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Template synthesis and characterization of well-aligned nitrogen containing carbon nanotubes

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Abstract

The synthesis of well-aligned nitrogen containing carbon nanotubes by pyrolysis of polyvinyl pyrrolidone (PVP) on alumina membrane template is described. The nanotubes were characterized by elemental analysis, electron microscopic analyses, Raman, IR and X-ray photoelectron (XPS) spectroscopic techniques. SEM, transmission electron microscopy (TEM) and AFM images reveal the hollow structures and vertically aligned features of the nanotubes. Raman spectrum shows the characteristic bands at 1290 cm^{-1} (D-band) and 1590 cm^{-1} (G-band). IR spectral bands indicated the characteristic C–N bonds in carbon nanotubes. This confirms the presence of nitrogen atoms in the carbon framework. The XPS and elemental analyses further indicate significant amount of nitrogen in the nanotubes. IR, elemental and XPS analyses clearly provide evidence for the presence of nitrogen in carbon nanotubes.

Keywords: Nitrogen containing carbon nanotubes; Template synthesis; Alumina template; Carbonization

1. Introduction

Since the discovery of carbon nanotubes (CNTs) by Ijima [1], a number of studies on CNTs and related nanostructures have been carried out. The extraordinary mechanical and electronic properties of these structures have led to several applications, including nanoscale fibres [2], nanoelectronic devices [3], probe tips for scanning probe microscopy [4] and field emitter arrays [5]. Carbon nanotubes are promising materials for catalyst supports [6] and electrodes for supercapacitors [7,8]. Furthermore, it has been proved that CNTs have better conductivity than graphite. The nanostructured morphology, higher surface area and suitable electronic properties suggest that carbon nanotubes have potential ability to promote electrochemical reactions in fuel cells [9]. Doping carbon nanotubes with heteroatom could be particularly an interesting way for tuning the surface and electronic properties. Incorporation of nitrogen in carbon nanotubes results in the enhancement of conductivity, due to the additional electron contributed by the nitrogen atom [10,11]. Doping with high-nitrogen concentrations leads to an increase in the conductivity due to raise of Fermi level towards conduction band [12,13]. The presence of nitrogen atoms in the carbon framework generates specific surface properties including the enhanced polarity, basicity and heterogeneity in terms of hydrophilic sites. The presence of nitrogen functional groups in the carbon framework also has a substantial effect on their catalytic activity [14,15]. Various routes have been evolved for synthesis of the heteroatom-doped nanotubes including arc discharge [16], laser ablation [17], substitution reaction [18], pyrolysis [19] and various chemical vapor deposition (CVD) methods [20]. Although arc discharge and laser ablation techniques produce CNTs, difficulties are encountered in the control of size and alignment of the nanotubes. Further, these techniques require purification processes to separate the CNTs from the catalyst particles used in the synthesis.

The template synthesis method has been widely used for preparing micro and nanostructured materials [21,22], which involves the synthesis of the desired material within the pores of a membrane to generate nanotubes of cylindrical nature with uniform diameter. Che et al. [23] and Kyotani et al. [24]

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used a combination of CVD and template synthesis methods to synthesize highly aligned, uniform, hollow and open ended (suitable for filling with other materials) CNTs with diameters ranging from 20 to 200 nm. Among all the methods of preparation of CNTs, the template synthesis method has the advantage of controlling composition, morphology and the size of the nanotubes [25]. Nitrogen containing carbon nanotubes prepared by template synthesis using precursors such as polyacrylonitrile [26] and polypyrrole [27], have been reported.

In this letter, use of polyvinylpyrrolidone as a new precursor for the synthesis of nitrogen containing carbon nanotubes by template synthesis is discussed. The well-aligned nitrogen containing CNTs have been formed. The morphology and structural features of the nanotubes have been investigated using electron microscopy and Raman spectroscopy. The composition and bonding of the nanotubes were determined using IR and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Chemicals

All the chemicals used were of analytical grade. Polyvinyl pyrrolidone (Sisco Research Laboratories, India), dichloromethane and concentrated HF (both from Merck) were used. Alumina template membranes were obtained from Whatman Anopore Filters.

2.2. Synthesis of nitrogen containing carbon nanotubes

Polyvinylpyrrolidone (PVP, 5 g) was dissolved in dichloromethane (20 ml) and impregnated directly into the pores of the alumina template by wetting method [28]. After complete solvent evaporation, the membrane was placed in a quartz tube (30 cm length, 3.0 cm diameter) kept in a tubular furnace and carbonized at 1173 K under Ar gas flow. After 3 h of carbonization, the quartz tube was naturally cooled to room temperature. The resulting carbon–nitrogen composite was immersed in 48% HF at room temperature for 24 h to remove the alumina template and the nitrogen containing CNTs were obtained as an insoluble fraction. The nanotube were then washed with distilled water to remove the residual HF and was dried at 393 K.

2.3. Characterization

The total chemical composition of the nanotubes was determined by elemental analysis using Hereaus CHN analyzer after the removal of alumina template. The scanning electron micrographs were obtained using JEOL JSM-840 model working at 15 keV. For transmission electron microscopic studies, the nanotubes dispersed in ethanol were drop cast on to a carbon-coated copper grid followed by solvent evaporation in air at room temperature and the images were obtained using Phillips 420 model, operating at 120 keV. The nanotubes were sonicated in acetone for 20 min and then were dropped on cleaned Si substrates and AFM imaging was performed in air using a Nanoscope IIIA atomic force microscope (Digital Instruments, St. Barbara, CA) operated in contact mode.

The CNTs placed in glass capillary tubes were used for recording Raman spectrum at the room temperature with 514.5 nm excitation in backscattered mode using Bruker FRA106 FT-Raman instrument. The IR spectrum was recorded with Perkin-Elmer (L-710) spectrophotometer. The X-ray photoelectron spectroscopic analysis was carried out using VG ESCALAB 220 iXL instrument at Al Kα (1486.5 eV) radiation.

3. Results and discussion

Elemental analysis was first conducted to examine whether nitrogen has really entered the carbon nanotube framework. It has been found that the samples prepared contained about 87.2% carbon and 6.6% nitrogen (w/w).

Scanning electron microscopic images given in Fig. 1 shows the morphology of the nitrogen containing CNTs after the removal of alumina template. The nanotubes are aligned and grouped into high-density arrays, appearing like the bristles of a brush (Fig. 1a) and this reflects the highly dense straight pores of the alumina membrane ($\sim 10^9$ pores cm^{-2}). Images b and c of Fig. 1 show the lateral view of the well-aligned nanotubes of the length 50–60 μm with open ends (indicated by arrows in Fig. 1c) similar to the thickness of the alumina membranes. Moreover, we performed transmission electron microscopy (TEM) analysis to determine the morphology and the diameter of the nanotube.

Transmission electron microscopy images of the nitrogen containing carbon nanotubes prepared from polyvinylpyrrolidone are shown in Fig. 2. The carbonized specimens are found to have a hollow structure with open ends. Because the channels of the membranes being cylindrical with uniform diameter and the tube diameter closely matching the pore size of the template used, monodispersed nanotubes of the desired material were obtained. Since no catalyst has been used for synthesis of nitrogen containing carbon nanotubes, it is worth pointing out that the nanotubes produced by template synthesis under normal experimental conditions are almost free from impurities.

AFM images of the nitrogen containing carbon nanotubes deposited on a silicon substrate are shown in Fig. 3. The AFM tip was carefully scanned across the tube surface in a direction perpendicular to the tube axis. From the AFM images, a part of the long nanotube is appeared to be cylindrical in shape and to be terminated by a symmetric hemispherical cap.

Raman spectrum is a unique tool to characterize the nanotubes under study, since the amount of ordering and degree of sp^2 and sp^3 bonding leaves a characteristic Raman "finger print". Thus, the graphitic nature of the nitrogen

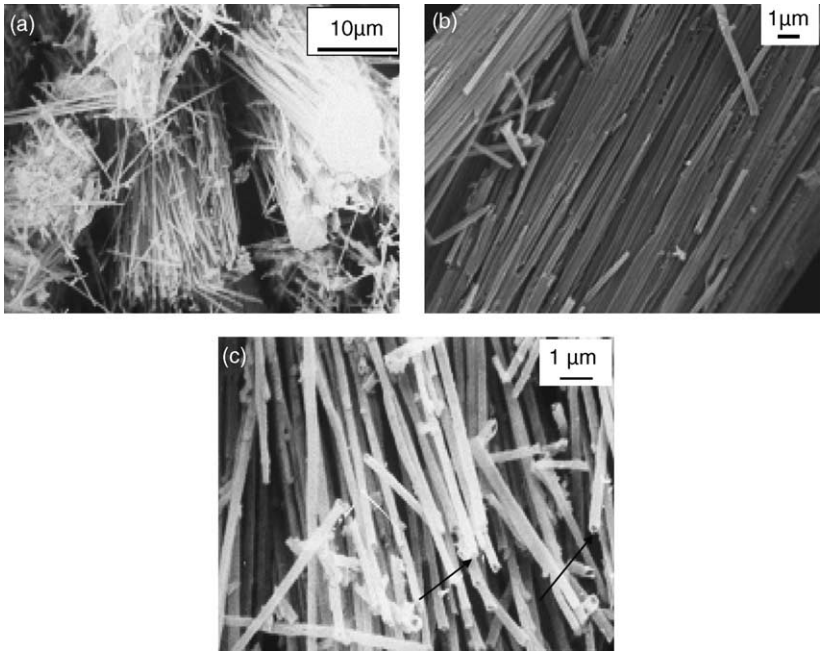

Fig. 1. SEM images of the nitrogen containing carbon nanotubes: (a) the top view of the nanotubes, (b) side view of the vertically aligned nanotubes and (c) high-magnification lateral view of the nanotubes.

containing carbon nanotubes obtained from the carbonization of polyvinylpyrrolidone was investigated by Raman spectroscopy. Fig. 4 shows Raman spectrum of the sample. It shows two peaks at 1290 and 1590 cm^{-1}. The peak at 1590 cm^{-1} (G-band) corresponds to the high frequency E_{2g} first-order mode, which can be attributed to the opposing movement of two-neighboring carbon atoms in a graphite sheet [29,30]. The peak at 1290 cm^{-1} (D-band) could be as a result of defects in the curved graphitic sheets, tube ends and finite size crystalline domains of the tubes [31]. The D-band appears to be significantly stronger than the G-band indicating the amorphization of the graphite network is due to much higher nitrogen content in the carbon nanotubes [32]. Although the carbon nanotubes prepared from polyvinylpyrrolidone show graphitic band, they have lesser graphitic structure as judged from the intensity and line width of the peak. And the carbonized specimen is found to have a poorly ordered graphite structure in the form of a hollow nanotube.

The nature of chemical bonding between the elements was analyzed using infrared and X-ray photoelectron spectroscopic techniques. Infrared spectrum of the nitrogen containing carbon nanotubes is similar to those reported for other carbon nitride materials [33]. FT-IR spectrum (Fig. 5)

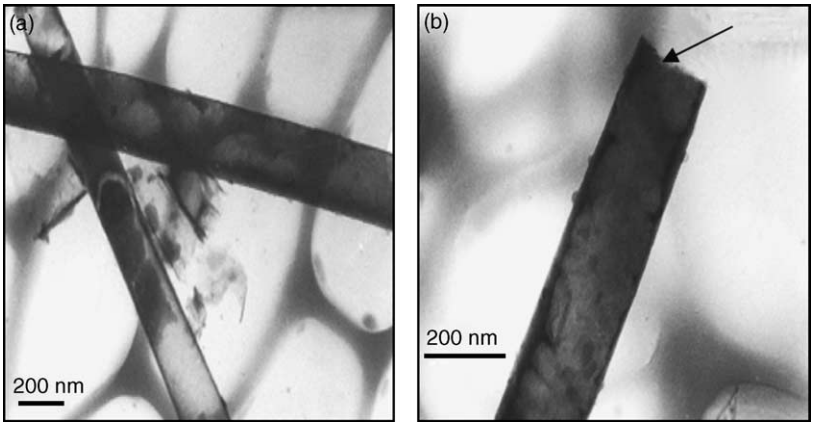

Fig. 2. (a) TEM image of the nitrogen containing carbon nanotubes and (b) higher magnification image of the individual nanotube (an arrow indicating the open end of the tube).

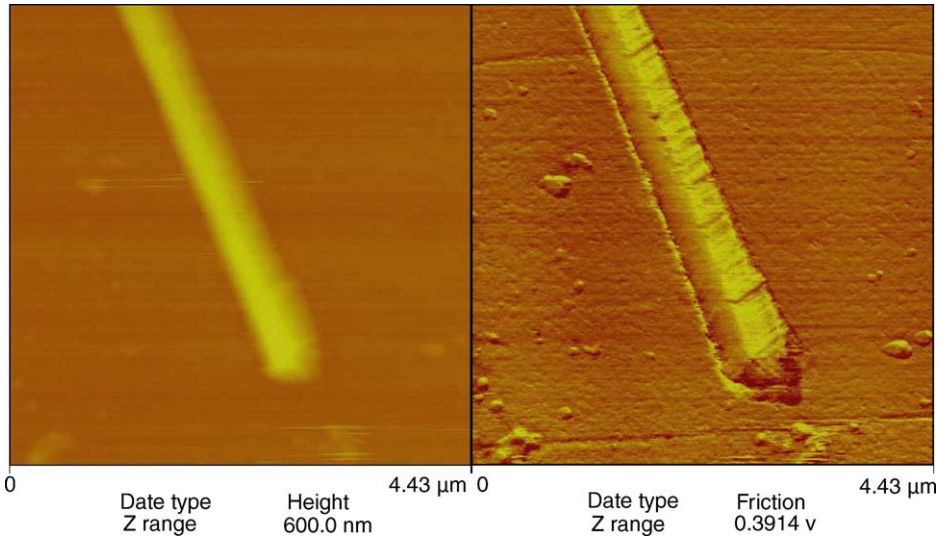

Fig. 3. AFM image of the nitrogen containing carbon nanotubes.

shows the stretching and deformation mode of NH_2 group at 3420 and 1640 cm^{-1}, respectively. The peaks at 2928 and 2855 cm^{-1} were observed only in amorphous CNTs and were assigned to C–H bonding [33,34]. Moreover, the presence of nitrogen in the carbon nanotubes induces CNTs to show G- and D-bands in FT-IR spectrum. The Peak at 1594 cm^{-1} is attributed to C=N stretching modes [35,36], while the other sharp peaks at 1381, 1124 and 1084 cm^{-1} corresponds to the characteristic absorbance of single C–N bonds [37]. These are the strong evidences of incorporated nitrogen in the carbon nanotubes. And also a band at 780 cm^{-1} is attributed to graphitic sp^2 domains [35].

The composition and the nature of chemical bonding of the prepared nanotube sample were studied by XPS measurement. The gross chemical composition estimated from the XPS results gave an N/C ratio of about 0.06. The deconvoluted C 1s and N 1s XPS spectra of nitrogen containing carbon nanotubes are shown in Fig. 6. The C 1s can be deconvoluted in to two lines peaked at 284.5 and 287.05 eV. By comparing with urotropine ($C_6H_{12}N_4$, sp^3 binding energy: 286.9 eV) [37] and pyridine (C_5H_5N, sp^2 binding energy: 285.5 eV) [38], the carbon peak at 287.05 and 284.5 eV are assigned due to sp^3 and sp^2 bondings, respectively. The N 1s also can be deconvoluted in to two lines peaked at 397.6 and 399.4 eV. These two peaks are attributed to sp^2 N, i.e. substitutional N in the graphite sheet [39]. The observed C 1s and N 1s binding energies are comparable to those found in melamine ($C_3N_6H_6$) molecules with covalent C–N bonds, which is similar to the C–N bonds of graphitic carbon nitride (C_3N_4) [40]. Together with the XPS results, it is inferred that the nitrogen atom is chemically bonded to the three neighboring carbons in a graphitic basal plane, and therefore the presence of the nitrogen in the carbon framework is confirmed.

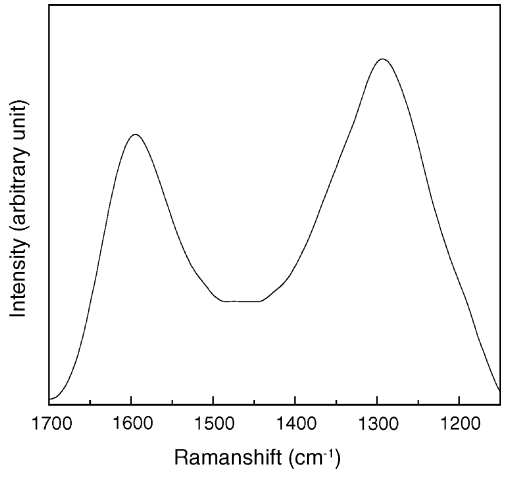

Fig. 4. Raman spectrum of the nitrogen containing carbon nanotubes.

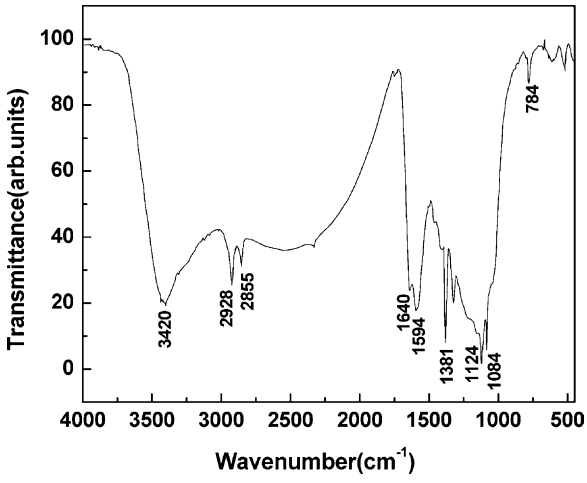

Fig. 5. FT-IR spectrum of the nitrogen containing carbon nanotubes.

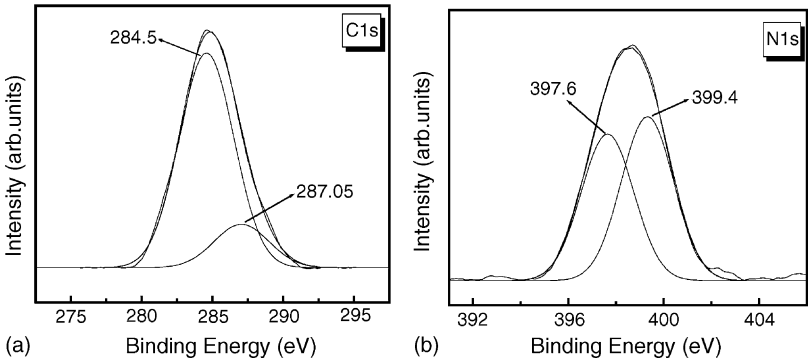

Fig. 6. XPS spectra of the nitrogen containing carbon nanotubes after the removal of alumina template: (a) C 1s and (b) N 1s.

4. Conclusions

In summary, polyvinylpyrrolidone is a highly efficient polymer precursor for synthesis of nitrogen containing carbon nanotubes and the adopted template method is effective for the synthesis of well-aligned nitrogen containing carbon nanotubes with control over the packing density. The nitrogen containing carbon nanotubes with controlled morphology and composition has been achieved. The morphology of the aligned nanostructures has been verified by SEM, TEM and AFM. Raman spectroscopic studies show a higher degree of disorder, indicates a distortion of the graphitic network is due to nitrogen incorporation in the carbon nanotubes. The presence of carbon–nitrogen bond in CNTs has been confirmed by infrared spectrum and XPS analysis.

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