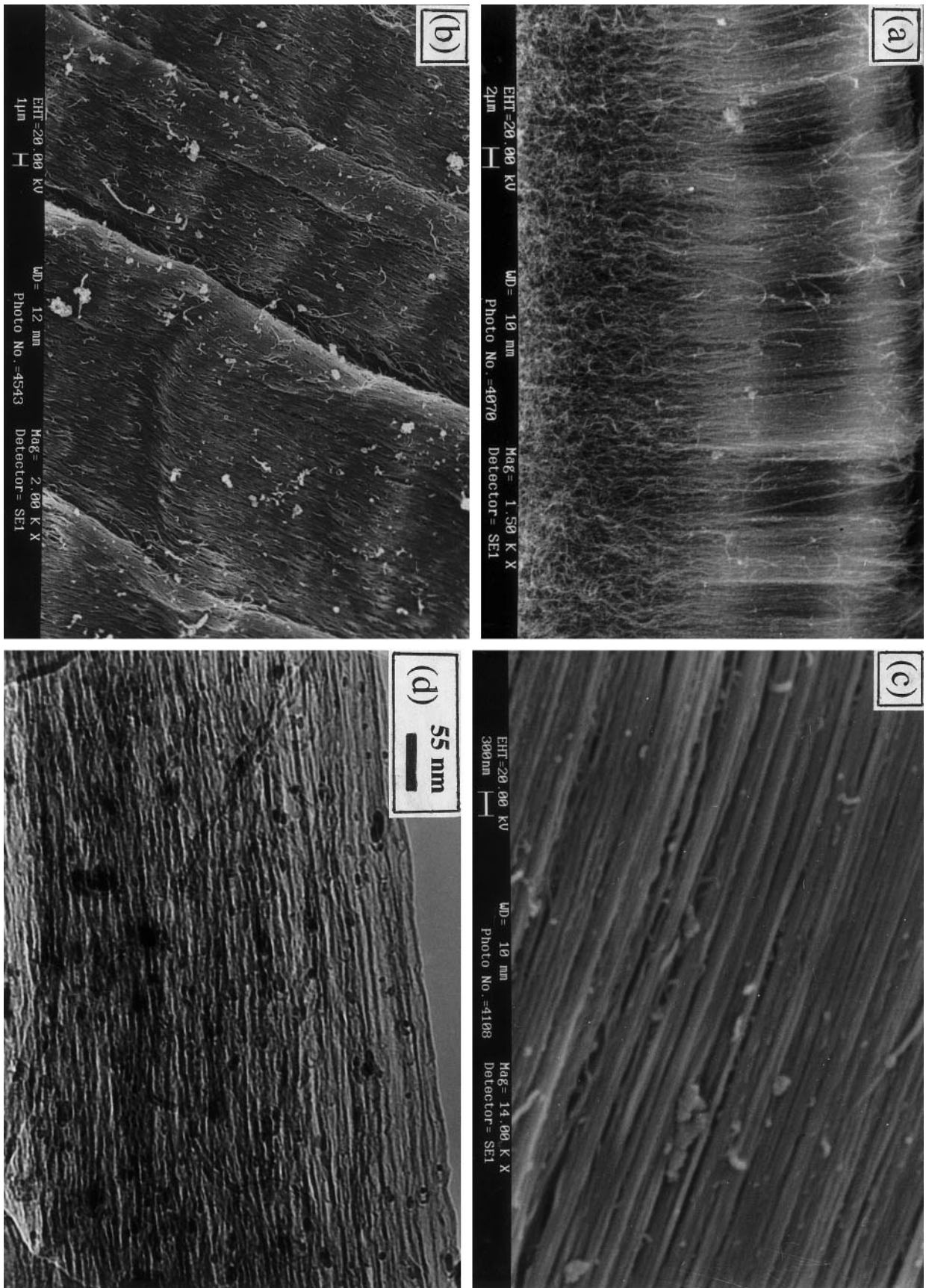
Fig. 9a–d SEM image of aligned-nanotube bundles obtained by the pyrolysis of ferrocene at 1373 K under a flow of C_2H_2 (5 sccm) and Ar (1000 sccm) (**a**). shows the SEM image of aligned-nanotube bundles obtained under C_2H_2 flow of 50 sccm (**b**). show respectively the SEM and TEM images of densely packed aligned nanotubes obtained with a higher proportion of C_2H_2 (85 sccm) in the reaction mixture (**c** and **d**)

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with a cobaltocene-ferrocene mixture at 1373 K in a flow of Ar (flow rate=975 sccm) and H_2 (flow rate=25 sccm). Figure 5(b) and (c) show the HREM images of a SWNT from the pyrolysis of acetylene with a nickelocene-cobaltocene mixture and a ferrocene-nickelocene mixture respectively, obtained under similar conditions. We have not found major differences in the yields of SWNTs by using binary mixtures of metallocenes instead of a single metallocene. However, the nanotubes are somewhat cleaner with the use of the mixture. Occasionally SWNT bundles are obtained when binary mixtures of metallocenes are used as metal precursors.

We have employed $Fe(CO)_5$ as a source of the metal instead of metallocenes and carried out the pyrolysis of acetylene in mixture with the carbonyl at 1373 K. Interestingly, SWNTs were obtained by this method as well. The flow rate of acetylene was maintained at 50 sccm and the Ar flow rate at 1000 sccm. The TEM image in Fig. 6(a) shows the presence of a few SWNTs along with metal encapsulated graphite nanoparticles. The image in Fig. 6(b) show single-walled tubes with diameters in the 0.9–1.5 nm range. SWNT bundles are more frequently found when $Fe(CO)_5$ is used as the organometallic precursor.

It appears from the above study that the type of the nanotubes produced depends somewhat on the nature of the organometallic precursor used. Table 1 summarizes the nature of the carbon nanotubes and other species obtained by the pyrolysis of acetylene along with different organometallic precursors. Precursors like nickelocene and cobaltocene favor the formation of SWNTs, while ferrocene favors the formation of aligned MWNTs. It is noteworthy that pyrolysis of mixture of ferrocene with nickelocene or cobaltocene along with acetylene yields aligned MWNTs at the inlet and SWNTs at the outlet. The nature of nanotubes and nanoparticles formed by the pyrolysis of a mixture of an organometallic and a hydrocarbon not only depends on the organometallic precursor but also on the hydrocarbon source. Table 2 summarizes the different types of nanostructures formed by the pyrolysis of organometallic precursors along with different hydrocarbon sources. Pyrolysis of ferrocene alone yields metal-filled MWNTs and an additional hydrocarbon source the yield of MWNTs is increased. The pyrolysis of nickelocene or cobaltocene also yields metal-filled MWNTs at the inlet and metal-encapsulated graphite nanoparticles at the outlet. The inclusion of acetylene however yields MWNTs at the inlet and SWNTs at the outlet. Further increase in the carbon content of the hydrocarbon source, by using benzene, gives high yields of MWNTs. Pyrolysis of $Fe(CO)_5$ alone gives metal-encapsulated graphite nanoparticles. With an additional carbon source such as CO or CH_4, which has less carbon, yields spherical carbon coated metal particles, but no nanotubes. Nanotubes are obtained by increasing the carbon content in the hydrocarbon source. Thus, pyrolysis of acetylene and $Fe(CO)_5$ yields SWNTs at the outlet of the furnace. MWNTs are obtained in the inlet of the furnace by the same procedure. Use of benzene yields nanorods at the inlet and metal encapsulated graphite nanoparticles at the outlet end of the furnace. Since the SWNTs ob-

tained are around 1 nm diameter, the metal particles produced from the pyrolysis of the organometallic precursors must be of this diameter atmost.

Most of the SWNTs as synthesized are closed at one end. They can be opened by stirring in HCl [16]. They are cleaned by refluxing in nitric acid (Fig. 7a). Acid-washed SWNTs can be decorated by metal nanoparticles (Fig. 7b). In Fig. 7(c) we show the HREM image of a SWNT opened at one end by stirring in HCl for 5 h at room temperature. It is known that MWNTs get opened by boiling in HNO_3 [17, 18]. The opened SWNTs can be filled by metals. For example, they were stirred in a saturated solution of $PdCl_2$ for 48 h, washed with distilled H_2O several times and then centrifuged. The black residue was dried in oven at 333 K overnight and then reduced in H_2 at 573 K for 1 h. Figure 7(d) shows a HREM image of a SWNT filled with Pd.

Since the method followed by us to prepare nanotubes by the pyrolysis of organometallic precursor-hydrocarbon mixture permits us to vary the partial pressure of the organometallic precursor and the hydrocarbon, we carried out several pyrolysis experiments with high concentrations of the metallocene in order to see whether aligned nanotubes could be obtained by this means.

In Fig. 8(a), (b) and (c), we show the SEM images of the nanotubes obtained by carrying out the pyrolysis of ferrocene at 1373 K in the apparatus shown in Fig. 1(b), with a fast heating rate of ferrocene (100 deg min^{-1}) and a high flow rate of Ar (1000 sccm). The images in Fig. 8(a) and (b) which are recorded in two different directions with respect to the axis of the nanotubes clearly reveal the extraordinary alignment. The image in Fig. 8(c) shows bundles of aligned nanotubes. TEM images of these nanotubes reveal that they are multi-walled, some of them partially filled with iron metal. Pyrolysis of ferrocene at 1170 K at a slow heating rate of 1 deg min^{-1} under vacuum (10^{-5} Torr) also yielded good quantities of aligned-nanotube bundles. In Fig. 8(d) we show the top view of such nanotubes. When the rate of heating of ferrocene (1 deg min^{-1}) and the flow rate of argon (10 sccm) were low, fewer aligned nanotubes were obtained at a pyrolysis temperature of 1373 K.

We have carried out the pyrolysis of ferrocene along with acetylene, by passing a mixture of argon and acetylene through the quartz tube. In Fig. 9(a), we show a SEM image of the aligned nanotubes obtained by the pyrolysis of a mixture of ferrocene and acetylene (5 sccm) at 1373 K carried out with the apparatus in Fig. 1(b), in flowing Ar (1000 sccm). The alignment could be further improved by increasing the flow rate of C_2H_2. The SEM images in Fig. 9(b) and (c) obtained in this manner, show densely packed aligned nanotubes. The flow rate of acetylene in (b) was 50 sccm and in (c) was 85 sccm. The TEM image in Fig. 9(d) reveals how well aligned these nanotubes are. The nanotubes in the bundles were generally closed and were 5–10 microns in length. Aligned nanotube bundles were also obtained by the pyrolysis of a mixture of two metallocenes along with acetylene. Thus pyrolysis of a mixture of ferrocene and nickelocene at 1373 K along with acetylene (flow rate=50 sccm) un-
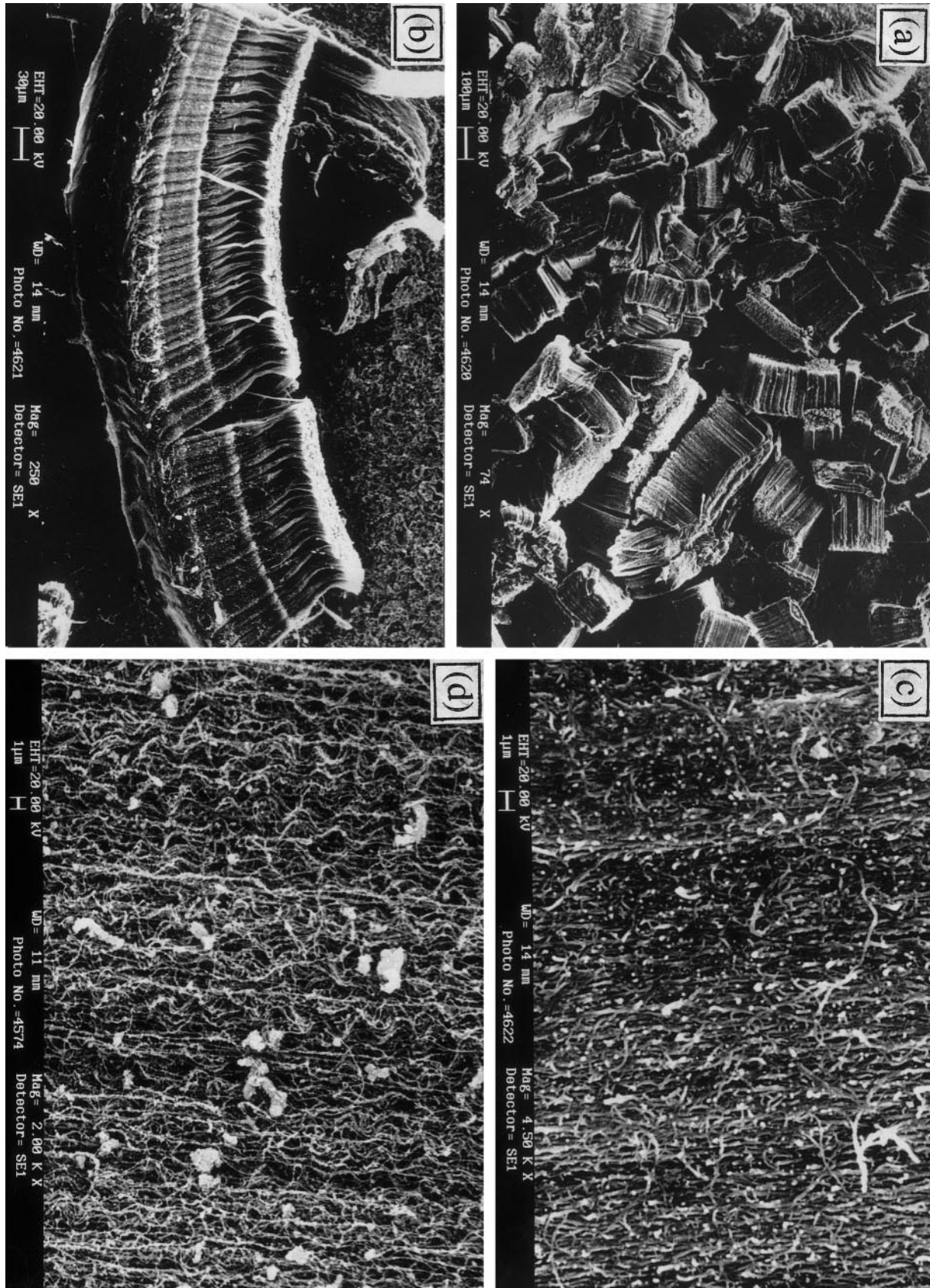
Fig. 10 (**a**), (**b**) and (**c**) show the SEM images of aligned-nano-tube bundles obtained by the pyrolysis of a 1:1 mixture of ferrocene and nickelocene at 1373 K under a flow of C_2H_2 (50 sccm), Ar (975 sccm) and H_2 (25 sccm). (**d**) shows aligned nanotubes obtained by the pyrolysis of a 1:1 mixture of ferrocene and cobaltocene at 1373 K in C_2H_2 (50 sccm), Ar (975 sccm) and H_2 (25 sccm) flow
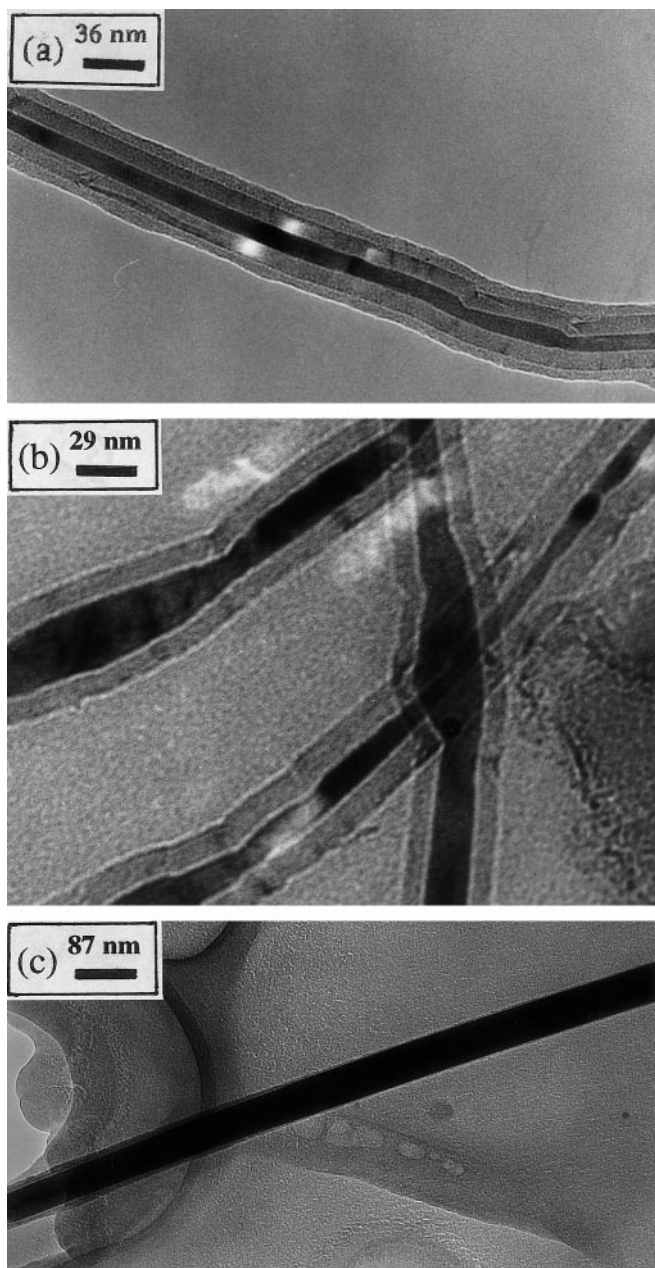
Fig. 11a–c TEM images of carbon coated iron nanorods obtained by the pyrolysis of ferrocene: (**a**),(**b**) at 1173 K under vacuum (10^{-5} Torr) and (**c**) at 1373 K in Ar flow of 10 sccm

der a flow of Ar and H_2 (total flow rate=1000 sccm) yielded aligned nanotube bundles as shown by the SEM images in Fig. 10 (a), (b) and (c). Fig. 10 (d) shows a SEM image of aligned nanotubes obtained by the pyrolysis of ferrocene and cobaltocene at 1373 K in C_2H_2 (50 sccm) and Ar+H_2 (1000 sccm) flow.

Pyrolysis of ferrocene was also carried out at a relatively fast heating rate of 50 deg min^{-1} by applying a vacuum (10^{-5} Torr) at the exit end of the quartz tube. Here, the ferrocene sublimed under vacuum and the vapour got sucked into the pyrolysis zone. We mainly obtained carbon-coated iron nanorods (yield≥60%) in these

experiments. In Fig. 11(a) and (b), we show the TEM images of iron nanorods with thick carbon coating, obtained by the pyrolysis of ferrocene at 1173 K under vacuum. We also obtained a fair proportion of nanorods when flow rate of Ar was low (10 sccm). In Fig. 11(c) we show the TEM image of a nanorod obtained by the pyrolysis of ferrocene at 1373 K at a Ar flow of 10 sccm. Such nanorods have been reported in the literature, by the reaction of carbon nanotubes with volatile oxide or halide species [19]. The present method of producing nanorods is however much simpler. The formation of iron metal in the form of particles or rods in the pyrolysis of ferrocene suggests that the mechanism of alignment of the nanotubes may be related to the magnetic nature of the nanorods or particles of iron.

Conclusions

In conclusion, the present study shows that the pyrolysis of hydrocarbon-organometallic mixtures provides an excellent route to produce different types of nanotubes. Benzene-metallocene mixtures yield MWNTs whereas the dilute acetylene-metallocene mixtures yield SWNTs. This may be because the carbon content in the former precursor is high. The use of hydrogen in the flow gas along with Ar minimizes the amorphous carbon coating on the nanotubes. Binary metallocene mixtures also yield isolated SWNTs. Fe(CO)$_5$ is a good organometallic precursor to produce SWNTs by acetylene pyrolysis. The diameters of the SWNTs obtained in the present study are all around 1 nm. Thus, the study confirms that on pyrolysis, the organometallic precursor molecules produce very small metal particles of ~1 nm diameter, necessary for the formation of SWNTs. In the case of MWNTs the metal particles would be somewhat bigger (1–10 nm diameter). Pyrolysis of ferrocene or ferrocene-acetylene mixture yields copious quantities of aligned nanotube bundles and such a ready method for the synthesis of nanotube bundles is of considerable importance. The alignment depends on the flow rate of the gases, heating rate of ferrocene and the diameter of the quartz pyrolysis tube. Nanorods have been obtained by carrying out the pyrolysis of ferrocene under vacuum or at low flow rate of argon gas.

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