Aligned N-Doped Carbon Nanotube Bundles Prepared via CVD Using Zeolite Substrates

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We report the synthesis of aligned N-doped carbon nanotube bundles via CVD (over the temperature range 700−800 °C) using ammonium-exchanged zeolite-β as the substrate, ferric nitrate as the catalyst, and acetonitrile as the carbon precursor. Ammonium exchange of the zeolite was found to be necessary for the formation of aligned N-doped carbon nanotubes (CNTs). The optimal temperature for the production of large amounts of aligned N-doped CNTs was found to be 750−800 °C. The N-doped CNTs had nitrogen content of between 6 and 9 wt %. The aligned CNTs grew in bundles along the verges, perpendicular to the surface of the hexagonal zeolite-β particles, and retained their aligned order after removal of the zeolite substrate. The length of the CNTs was in the range 2−10 μm depending on CVD temperature, with inner and outer diameters of ca. 10 and 30 nm, respectively. The CNTs exhibited high levels of graphitic ordering and thermal stability in air and had relatively high surface area (226−886 m^2/g) and pore volume (0.3−0.81 cm^3/g). The aligned N-doped CNTs had a bamboolike morphology with transverse carbon bridges forming compartments.

Introduction

Since their discovery in 1991,[1] carbon nanotubes (CNTs) have attracted much attention due to their extraordinary mechanical and electrical properties.[2,3] A wide range of potential applications for CNTs have been proposed, including use as field emission sources,[4] as hydrogen storage media,[5−7] and in microelectronics.[8−10] For this reason, much effort has been devoted to the synthesis of CNTs of good quality via simple and reliable techniques. Controlled growth of CNTs is desirable especially for applications in electronic devices and composite materials. CNTs have been synthesized using various methods including arc discharge,[11,12] condensation of a laser-vaporized carbon−nickel−cobalt mixture,[13] catalytic pyrolysis of hydrocarbons,[14−17] and plasma-enhanced[18] or thermal chemical vapor deposition (CVD).[19−23] Among these synthesis methods, CVD is attractive because it can offer low-temperature and large-scale production of CNTs and allows control over the alignment, density, and diameter of CNTs.[4,14,18−20,24]

Aligned CNTs can be obtained via CVD with[14,18,19] or without[25] substrates. Metals such as Fe, Co, and Ni are widely used as catalysts in carbon nanotube preparations.[16,17,26−28] Substrates including glass,[18] quartz,[16,29] silicon,[4,24,28,30] silica,[17,19,26,27,31,32] or SiO_2/Si wafers[20,22] have been extensively

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studied. In some cases the substrates are prepatterned to enhance the controlled growth of CNTs.[4,14,33] For example, Liu and co-workers used photolithographic patterning to deposit the catalyst and thereby control the location and length of individual single-walled nanotubes (SWNTs).[21,22]

A recent prediction that carbon nitrides are superhard and metallic in comparison with pure carbon structures has spurred interest in nitrogen-containing CNTs.[34,35] As a result, the synthesis of carbon−nitrogen nanotubes has attracted considerable attention. So far the preparation of carbon−nitrogen nanotubes or nanofibers has been investigated extensively by pyrolysis[14,25,26,36−39] and CVD.[40−44] Most reports to date show bamboo-shaped structures for the carbon−nitrogen nanotubes.[25,37,38,40,42−44] Some of the methods used in the synthesis of carbon−nitrogen nanotubes result in aligned nanotubes. For example, Terrones et al. prepared aligned N-doped carbon nanofibers (containing 2−10% nitrogen) and carbon nanotubes by pyrolyzing various C/N sources including triazine,[14] melamine,[45] ferrocene/melamine mixture,[36,39] and ferrocene/C_{60} mixtures in ammonia atmosphere.[37] Rao and co-workers produced good quantities of aligned carbon−nitrogen nanotube bundles by pyrolysis of pyridine.[26,35] Lee and co-workers prepared large quantities of aligned carbon−nitrogen nanotubes by pyrolysis of iron pentacarbonyl ($Fe(CO)_5$) and cetylene (C_2H_2) mixtures with ammonia.[25] Ma et al. obtained aligned N-containing carbon nanofibers on a large scale using microwave plasma-assisted CVD with a mixture of methane and nitrogen.[46]

Zeolite particles have been seldom used as substrates for the growth of CNTs.[47−49] Fonseca and co-workers prepared CNTs using transition metal incorporated zeolite supports.[47] Shinohara and co-workers reported the bulk production of quasi-aligned CNT bundles grown on zeolite substrates.[49] However, the growth of aligned CNTs on zeolite particles has so far not been achieved. Zeolites are excellent support materials that have not been sufficiently explored as substrates for aligned CNT growth. Unlike other types of substrates, zeolites offer the opportunity of positioning metal catalysts within their pore channels rather than only on the external surface of particles. Here we report the synthesis of aligned N-doped carbon nanotubes via CVD (over the temperature range 700−800 °C) using ammonium-exchanged zeolite-β as the substrate, ferric nitrate as the catalyst, and acetonitrile as the carbon precursor. We show that the use of ammonium-exchanged zeolite β as substrate promotes the formation of bundles of well-aligned CNTs. The properties (morphology, graphitic ordering, textural parameters, C−N binding, thermal stability) of the CNTs were probed using electron microscopy, X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy, nitrogen sorption analysis, and thermogravimetric analysis. The effect of CVD temperature and duration on the production of aligned N-doped carbon nanotubes was also studied.

Experimental Section

Zeolite β was obtained by following the procedures reported by Davis and co-workers.[50] The zeolite was calcined at 500 °C for 6 h. Ammonium-exchanged, NH_4-zeolite β was obtained by adding 1 g of zeolite β to 20 mL of 0.02 M ammonium nitrate (NH_4NO_3) solution under stirring for 2 h, followed by filtration. This exchange−filtration procedure was repeated twice. The final NH_4-zeolite β was recovered by filtration and air-dried at room temperature. Both the original (Na-containing) zeolite β and NH_4-exchanged zeolite β were impregnated with Fe. The Fe was impregnated from ferric nitrate in ethanol under stirring at an Fe/Si molar ratio of 0.05, followed by overnight drying at 100 °C to remove the ethanol. The ferric nitrate impregnated zeolites were then used as substrate for the synthesis of CNTs via CVD. In brief, an alumina boat with 0.2 g of ferric nitrate impregnated zeolite (Na or NH_4 containing) was placed in a flow through tube furnace, which was then heated to the required temperature (in the range 700−900 °C) under a flow of argon. The temperature of the furnace was maintained at the target temperature for a specific duration (1, 10, or 20 h) under a flow of argon saturated with the carbon precursor, acetonitrile. The resulting zeolite/carbon nanotube (zeolite/CNT) composites were recovered and washed with 10% hydroflouric (HF) acid several times, followed by further washing by refluxing in concentrated HCl at 60 °C to remove the zeolite substrate. The resulting CNTs were dried in an oven at 120 °C prior to further characterization. As-synthesized zeolite/CNT composites prepared from NH_4-exchanged zeolite β were denoted as CTubeA1, CTubeA2, CTubeA3, and CTubeA4 corresponding to CVD temperature of 700, 750, 800, and 900 °C, respectively. Zeolite-free CNTs (i.e., after treatment with HF and refluxing in HCl) were denoted as CTube1, CTube2, CTube3, and CTube4 corresponding to CVD temperature of 700, 750, 800, and 900 °C, respectively.

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Material Characterization. The CNTs were characterized by powder X-ray diffraction (XRD), nitrogen sorption analysis, elemental analysis, thermogravimetric analysis (TGA), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS). Powder XRD analysis was performed using a Philips 1830 powder diffractometer with Cu Kα radiation (40 kV, 40 mA). Nitrogen sorption isotherms and textural properties of the CNTs were determined at −196 °C using nitrogen in a conventional volumetric technique by a Micromeritics ASAP2020 sorptometer. Before analysis the samples were oven dried at 150 °C and evacuated for 12 h at 200 °C under vacuum. The surface area was calculated using the BET method on the basis of adsorption data in the partial pressure (P/P_0) range 0.05−0.2, and total pore volume was determined from the amount of the nitrogen adsorbed at P/P_0 = ca. 0.99. Elemental analysis was carried out using a CHNS analyzer (Fishons EA 1108). Thermogravimetric analysis (TGA) was performed using a Perkin-Elmer Pyris 6 TG analyzer at a heating rate of 2 °C/min under static air conditions. Scanning electron microscopy (SEM) images were recorded using a JEOL JSM-820 scanning electron microscope. Samples were mounted using a conductive carbon double-sided sticky tape. A thin (ca. 10 nm) coating of gold sputter was deposited onto the samples to reduce the effects of charging. Transmission electron microscopy (TEM) images were recorded on a JEOL 2000-FX electron microscope operating at 200 kV. Samples for analysis were prepared by spreading them on a holey carbon film supported on a grid. Raman spectra were obtained with 532 nm excitation wavelength on a Nicolet Almega Dispersive Raman microscope. Raman spectra were collected by manually placing the probe tip near the desired point of the sample on a glass slide at room temperature. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos AXIS ULTRA spectrometer with a monochromated Al Kα X-ray source (1486.6 eV) operated at 10 mA emission current and 15 kV anode potential. The analysis chamber pressure was better than 1.3×10^{-12} bar. The FAT (fixed analyzer transmission) mode was used, with pass energies of 160 eV (or 80 eV) for survey scans and 40 eV for high-resolution scans. A magnetic immersion lens system allowed the area of analysis to be defined by apertures, a "slot" aperture of 300×700 μm for wide/survey scans and a 110 μm aperture for high-resolution scans. The take off angle for the photoelectron analyzer was 90°, and the acceptance angle was 30° (in magnetic lens modes).

Results and Discussion

We first investigated the influence of length of time allowed for chemical vapor deposition (i.e., CVD duration) on the formation of CNTs using Na-containing zeolite β (Na-zeolite β) or NH_4-exchanged zeolite β (NH_4-zeolite β) as substrates. A heating ramp rate of 5 °C/min and a final temperature of 800 °C were used. Figure 1 shows representative SEM images of CNTs obtained after various CVD durations (1, 10, or 20 h) on ferric nitrate impregnated zeolite substrates. CNTs prepared from Na-zeolite β (Figure 1a−c) appear to be randomly oriented regardless of the CVD duration.[46,48] CNTs obtained from NH_4-zeolite β are either randomly oriented (for CVD duration of 1 or 10 h, Figure 1A,B) or are arranged in isolated bundles with good alignment (for 20 h CVD duration, Figure 1C). The SEM images in Figure 1 strongly suggest that use of NH_4-zeolite β as substrate at CVD duration of 20 h optimized the production of aligned CNTs. For this reason, the NH_4-zeolite β substrate and a heating ramp rate of 5 °C/min and CVD duration of 20 h were adopted for further studies on the production of aligned N-doped CNT in the temperature range 700−900 °C.

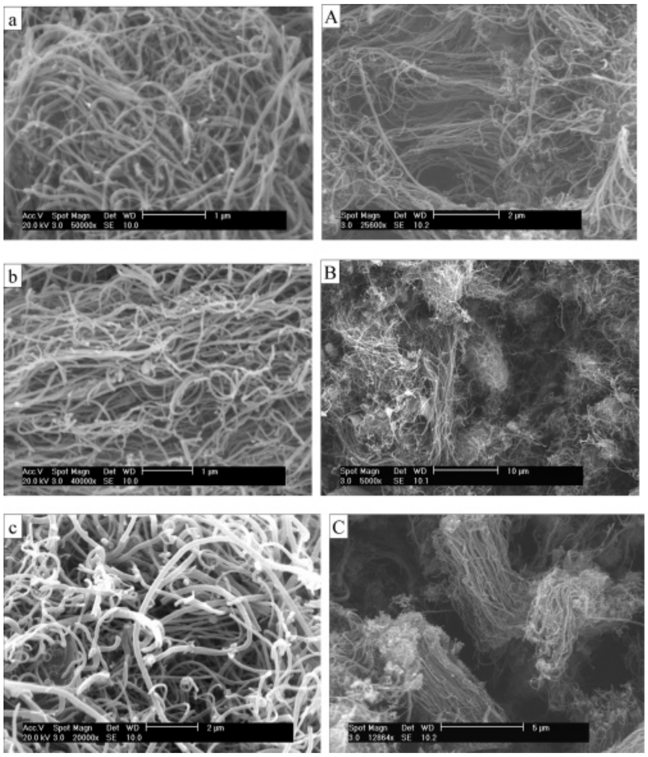

Figure 1. SEM images of carbon nanotubes prepared via CVD at 800 °C using Na-zeolite β (a−c) or NH_4-zeolite β (A−C) as substrate and acetonitrile as carbon source for various CVD durations: (a, A) 1 h; (b, B) 10 h; (c, C) 20 h.

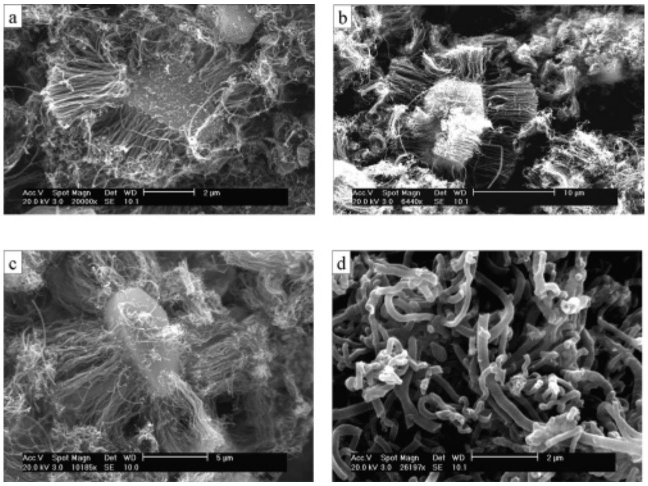

Figure 2. SEM images of as-synthesized zeolite β/carbon nanotube composites prepared for a CVD duration of 20 h, using NH_4-zeolite β as substrate and acetonitrile as carbon source, at various CVD temperatures: (a) 700 °C; (b) 750 °C; (c) 800 °C; (d) 900 °C.

Figure 2 shows SEM images of as-synthesized zeolite/carbon nanotube composites (i.e., CTubeA samples) prepared at various CVD temperatures using ferric ion impregnated NH_4-zeolite β as substrate. For CTubeA1, CTubeA2, and CTubeA3 composites prepared at 700, 750, 800 °C, respectively, the particles of the zeolite β substrate are clearly observed along with aligned CNTs that grow along the verges of the hexagonal particles. However, only

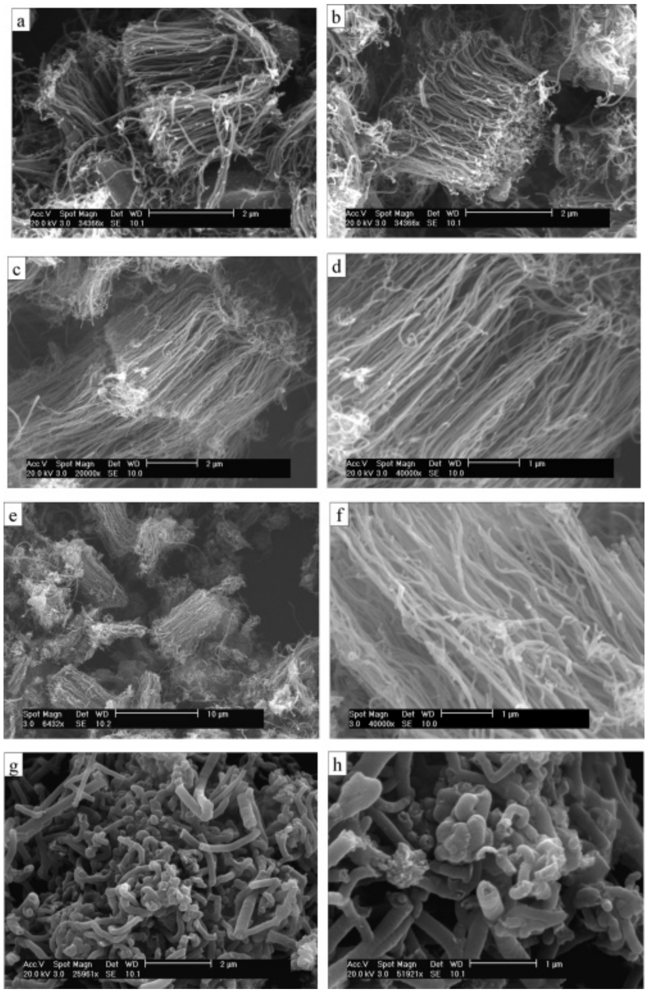

Figure 3. SEM images of carbon nanotubes prepared for a CVD duration of 20 h, using NH_4-zeolite β as template and acetonitrile as carbon source at various CVD temperatures: (a, b) 700 °C; (c, d) 750 °C; (e, f) 800 °C; (g, h) 900 °C.

randomly oriented and broken CNTs are observed for the composite prepared at a CVD temperature of 900 °C (Figure 2d).

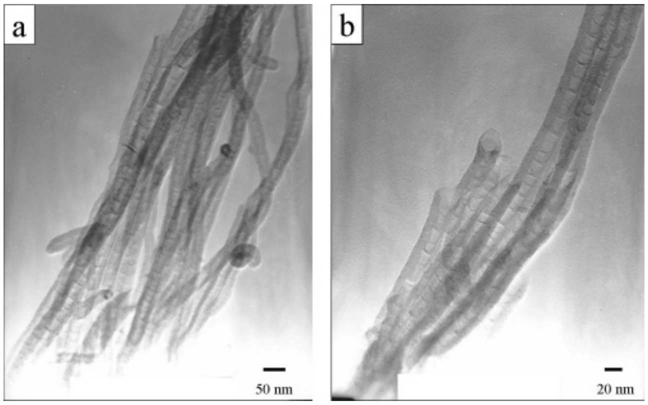

Figure 4. TEM images of carbon nanotubes prepared at 800 °C for a CVD duration of 20 h, using NH_4-zeolite β as template and acetonitrile as carbon source.

Figure 3 shows SEM images of zeolite-free CNTs (i.e., after treatment with HF and refluxing in HCl) prepared at various CVD temperatures. As expected, the particles of the zeolite are not present and instead bundles of aligned CNTs are observed for samples prepared at CVD temperatures lower than 900 °C. The SEM images in Figure 3 confirm that aligned CNTs are obtained after 20 h CVD duration at 700, 750, and 800 °C. The length of the aligned CNTs varies between 2 and 10 μm. In particular Figure 3e shows that large amounts of isolated bundles of CNTs, of length up to 10 μm, are present for sample CTube3 which was prepared at 800 °C. Sample CTube4, which was prepared at 900 °C, presents randomly oriented and broken nanotubes of various lengths. The diameter of these short nanotubes is much larger than that of the aligned nanotubes obtained at lower CVD temperature. Representative TEM images of the CNTs prepared at 800 °C are shown in Figure 4. The TEM images show that the CNTs are well aligned in accord with the SEM images (Figures 2 and 3). The CNTs are multiwalled and show a bamboolike morphology with transverse carbon bridges forming compartments. The CNTs have comparable widths with inner and outer diameters of ca. 10 and 30 nm, respectively, and are free of Fe particles.

On the basis of the SEM and TEM images, we propose the following tentative explanation for the production of the aligned CNTs. When Na-zeolite β is used as substrate, the ferric ions are mainly located on the surface of the zeolite particles. It is unlikely that the ferric ions will displace Na ions located within the zeolite framework. Consequently, the CNTs grow from the surface of the hexagonal zeolite particles in a random manner (Figure 1a−c) in agreement with previous reports.[47,49] However, for the NH_4-zeolite β substrate, the sodium ions on the zeolite framework are already exchanged with ammonium ions. During the (ferric nitrate) impregnation step, some of the ammonium ions may be exchanged (displaced) by ferric ions. Such an exchange results in the presence of some ferric species within the framework of zeolite β substrate. Consequently, CNTs may grow from Fe particles located within the framework (surface/near surface region) of the hexagonal zeolite particles (via defects or cracks), which results in alignment of the nanotubes. The CVD temperature and duration also play a role in the production of aligned CNTs; temperatures lower than 700 °C and CVD durations of 10 h or less may not be sufficient to produce large amounts of carbon nanotube bundles at once. Indeed we observed no formation of CNTs at 600 °C. On the other hand, a CVD temperature of 900 °C may be so high that the nanotubes aggregate quickly to produce short nonaligned nanotubes with larger diameter (Figures 2d and 3g,h). A CVD temperature of 750−800 °C and duration of 20 h appears to be optimal for the production of large quantities of aligned CNTs.

Figure 5 shows the powder X-ray diffraction (XRD) patterns of CNTs prepared using NH_4-zeolite β substrate at various CVD temperatures. For ease of comparison, the XRD pattern of the zeolite β substrate is included. The as-synthesized zeolite/carbon nanotube composites (Figure 5A) have XRD patterns that exhibit a peak at $2\theta = 22°$ and other higher angle peaks corresponding to the zeolite β substrate. The intensity of the peak at $2\theta = 22°$ decreases for composites prepared at higher CVD temperature. In addition, XRD pattern of composites prepared at 800 and 900 °C exhibit a peak at $2\theta = 26°$, which is the (002) diffraction from graphitic carbon. However after removal of the zeolite

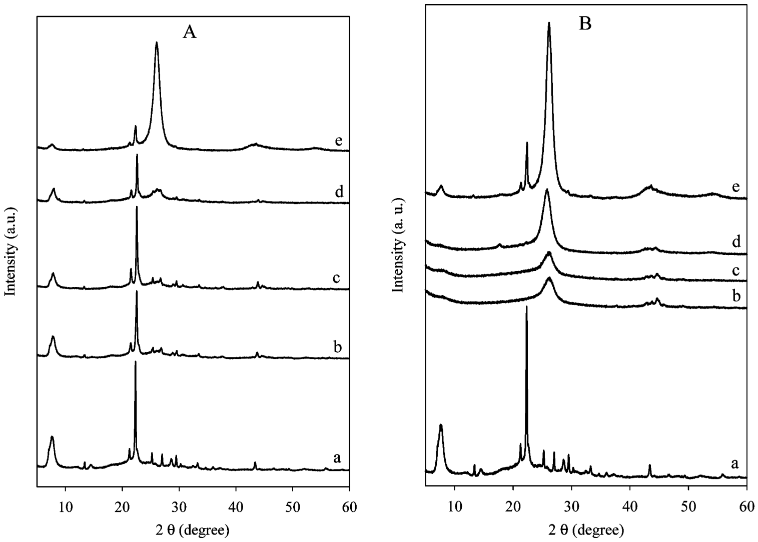

Figure 5. XRD patterns of zeolite β (a), zeolite β/carbon nanotube composites (A), and carbon nanotubes (B) prepared via CVD using NH_4-zeolite β as substrate and acetonitrile as carbon source at various CVD temperatures: (b) 700 °C; (c) 750 °C; (d) 800 °C; (e) 900 °C.

substrate, the CNTs have XRD patterns (Figure 5B) that are dominated by peaks ascribable to graphitic carbon. These are the (002) diffraction at $2\theta = 26°$ and two other peaks at ca. $2\theta = 44$ and 54° (corresponding to the (101) and (004) diffractions of graphitic carbon, respectively), which are observed for CNTs prepared at 800 and 900 °C. The intensity of the graphitic peaks increases for CNTs prepared at higher CVD temperature. In addition to the graphitic peaks, a group of very weak peaks in the 2θ range of 43−46° is observed. These peaks are ascribable to FeC_3, indicating that there is a small amount of FeC_3 in the CNT samples. It is noteworthy that no peaks corresponding to zeolite β appear in the XRD patterns of CNT samples prepared at temperatures lower than 900 °C. This suggests that the substrate extraction process was successful in removing the zeolite β (at least within the detection limit of XRD). However, we note that some peaks ascribable to zeolite β are observed for CNTs prepared at 900 °C, despite thorough washing with HF and refluxing in concentrated HCl. A possible explanation for these peaks, i.e., transfer of the zeolite structure to carbonaceous material formed at 900 °C, is currently under investigation.

Raman spectroscopy is often used to evaluate the crystallinity of CNTs. The Raman spectrum of CNTs (sample CTube3) prepared at 800 °C is shown in Figure 6. The spectrum shows two bands at ca. 1355 cm^{-1} (D band) and ca. 1590 cm^{-1} (G band). The G band corresponds to the C−C stretching (E_{2g}) mode for typical graphite. The D band arises from defects and disorder in graphene sheets and is consistent with the presence of MWNTs.[51] Some of the defects and disorder may be related to the presence of N in the graphene sheets.[52] However, the presence of a relatively high intensity G band provides further evidence for the generally high graphitic ordering in the CNTs. The Raman spectrum is therefore in agreement with the XRD patterns in showing that the CNTs obtained at 800 °C are highly graphitized.

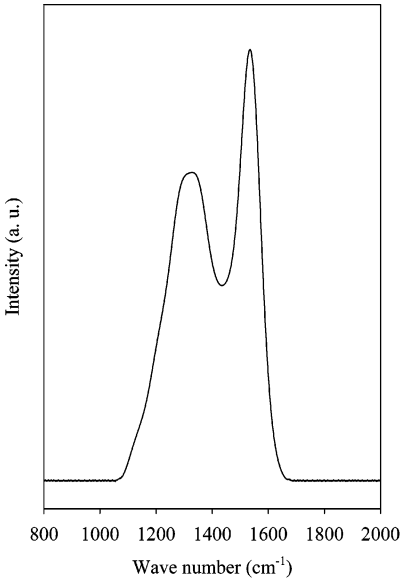

Figure 6. Raman spectrum of carbon nanotubes prepared via CVD using NH_4-zeolite β as substrate and acetonitrile as carbon source at 800 °C. An excitation wavelength of 532 nm was used.

Thermogravimetric analysis (TGA) is useful in determining the level of graphitization in CNTs. TGA curves and corresponding differential thermogravimetric (DTG) profiles for the present CNTs are shown in Figure 7. The CNT samples exhibit one apparent mass loss event of more than 90% regardless of the CVD temperatures at which they were prepared. This implies that the CNT samples consist of more than 90% carbon, which is in agreement with the results (91−94%) obtained from the elemental analysis. The onset temperature for the mass loss in the TGA curves increases for CNT samples prepared as higher CVD temperature. The mass loss maxima (obtained from the DTG profiles, Figure 7B) shifts from 540 to 620 °C with increase in the CVD temperatures at which the CNTs were prepared. The shift in the mass loss maxima suggests a higher degree of graphitic ordering for CNT samples prepared at higher CVD temperature, which is in agreement with the XRD patterns (Figure 5).

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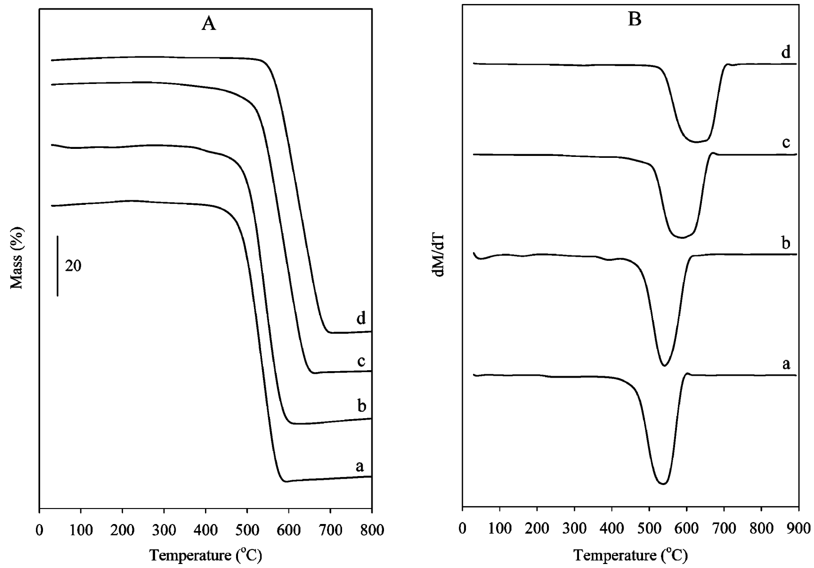

Figure 7. TGA curves (A) and corresponding DTG profiles (B) of carbon nanotubes prepared via CVD using NH_4-zeolite β as substrate and acetonitrile as the carbon source at various CVD temperatures: (a) 700 °C; (b) 750 °C; (c) 800 °C; (d) 900 °C.

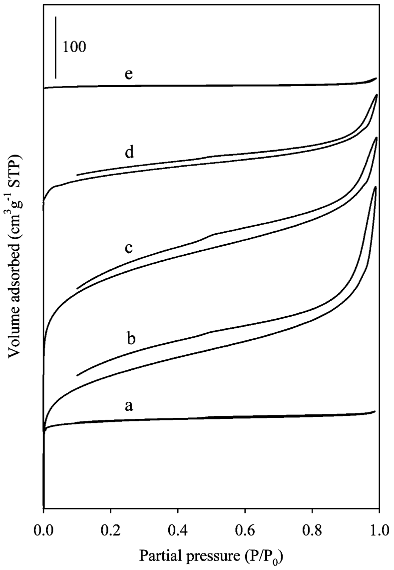

Figure 8. Nitrogen sorption isotherms of zeolite β (a) and carbon nanotubes prepared via CVD using NH_4-zeolite β as substrate and acetonitrile as carbon source at various CVD temperatures: (b) 700 °C; (c) 750 °C; (d) 800 °C; (e) 900 °C.

To be used as gas storage media, it is desirable that the nanotubes possess high surface area and pore volume. The nitrogen sorption isotherms of the zeolite β substrate and the CNT samples are shown in Figure 8. The zeolite and the CNT sample prepared at 900 °C only show micropore filling and capillary condensation at very low partial pressures ($P/P_0 < 0.02$). However, CNT samples prepared at 700, 750, and 800 °C exhibit considerable adsorption at $P/P_0 > 0.2$ in addition to the micropore filling and capillary condensation below $P/P_0 = 0.02$. The adsorption at $P/P_0 > 0.2$ may be attributed to textural porosity perhaps arising from interparticle (voids) mesopores. The textural properties of zeolite β and carbon nanotube samples are summarized in Table 1. CNT samples (CTube1 and CTube2) prepared at lower temperature (700 and 750 °C) have much higher surface area (745 and 886 m^2/g, respectively) and pore volume (0.81 and 0.75 cm^3/g, respectively). The surface area of the bundles of aligned CNTs prepared at 800 °C is also relatively high (226 m^2/g). However, the textural parameters of the short CNTs prepared at 900 °C are much lower.

Table 1. Textural Properties and Nitrogen Content of Carbon Nanotubes Prepared via Catalyzed Chemical Vapor Deposition (CCVD) Using NH_4-Exchanged Zeolite β as Substrate and Acetonitrile as Carbon Source at Various Temperatures

sample	CVD conditions (°C)/duration (h)	N content (wt %)	surf area (m^2/g)	pore vol (cm^3/g)
CTube1	700/20	6.4	745	0.81
CTube2	750/20	6.8	886	0.75
CTube3	800/20	7.2	226	0.30
CTube4	900/20	8.9	24	0.03
zeolite β			487	0.25

All the CNTs contain significant amounts of nitrogen that arises from the use of acetonitrile as carbon precursor. The N content for all the samples varies between 6 and 9 wt % as shown in Table 1. The nitrogen content of the CNTs is comparable to that previously reported by Terrones and coworkers.[39] The XPS spectra of the N-doped CNT samples shown in Figure 9 indicate a N 1s signal which was split into two peaks. The N1s signal was split into two peaks centered at 398.6 and 400.5 eV for samples CTube3 and CTube4 prepared at 800 and 900 °C, respectively. The peaks at binding energy of 398.6 and 400.5 eV correspond to "pyridinic" (i.e., pyridine-like) and "graphitic" nitrogen, respectively.[39,53,54] The term "pyridinic" is used to refer to N atoms which contribute to the π system with one p-electron, whereas "graphitic" nitrogen corresponds to highly coordinated (quaternary) N atoms substituting inner C atoms on the graphene layers. The C 1s peak for the N-doped CNTs (Figure 9B) was observed at ca. 284.7 eV and is consistent with sp^2 graphitic carbon.

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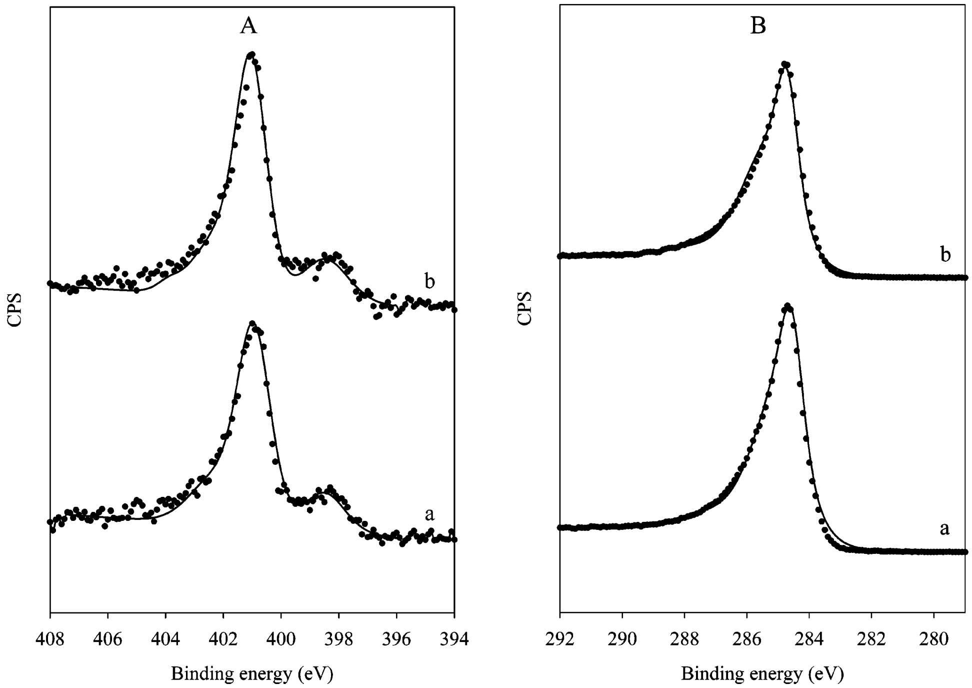

Figure 9. XPS spectra showing N1s (A) and C1s (B) peaks for N-doped carbon nanotubes prepared via CVD using NH_4-zeolite β as substrate and acetonitrile as carbon source at various CVD temperatures: (a) 800 °C; (b) 900 °C.

Conclusion

In conclusion, we have prepared bundles of aligned N-doped carbon nanotubes by a simple CVD method, in which ammonium-exchanged zeolite-β was used as the substrate, ferric nitrate as the catalyst, and acetonitrile as the carbon precursor. Well-aligned bundles of N-doped carbon nanotubes with bamboolike structure were obtained over the temperature range 700−800 °C. The nitrogen content of the nanotubes varied between 6 and 9 wt % depending on the CVD temperature at which they were prepared. We believe that the use of zeolite substrates as demonstrated here is of general application and not restricted to the reported N-doped CNTs. The optimal conditions for the production of large amounts of aligned and highly graphitized CNT were found to be a CVD temperature of 750−800 °C and duration of 20 h. The length of the aligned nanotubes varied between 2 and 10 μm, with an inner diameter of ca. 10 nm and outer diameter of 30 nm.

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