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FTIR studies of nitrogen doped carbon nanotubes

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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_x 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

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Ni on copper foil was performed in an electroplating bath. The copper substrate (1 cm × 1 cm × 0.1 mm) was used as cathode and a thin platinum wire was used as the anode. Commercial grade nickel sulfate ($NiSO_4 \cdot 7H_2O$) (275 g/l) and nickel chloride ($NiCl_2 \cdot 6H_2O$) (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

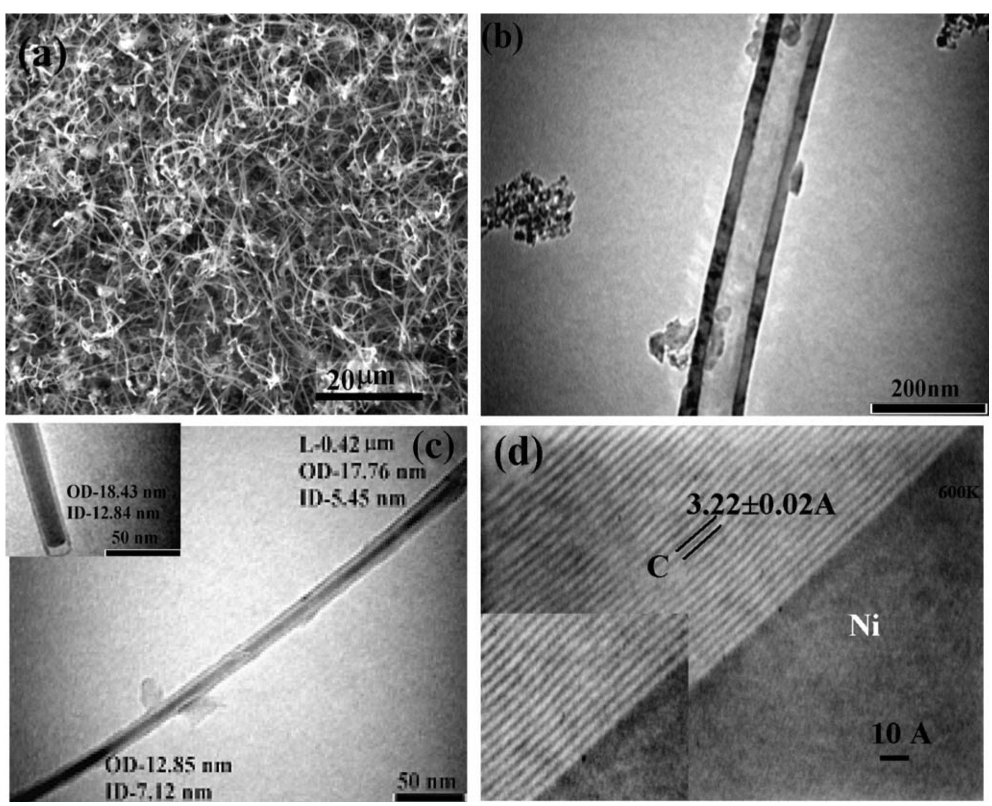

Fig. 1. (a) SEM micrograph of a sample of multiwalled carbon nanotubes deposited on a copper substrate. The high density of tubes is noteworthy. (b)–(c) TEM images of the multiwalled carbon nanotubes free of encapsulated and with encapsulated catalytic nickel particles, respectively. (d) High-Resolution Transmission Electron Microscopy (HRTEM) image of graphitic walls of a typical MWCNT.