FTIR studies of nitrogen doped carbon nanotubes

Abha Misra, Pawan K. Tyagi, M.K. Singh, D.S. Misra *

Department of Physics, Indian Institute of Technology, Bombay, Mumbai-400076, India

Abstract

Purified and defect free carbon nanotubes have great potential for applications in electronic, polymer composites and biological sciences. The removal of impurities (carbon nanoparticles and amorphous carbon) is an important step before the CNT applications can be realized. We report the results of FTIR and TGA/DTA studies of the impurities present in the carbon nanotubes. The multiwalled CNTs were grown using Microwave Plasma Chemical Vapor Deposition (MPCVD) technique. Fourier transform infrared (FTIR) spectroscopy was carried out in the range of 400–4000 cm\(^{-1}\) to study the attachment of the impurities on carbon nanotubes. FTIR spectra of the as-grown MWCNTs show dominant peaks at 1026, 1250, 1372, 1445, 1736, 2362, 2851, 2925 cm\(^{-1}\) that are identified as Si–O, C–N, N–CH\(_3\), CNT, C–O, and C–H respectively. The peaks are sharp and intense showing the chemisorption nature of the dipole bond. The intensity of the peaks due to N–CH\(_3\), C–N and C–H reduces after annealing and the peaks vanish on annealing at high temperature (900 °C). The presence of C–N peak may imply the doping of the CNTs with N in substitution mode. TGA/DTA measurements, carried out under argon flow, show that the dominant weight loss of the sample occurs in the temperature range 400–600 °C corresponding to the removal of the impurities and amorphous carbon.

Keywords: MWCNTs; FTIR spectroscopy; TGA/DTA

1. Introduction

Carbon nanotubes [1] (CNTs) are found attractive on account of their potential for applications in hydrogen storage, nanoscale devices and sensor [2–6]. High quality and well-aligned carbon nanotubes are essential for the applications in the field of nanoelectronics and many of these applications are dependent upon the chirality and diameter of CNTs [7]. The nanotubes can be either metallic or semiconducting depending upon their diameter and chirality. The presence of defects and impurities that are electronically and chemically active can change these properties. Therefore, the control of the defects and impurities has become important for many applications of CNTs. Doping is a practical way to tailor the electrical properties of the CNTs. The nitrogen doped CNT shows n-type semiconducting behavior regardless of tube chirality [8].

A great deal of attention has been devoted to the N-doped CNTs. Several groups have produced carbon nanotubes containing nitrogen or nitrogen and boron. The specific interest in CN\(_x\) tubes is due to the fact that substituted N makes exclusively semiconducting tubes. Many groups have proposed that the electronic structure of N doped pyridine-like, pyrolic, and graphite like structure (Carbon atom has been replaced by N atom in graphite layers) is similar to triple-bonded CN [9–11]. Another group has proposed that N atoms might exist mainly inside the inner core of CNTs [12]. In this paper we investigate the nitrogen doped multiwalled carbon nanotubes using Fourier transform infrared (FTIR) spectroscopy and thermo gravimetric analysis (TGA).

2. Experimental

CNTs were grown onto nickel electroplated copper foil substrates. The commercial grade copper foils (purity, 98%), polycrystalline in nature, were used without any special pre-treatment to improve their smoothness. The electroplating of
Ni on copper foil was performed in an electroplating bath. The copper substrate (1 cm x 1 cm x 0.1 mm) was used as cathode and a thin platinum wire was used as the anode. Commercial grade nickel sulfate (NiSO$_4$·7H$_2$O) (275 g/l) and nickel chloride (NiCl$_2$·6H$_2$O) (60 g/l) were used as electrolytes in a dc electroplating process. The bath temperature and current were maintained at 60 °C and 80 mA, respectively. The nickel layers having a thickness of 5–10 μm were treated in the plasma of ammonia (NH$_3$) gas for 10 s. Ammonia plasma treatment was performed for 10 s in the temperature range of 300–750 °C at 10 Torr for the formation of nano-sized nickel catalyst, which was the precursor for subsequent CNTs growth using chemical vapor deposition (CVD). The flow rate of ammonia was kept at 180 sccm. Methane (CH$_4$) and hydrogen (H$_2$) were used with respective flow rates of 6 and 40 sccm. The temperature of the substrate was maintained at 820 ± 20 °C at deposition pressure 40 Torr. The deposition time was 5 min. Nitrogen doping was achieved by adding ammonia gas with flow rate of 180 sccm in the gas mixture at the time of deposition.

Thermal Gravimetric Analysis (TGA) were carried out on Mettler–Toledo (TGA/SDTA851) thermal analyzer under argon flow at the heating rate of 5°/min to obtain information on the decomposition and the burning properties of carbon nanotubes and impurities present in it. The temperature of the sample was varied from room temperature to 900 °C. The Fourier transform infrared (FTIR) spectrometer were recorded on Nicolet Magna 550 FT-IR Spectrum. The samples for FTIR studies were prepared by suspending approximately 6 mg of MWCNT materials in ~15 ml isopropyl alcohol by sonication with an ultra sonic probe for several minutes. One drop of this solution was sprayed onto silicon wafer and a uniform thin MWNT film on the IR transparent silicon substrate was thus obtained. FTIR studies were carried out in the range of 400–4000 cm$^{-1}$ in the absorbance mode. The FTIR results with the support of TGA results give a reasonably good picture of the attachment on the carbon nanotubes.

3. Results and discussion

Fig. 1(a) shows the SEM micrograph of high density MWCNTs grown on nickel electroplated copper substrate after ammonia plasma treatment for 2 min. The average length and diameter of the tubes are 100 μm and 20 nm respectively. Fig. 1 (b–c) show TEM images of the multiwalled carbon nanotubes free of encapsulated and with encapsulated catalytic nickel particles, respectively. The inset in Fig. 1(c) shows that the inner and outer diameter of the CNT is 12.84 and 18.43 nm respectively and the tips of the CNTs are closed. Fig. 1(d) is the High-Resolution Transmission Electron Microscopy (HRTEM) image of graphitic walls of a typical MWCNT.
graphitic walls of a MWCNT. The separation between two consecutive walls is 3.22 Å.

FTIR is used to characterize the functional elements absorbed by carbon nanotubes. Fig. 2 (a–d) shows the FTIR spectra in the range of 400–4000 cm\(^{-1}\) of a) as-grown tubes, b) of the tubes collected after TGA at 400 °C, c) of the tubes annealed at 600 °C, and d) of the tubes collected after TGA at 900 °C. FTIR of a) shows dominant peaks at 1026, 1250, 1372, 1445, 1736, 2362, 2851, 2925 cm\(^{-1}\) which corresponds to Si–O, C–N, N–CH\(_3\), CNT, C–O, C–H\(_x\) respectively. The infra-red absorbance at 1026 cm\(^{-1}\) is consistent with Si–O stretching vibrations due to slightly different concentrations in the native oxide layer of the silicon before and after coating with MWCNTs film [13].

Out of the above identified bonds, the presence of C–N and N–CH\(_3\) bonds at 1250 and 1372 cm\(^{-1}\) is most interesting. The strong peaks at 1250 and 1372 cm\(^{-1}\) are consistent with C–N and N–CH\(_3\) stretching vibrations attributed by Choi et al. [14] to the presence of intercalated N atoms between the graphite layers at the inner part of the nanotube walls. However, in our opinion the intercalated nitrogen atoms in between the graphite walls may not be strongly IR active. The halfwidths of the C–N and N–CH\(_3\) peaks are 36.72 and 18.53 cm\(^{-1}\) respectively, and suggest that the chemisorption process may be dominant implying chemical bonding between carbon and nitrogen atoms. It has been pointed out [15–18] that substituting a N atom in place of a C atom in a \(sp^2\) bonded carbon network will induce strong IR activity; consequently the absorption in the 1200–1600 cm\(^{-1}\) region is expected if the N atoms are bonded into the carbon network. We therefore strongly believe that N doping of graphene sheets may be taking place and a C–N bond identical to the \(sp^3\) bonded carbon nitride sample may be forming. Features at 1445 and 1736 cm\(^{-1}\) attributed to MWCNT vibrational modes are also apparent [19]. The peak at 2362 cm\(^{-1}\) corresponds to the C–O bonds and the features between 2851 and 2925 cm\(^{-1}\) are consistent with C–H\(_x\) stretching vibrations of chemisorbed hydrogen of various types presents in all carbon films [20,21].

The intensity of the peaks due to N–CH\(_3\), C–N and C–H are gradually suppressed, after annealing at 400 °C. The suppression of the peaks would be related to the gradual removal of nitrogen and hydrogen bonded species as impurity. The bonding of N to carbon atom in graphene sheet will give rise to a defect in structure, which would get annealed, at high temperature. This results in the reduction of the intensity of the IR peaks with annealing. Further annealing of the sample at 600 °C does not induce any appreciable change. It is interesting to note that these peaks vanish on annealing at higher temperature (900 °C) implying that at high temperature the defects inside the tubes are getting strongly mobile leading to the destruction of the attachments along with the tubes.

TGA/DTA curve in Fig. 3 reveals a small weight loss due to water removal around 80 °C. The dominant weight loss steps are due to the removal of carbon materials and also due to the decomposition of nanotubes [22–24] taking place in the temperature range between 400 and 600 °C. The weight loss starts near 400 °C and the process completes by 600 °C. This result agrees with the FTIR spectra in Fig. 1(b–c) discussed above where we have shown a significant decrease in the intensity of IR peaks upon annealing to 400 °C. The MWCNTs are completely destroyed at 900 °C, suggesting that at this temperature amorphous carbon as well as MWCNTs converts to gaseous form. The complete removal of all the dominant peaks from the FTIR spectra in Fig. 1(d) confirms the burning of MWCNTs at 900 °C resulting in the change of the color of the sample.

4. Conclusion

FTIR technique gives information about gaseous elements attached to the tube. Nitrogen attachment is evident from strong and intense IR peaks at 1250 and 1372 cm\(^{-1}\). From the intensity and halfwidth of these peaks we conclude that the N atom is incorporated at substitutional
sites in the carbon network. TGA/DTA has been used to study the weight loss of carbon nanotube as a function of temperature. We found that the dominant weight loss occurs between 400 and 600 °C range and agrees well with disappearance of IR peaks corresponding to N-attachment. TGA can be used to get the information about the weight loss of the sample.

Acknowledgements

The authors would like to thank Dr. P.V. Satyam of Institute of Physics Sachivalaya Marg, Bhubaneshwar for high-resolution transmission electron microscopy (HRTEM) measurements.

References