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Production of bundles of aligned carbon and carbon-nitrogen nanotubes by the pyrolysis of precursors on silica-supported iron and cobalt catalysts

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Abstract

Pyrolysis of acetylene over iron or cobalt nanoparticles well dispersed on silica substrates gives copious yields of aligned carbon nanotube bundles. By carrying out the pyrolysis of pyridine over these catalyst surfaces, good quantities of aligned carbon-nitrogen nanotube bundles have been produced. The composition of the carbon-nitrogen nanotubes varies between $C_{10}N$ and $C_{33}N$, depending on the catalyst. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon nanotubes and related materials have gained increasing importance in the last few years because of their possible technological applications [1]. Aligned carbon nanotube bundles, which are specially useful in some of the applications, have been synthesized using alumina membranes [2,3], mesoporous silica [4] and patterned silica substrates covered with Co [5]. Good quantities of aligned nanotube bundles have been obtained by the pyrolysis of ferrocene and other organometallic precursors [6,7]. In spite of these efforts, there is still a need for

newer methods for making aligned nanotube bundles. Pan et al. [8] reported recently that aligned carbon nanotubes can be obtained by carrying out the pyrolysis of acetylene over silica surfaces containing evenly positioned iron-silica nanocomposite particles while Mukhopadhyay et al. [9] have produced quasi-aligned carbon nanotubes by catalytic chemical vapour deposition. This led us to explore whether pyrolysis of simple organic precursor molecules over metal-silica catalyst surfaces can be usefully employed for this purpose. With this objective, we have carried out the pyrolysis of acetylene over the surfaces of silica-supported iron and cobalt catalysts prepared by the sol-gel route and obtained good results. More importantly, we have carried out the pyrolysis of pyridine over these catalyst surfaces to obtain carbon-nitrogen nanotube bundles. Car-

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bon-nitrogen nanotubes were first synthesized by Sen et al. [10] by the pyrolysis of pyridine over cobalt nanoparticles. Carbon-nitrogen nanotubes or nanofibres have since been prepared by means of a microwave-excited plasma of $C_2H_2-N_2$ mixtures [11], reactive/magnetron sputtering of graphite [12], pyrolysis of melamine on laser-patterned Fe/Ni substrates [13] and pyrolysis of ferrocene-melamine mixtures [14]. Some of these preparations yielded fully or partially aligned nanotubes. The present study reports good quantities of aligned carbonnitrogen nanotubes obtained by pyridine pyrolysis over the catalysts. These *n*-type nanotube bundles are likely to be more useful because of their desirable electronic properties.

2. Experimental

The iron-silica catalyst surfaces were prepared by employing two procedures. In procedure 1, 2 ml of tetraethylorthosilicate (TEOS) was mixed with 2 ml absolute ethanol and 9 ml of 1.5 M aqueous solution of $Fe(NO_3)_3$, and stirred for 20 min. This corresponds to a loading of 1.04 at.% of iron on silica. Few drops of concentrated HF solution were added to the mixture and stirred for another 20 min, to achieve slow gelation. The resulting gel was deposited on glass substrates and dried in an oven at 60°C for 12 h. The gel so deposited fragmented into smaller sections of 2-8 mm² area; it was then calcined at 450°C for 1 h under vacuum (10^{-3} Torr) and reduced in hydrogen at 500°C for 2 h. In procedure 2, iron acetylacetonate was used as the metal precursor. A desired quantity of the acetylacetonate (1.5 mmol) was dissolved in 100 ml methanol and then mixed with TEOS (2 ml) and the gel obtained by a procedure similar to the one mentioned earlier. This procedure was also employed to prepare Co/silica catalysts starting with cobalt acetylacetonate. The catalyst samples were examined by scanning and transmission electron microscopy (SEM and TEM) using LEICA S440i and JEOL JEM-3010 microscopes, respectively.

In order to prepare bundles of aligned carbon nanotubes, acetylene was pyrolysed over the catalyst surfaces. The pyrolysis set-up consisted of stainless steel gas flow lines, fitted to a quartz tube (25 mm inner diameter) placed in a furnace operating at a temperature in the 700–900°C range, depending on the requirement. The flow rates of the gases were controlled using UNIT mass flow controllers. Fragmented sections of the calcined catalyst were first



Fig. 1. SEM image of the Fe/silica catalyst (obtained from procedure **1** employing iron nitrate) showing the uniform distribution of Fe nanoparticles. (b) TEM image showing the uniform sized Fe nanoparticles obtained by the sol–gel process followed by calcination and reduction. (c) SEM image of the Fe/silica catalyst obtained by using iron acetylacetonate (procedure **2**).

Catalyst preparation	Carbon nanotubes				Carbon-nitrogen nanotubes			
	Flow rates (sccm)		Pyrolysis temperature	Duration	Flow rates (sccm)		Pyrolysis temperature	Duration
	$\overline{C_2H_2}$	Ar			Pyridine	Ar/H_2		
Procedure 1	15	85	700°C	1 h	30	120 (Ar)	900°C	1.5 h
Procedure 2 (Iron)	15	85	700°C	30 min	40	$60(H_2)$	900°C	10 min
Procedure 2 (Cobalt)	15	85	700°C	30 min	45	55 (H ₂)	900°C	30 min

 Table 1

 Conditions for the synthesis of aligned nanotubes

placed in the quartz tube and reduced under hydrogen atmosphere at 500°C for 2 h. The temperature of the furnace was then raised to 700°C under a slow ramp rate and the pyrolysis of acetylene carried out with argon as the carrier gas. Aligned carbon–nitrogen nanotube bundles were prepared by a similar procedure except that pyridine was pyrolysed on the catalyst surface at 900°C. Typical pyrolysis conditions for the production of carbon and carbonnitrogen nanotubes, are listed in Table 1.

The aligned nanotubes were observed by scanning and transmission electron microscopy. For TEM



Fig. 2. SEM images of (a) aligned carbon nanotubes growing vertically from the iron-silica catalyst (prepared by procedure 1), obtained by the pyrolysis of acetylene, and (b) and (c) of aligned nanotubes in side view. (d) TEM image of the carbon nanotubes obtained with the Fe/silica catalyst.



Fig. 3. SEM images (a), (b) and (c) of the aligned carbon–nitrogen nanotubes obtained by the pyrolysis of pyridine over Fe/silica substrates (prepared by procedure 1). In (d) C 1s and N 1s XPS signals of the nanotubes are shown.

studies, the nanotube samples were ground, dispersed in carbon tetrachloride and deposited onto holey carbon copper grids. In the case of the aligned carbon-nitrogen nanotubes, the compositions were examined by X-ray photoelectron spectroscopy (XPS) using a VG scientific ESCA LAB V spectrometer. Electron energy loss spectroscopy (EELS) was also carried out concurrently with high-resolution electron microscopy.

3. Results and discussion

In Fig. 1a we show a SEM image of the iron-silica catalyst surface, obtained by procedure **1**, subjected

Fig. 4. SEM images of aligned nanotubes: Carbon nanotubes grown on (a) Fe/silica surfaces (prepared by procedure 2), by pyrolysis of acetylene (flow rate, 15 sccm) at 700°C for 30 min under a flow of Ar (85 sccm), and (b) on Co/silica surfaces (by procedure 2) by pyrolysis of acetylene (flow rate, 15 sccm) at 700°C for 30 min under Ar (70 sccm). Carbon–nitrogen nanotubes grown on (c) Fe/silica surface (obtained by procedure 2) by pyrolysis of pyridine at 900°C for 10 min with Ar (40 sccm) as the carrier gas and under a flow of hydrogen (60 sccm), and (d) on Co/silica surfaces (by procedure 2) by pyrolysis of pyridine at 900°C for 30 min with Ar (40 sccm) as the carrier gas under a flow of hydrogen (55 sccm). XPS N 1s signals of the samples from (c) and (d) are shown next to the SEM images.

to calcination and reduction. The image shows a uniform distribution of iron-silica nanoparticles on

the surface. We show a TEM image of the catalyst surface in Fig. 1b. The image shows fairly uniform



sized iron nanoparticles. An analysis of the TEM images showed that most of the particles had diameters in the 5–20 nm range. In Fig. 2, we show the SEM images of aligned carbon nanotube bundles obtained by the pyrolysis of acetylene (flow rate, 15 sccm; sccm, standard cubic centimeter per minute) over the iron–silica surface at 700°C for 1 h under argon flow of 85 sccm. The low magnification image in Fig. 2a shows the bundles of aligned carbon nanotubes growing out perpendicularly from the catalyst surface. Fig. 2b,c show the SEM images of compact aligned nanotube bundles.

In Fig. 3a we show a SEM image of the nanotubes obtained from the pyrolysis of pyridine (flow rate, 30 sccm) at 900°C for 1.5 h, under Ar (120 sccm) flow on the iron-silica catalyst surface. The image clearly reveals the alignment of the nanotubes, perpendicular to the catalyst surface. The SEM images in Fig. 3b,c show side and top views of the aligned nanotubes, respectively.

In order to characterize the aligned nanotubes obtained by pyridine pyrolysis, XPS analysis was carried out. In Fig. 3d we show the C 1s and N 1s signals from these nanotubes. This C 1s signal is at 285 eV and the N 1s signal around 400 eV. The carbon to nitrogen ratio was estimated by taking the ratio of the integrated peak areas under the C 1s and N 1s signals and dividing them by the respective photoionization cross-sections. The average composition for the aligned carbon-nitrogen nanotube turns out to be around C₆N. A Gaussian fit of the N 1s spectrum, however, shows the presence of two peaks with binding energies of 399 and 401 eV. The 399 eV feature is characteristic of pyridinic nitrogen (sp² hybridization), probably present at nanotube ends, while the peak centered at 401 eV is due to nitrogen present in the graphene sheets [10]. The latter corresponds to trivalent nitrogen replacing the carbon in the hexagonal structure. If we take the intensity of only the 401 eV feature, the composition turns out to be $C_{10}N$. EELS measurements confirmed the presence of nitrogen in the nanotube preparations. The compositions estimated from EELS are generally close to those from XPS [10,15].

It has been proposed that nanotubes prepared by precursor pyrolysis using catalyst particles grow by the tip-growth mechanism [16]. According to this mechanism, the metal particles stick at the tip of the nanotube, rather than the growth starting at the surface of the particle. In order to examine this aspect, we carried out a TEM study of the aligned carbon nanotubes. In Fig. 2d, we show a typical TEM image of carbon nanotubes, with diameters in the range of 10–15 nm. The image shows the presence of few metal particles at the tips of the carbon nanotubes. Furthermore, the SEM image of the carbon nanotube bundles in Fig. 2a shows that the nanotubes lift the metal nanoparticles from the catalyst surface. The SEM image of carbon–nitrogen nanotube bundles in Fig. 3a also shows tip-growth. We see metal particles at the tips of some of the nanotubes in Fig. 3.

In Fig. 4a,b, we show the SEM images of bundles of carbon nanotubes obtained by the pyrolysis of acetylene over Fe and Co catalysts prepared from the acetvlacetonates (procedure 2). In Fig. 4c.d. we show the SEM images of carbon-nitrogen nanotube bundles obtained by pyridine pyrolysis over the Fe and Co catalysts prepared by procedure 2. XPS analysis of the carbon-nitrogen nanotubes obtained with these catalysts shows broad signals due to N 1s around 400 eV. Based on the total N 1s intensities the compositions of the nanotubes work out to be C_oN and $C_{18}N$, respectively, with the iron and cobalt catalysts. However, if we take the intensity of the signal at 401 eV obtained after spectral decomposition, the compositions work out to be C₁₈N and $C_{33}N$, respectively, with the iron and cobalt catalysts.

The TEM images of some of the carbon-nitrogen nanotubes exhibit interesting features. In Fig. 5 we present some of the unusual images of these nanotubes. The image in Fig. 5a shows a nanotube with bamboo-shaped morphology. Fig. 5b shows a nanotube having a nested cone-shaped cross-section, while that in Fig. 5c shows a somewhat unusual morphology involving a conical stacking sequence of the graphene sheets with intermittent hollow regions. The high-resolution TEM image in Fig. 5d shows that the graphene sheets are stacked in the form of nested cones. Clearly, doping with nitrogen modifies the morphology of the nanotubes drastically. It seems that doping favours the formation of quasi-continuous, cylindrical graphene fragments, which in turn facilitate the growth of the nanotube. It is to be noted that nitrogen can be present in pyridinic rings present at the edges of such graphene fragments. The conical



Fig. 5. (a)–(c) TEM images of carbon–nitrogen nanotubes obtained by the pyrolysis of pyridine (flow rate, 30 sccm) over Fe/silica substrates (prepared by procedure 1) at 900°C for 1.5 h under Ar (120 sccm) flow, showing various morphologies. (d) HREM image of a nanotube showing the nested cone-type stacking of graphene sheets in the hollow region.

sections sometimes enclose the catalyst particle as shown in Fig. 5c, lending some support to the tipgrowth mechanism. The conical curvature in the hollow regions could be due to the nitrogen doping, wherein nitrogen is present in the five-membered rings.

4. Conclusion

The present study shows that pyrolysis of appropriate organic precursors over iron-silica and cobalt/silica catalysts, prepared by the sol-gel method by using the metal nitrate or the acetylacetonate as the starting material, gives aligned bundles of carbon nanotubes as well as carbon-nitrogen nanotubes. The synthesis of copious quantities of aligned carbon-nitrogen nanotube bundles by this method is of significance since they are likely to possess more desirable electronic properties. The nanotube diameters obtained by us is in the range 15–150 nm, most of which have a stacked cone morphology. It would be therefore equally correct to consider them to be hollow carbon fibres, similar to those reported by Terrones et al. [13,14]. The carbon-nitrogen nanotube compositions obtained by us are in the range $C_{10}N-C_{33}N$. These are comparable to the compositions reported by Terrones et al. which are in the range $C_{13}N_r$ to $C_{49}N_r$ ($x \le 1$).

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