HIGH YIELD SYNTHESIS OF CARBON NANOTUBE ARRAYS BY PYROLYSIS OF BENZENE/METALLOCENE AEROSOLS

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Introduction
Carbon nanotubes are prepared by using various methods [1, ii, iii, iv]. Among them, pyrolysis of hydrocarbons in the presence of a metal catalyst constitutes a simple and efficient process [v]. Studies of pyrolysis often use gaseous [vi, vii] or easily vaporisable liquids [viii, ix] as hydrocarbon sources, passed over metal catalysts (e.g. metal powders or metallocenes). The advantage of using liquids lies in the possibility of preparing homogeneous solutions, containing both hydrocarbon source and catalyst precursor, which can be fed simultaneously into the pyrolysis reactor. Recent studies described the pyrolysis of solutions injected into a furnace, either with a syringe [i] or as a sprayed jet [ii], thus producing aligned carbon nanotubes. However, the pyrolysis of liquid aerosols containing both hydrocarbon source and metal catalyst precursors, homogeneously dispersed in the reactor, has not been reported hitherto.
Here we report the development of a pyrolysis process involving aerosols generated from benzene-based solutions using a compressed gas (Ar) driven atomiser and creating high yield of aligned nanotubes. The aim of the atomisation, using high Ar flow rates, is to produce minute hydrocarbon/catalyst droplets (aerosol), which homogeneously fills the reactor volume, favouring formation of evenly distributed metal clusters during pyrolysis. The characteristics of collected samples are determined with respect to their synthesis conditions.

Experimental
Benzene solutions of metallocene(s) were prepared by sonicationating metallocenes (2.5, 5 or 10 % by weight of ferrocene or ferrocene/nickelocene mixtures) in benzene for 5 min in a bath. The apparatus, described in details elsewhere [xii], consists of an atomiser, furnace, and water cooler followed by a trap (Fig. 1). The glass atomiser (pyrex), consisting of a reservoir and two orthogonally arranged nozzles (inner diameters ca. 0.45 mm), works on the same principles as a commercial air-driven atomiser. The solution is "atomised", and the resulting aerosol becomes evenly distributed within a quartz tube placed inside a temperature-controlled cylindrical furnace maintained at 800 or 950ºC for 5, 15 or 45 min. A water-cooler, followed by a gas trap is located at the other end of the quartz tube. After 5, 15 or 45 min at 800 or 950ºC, "atomisation" is discontinued and the argon flow rate is reduced (300-500 sccm; see Fig. 1, inlet C) in order to avoid oxidation of the products as the furnace is allowed to cool to room temperature. The synthesis conditions - metallocene concentrations, pyrolysis temperatures and experiment duration - are summarised in Table 1. The products, collected from the high temperature zone, always consists of black "flaky" powders deposited on the quartz tube walls.
As-collected samples are first analysed by scanning electron microscopy (SEM, Jeol JSM 6300F, equipped with an Noran Instrument EDX detector). Subsequently, samples are dispersed in acetone using an ultrasonic probe (Sonics and Materials, Vibra Cell) for the purpose of TEM and HRTEM observations (Hitachi 7100 operated at 120 kV and Jeol JEM 4000 EX operated at 400 kV, respectively). X-Ray powder diffraction studies (XRD, Siemens Diffractometer D5000, Cu-K radiation) are also carried out in order to identify the products and to determine their degree of crystallisation.

Results and discussion
For all metallocenes, the rate at which black material is deposited increases as the pyrolysis temperature increases. Thus, for identical metallocene concentrations and durations, the amount of black product generally increases by a factor of 3 to 5 for the higher temperature (e.g. 950 ºC). In addition, it is important to note that the catalysed production of black deposit derived from benzene is higher when ferrocene/nickelocene mixtures are used. Thus, for the same synthesis conditions (temperature, metallocene concentration), the amount of black material produced with ferrocene/nickelocene mixtures is increased by a factor of 3 to 5 as compared to the one produced with only ferrocene. This result demonstrates a strong catalytic effect of the metallocene mixtures on the decomposition of benzene.

SEM studies reveal that the products generally consist of carpet-like flakes exhibiting similar morphologies. These "carpets" (up to 1.5 mm², Fig. 2) contain both well-aligned elongated structures (30 to 150 m long) and agglomerated particles. The amount of elongated structures, as compared to particles, depends on the synthesis conditions such as the duration of the experiment, the chemical nature and the concentration of metallocene(s) and the pyrolysis temperature. Thus, samples obtained after prolonged pyrolysis (45 min) or with a high ferrocene concentration (10%) are impure.
(large quantities of particles as compared to elongated structures) and the particles seem to be surrounding the elongated structures (Fig. 2a). By contrast, among samples synthesised during 5 or 15 min with 2.5 or 5 % metalloocene solutions, higher purity and better alignment is evident (Fig. 2 b–f). It is noteworthy that, for both pyrolysis temperatures (800 or 950°C) and both metalloocene concentrations (2.5 or 5%), the use of ferrocene/nickelocene mixtures, especially with the 65:35 Fe: Ni ratio, significantly improves the alignment and the purity of the samples, which are, for all synthesis conditions, very pure and contain well-aligned elongated structures (Fig. 2 e and f). A comparison between samples obtained from ferrocene or ferrocene/nickelocene mixture at the same temperature and concentration demonstrates the absence of particles at the surface of the carpet produced from metallocene mixtures (Fig. 2 c and d). However, for samples prepared from 5% ferrocene/nickelocene (25:75 Fe: Ni ratio) mixture solutions, the purity and the alignment degree are significantly increased when the pyrolysis temperature reaches 950°C. For samples obtained from ferrocene solutions in benzene, the sample purity varies with synthesis conditions such as ferrocene concentration and pyrolysis temperature. Thus, for higher ferrocene concentrations (eg. 5%) and temperatures (eg. 950°C), the purity decreases and a high content of particles can be observed. Similar well-aligned elongated structures have been observed previously by SEM and shown to contain aligned nanotubes [10, xvi, xvii].

EDS analysis has been carried out on the “carpets”, both on the surface and on the cross-section. Samples prepared from solutions of ferrocene in benzene are mainly composed of carbon and iron, whereas samples obtained from solutions of ferrocene/nickelocene mixtures in benzene contain carbon, iron and nickel.

TEM observations, carried out on the purest samples (2.5 or 5% metalloocene solutions, 5 or 15 min), revealed a high yield of partly-filled nanotubes as compared to amorphous carbon and encapsulated particles (Fig. 3). These observations confirm that the well-aligned structures observed by SEM are nanotubes. It is important to note that the quantity of nanotubes obtained is higher for all samples involving solutions of metalloocene mixtures (especially Fe: Ni 65:35) in benzene as compared with ferrocene alone. However, the use of metalloocene mixture with Fe: Ni 25:75 ratio induces a significant decrease in the nanotube yield, only at 800°C. For samples obtained at higher temperature (e.g. 950°C), the nanotubes are sometimes still arranged in bundles even after ultra sound dispersion, suggesting strong alignment of the nanotubes. These results are in good agreement with SEM observations reported above.

The diameters of individual nanotubes vary over quite a large range (ca. 10-200 nm) and the distribution thereof seems to be bimodal. However, the diameters appear to be generally shorter for samples prepared with mixed metalloocene solutions as compared to samples prepared from only ferrocene solutions (large nanotubes: 60-120 nm and 90-200 nm o.d. range respectively; thin nanotubes: 10-40 nm and 10-70 nm o.d. range respectively).

For all metalloccenes dissolved in benzene, a decrease in metalloocene concentration involves a decrease in nanotube filling. In addition, for the same metalloocene concentration, nanowire lengths are lower for samples obtained from mixtures in solution as compared to samples prepared from ferrocene solutions. Thus, the length of the filling is only in the range 30-410 nm for nanotubes prepared from metalloocene mixtures whereas it is in the range 60-2060 nm for nanotubes prepared from only ferrocene. However, the diameter range of the filling is quite similar for all samples (ca. 10-40 nm).

HRTEM studies reveal the presence of multi-walled and partly-filled carbon nanotubes (interlayer spacing ca. 0.34 nm, Fig. 4); the nanotube filling being often well crystallised. Thick nanotubes exhibit a reasonable degree of "graphitisation" (Fig. 4) when compared to vapour-grown carbon fibres obtained by the pyrolysis of benzene vapour [°C]. The thick tubes are similar to nanofibers, but sometimes do not contain central hollow cores; the inner core is mainly composed of mixed graphite layers. However, in some cases, distortions can be observed in the graphene sheets due to the presence of defects within the carbon structure. Thin nanotubes sometimes exhibit less than ten graphene shells (e.g. 4 to 5 shells, diameter ca. 15 nm) and are often well "graphitised", especially in the filling area [°vii, xviii].

XRD patterns (Fig. 5) reveal the presence of graphite-like peaks in all samples. A small shift occurs, especially for the (001) reflections (e.g. d _002 = 0.34 nm), which is associated with the curvature of the rolled graphene sheets (e.g. cylinders) in nanotubes. The interlayer spacing found by XRD is consistent with that obtained from HRTEM and is characteristic of carbon nanotubes. For samples obtained from benzene/ferrocene solutions, Fe and Fe3C (cementite) phases were also clearly detected. In samples prepared from ferrocene/nickelocene mixture (65:35 Fe: Ni) solutions, only FeNi alloy (fcc structure containing 30% at Ni and above) was identified. In samples prepared with solutions containing a metalloocene mixture (25:75 Fe: Ni), FeNi as well as Ni3Fe (orthorhombic structure) alloys were detected. In addition, no peaks of Fe, Fe3C and Ni were observed in these samples. Considering the very high nanotube yield in these samples, the results strongly suggest that the FeNi alloy(s), present within the carbon nanotubes [17, xviii], catalyse only the tube growth and avoid the formation of metal encapsulated particles and other unwanted byproducts. It is
noteworthy that metal carbide phases are notably absent in this case. The significant presence of Fe3C in samples prepared from ferrocene solutions in benzene suggests that Fe3C plays a key role in nanotube growth [xiv]. However, this carbide also appears to be responsible for the generation of encapsulated particles.

**Conclusion**

This study demonstrates that pyrolysis of benzene/metallocene(s) aerosols, homogeneously distributed inside the reactor, is able to produce high yields of aligned multi-walled partly filled carbon nanotubes. The use of metallocene mixtures (e.g. ferrocene and nickelocene) dissolved in benzene strongly increases the production rate of black deposit and the nanotube yield which is high and similar for all temperatures and metallocene mixture concentrations.

The diameter distribution of individual nanotubes seems to be bimodal; thick and thin nanotubes are present. The use of benzene aerosols containing metallocene mixtures induces a decrease of nanotube diameter and of filling length as compared to the use of benzene aerosols containing ferrocene. For all chemical natures of metallocene, the filling degree is proportional to metallocene concentration and is generally low in nanotubes prepared from metallocene mixture solutions.

This synthesis process, involving the pyrolysis of aerosols, opens up new avenues in carbon nanotube synthesis using various liquids and catalysts. The advantage of this process is the continuous and simultaneous feeding of the reactor with homogeneous hydrocarbon/catalyst aerosols, which results in high yields of aligned carbon nanotubes. The alignment, can be directly accessed by this method without using any template catalyst substrate and may be advantageous for technological applications.

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**References**

Table 1. Synthesis conditions.

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<thead>
<tr>
<th>Metalloccenes</th>
<th>Synthesis conditions</th>
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<tbody>
<tr>
<td></td>
<td>Metallocene content (wt%)</td>
</tr>
<tr>
<td>Ferrocene</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>Ferrocene/nickelocene mixtures</td>
<td>5*</td>
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<tr>
<td>Fe:Ni = 65:35</td>
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<td>Fe:Ni = 25:75*</td>
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Figure 1. Aerosol pyrolysis apparatus.
Figure 2. SEM images of samples prepared from pyrolysis at 800°C of solutions containing 2.5% of ferrocene a) during 45 min b) c) during 15 min and pyrolysis of solutions containing 5% of ferrocene/nickelocene mixtures during 5 min d) at 800°C (65:35 Fe:Ni ratio) e) at 950°C (25:75 Fe:Ni ratio) f) at 950°C (65:35 Fe:Ni ratio).
Figure 3. TEM images of typical samples prepared at 950°C using benzene solutions of a) 2.5% ferrocene and b) 5% ferrocene.

Figure 4. HRTEM images of samples prepared at 950°C using benzene solutions of: a) b) 2.5% ferrocene, c) d) e) 5% ferrocene.
Figure 5. XRD patterns of samples prepared at 950°C from benzene solutions of a) ferrocene and b) ferrocene/nickelocene mixtures.