

Functionalization of Carbon Nanotubes Using Nitric Acid Oxidation and DBD Plasma

M. Vesali Naseh, A. A. Khodadadi, Y. Mortazavi, O. Alizadeh Sahraei, F. Pourfayaz, and S. Mosadegh Sedghi

Abstract—In this study, multiwall carbon nanotubes (MWNTs) were modified with nitric acid chemically and by dielectric barrier discharge (DBD) plasma in an oxygen-based atmosphere. Used carbon nanotubes (CNTs) were prepared by chemical vapour deposition (CVD) floating catalyst method. For removing amorphous carbon and metal catalyst, MWNTs were exposed to dry air and washed with hydrochloric acid. Heating purified CNTs under helium atmosphere caused elimination of acidic functional groups. Fourier transformed infrared spectroscopy (FTIR) shows formation of oxygen containing groups such as C=O and COOH. Brunauer, Emmett, Teller (BET) analysis revealed that functionalization causes generation of defects on the sidewalls and opening of the ends of CNTs. Results of temperature-programmed desorption (TPD) and gas chromatography (GC) indicate that nitric acid treatment create more acidic groups than plasma treatment.

Keywords—Carbon nanotubes (CNTs), chemical treatment, functionalization, plasma.

I. INTRODUCTION

CARBON nanotubes (CNTs) are an interesting new molecular form of carbon in the fullerene family, discovered by Iijima [1]. Due to unique electronic and mechanical properties of CNTs [2] and also their resistance to acid/basic media [3] they have attracted a special attention. These nano-materials are very promising for the development of gas sensors [4] and composites fabrication [5].

However, the hydrophobic and inert nature of the surface of as-prepared nanotubes is unfavorable for these applications [6]. In order to improve the interaction of CNTs and foreign

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molecules it is necessary to modify the surface of nanotubes. Oxygen-containing groups which are interesting to improve the interaction of CNTs with the solvent matrix are formed on the surface of nanotubes either by chemical treatment such as nitric acid [7] or dry treatment like DBD plasma in the oxygen-based atmosphere [8]. Due to its short period of its procedure, its low temperature, less damage and less pollution, plasma treatment is more paid attention by scientists in comparison with chemical treatment. The excited species, radicals, electrons and ions within the plasma atmosphere break the C-C bonds and creating active sites for bonding of functional groups [9].

It is known that the amount and type of oxygen-containing functional groups depends on the treatment methods. In the case of nitric acid, formation of acid groups like carboxyl, phenol and lactol are reported [10-11]. However, when oxygen plasma is under study, formation of functional group such as carbonyl, and lactone is observed [8,9]. In the present paper functionalization of CNTs by chemical and dry oxidation is investigated.

II. EXPERIMENTAL

The CNTs used in this study are multiwall carbon nanotubes (MWNTs) which are prepared by chemical vapour deposition (CVD) floating catalyst method. In this method, source of Fe catalyst is ferrocene which is dissolved in xylene as a liquid carbon source and this solution is carried to synthetic reactor by Argon. During synthesis process, amorphous carbon is also produced. For removing this impurity, the CNTs have been oxidized in the presence of dry air at 492°C for 40 minutes. In order to eliminate metal catalyst, the CNTs are refluxed in HCl for 2 hr. For excluding functional groups which are produced during these two purification processes, the CNTs were heated to 1000°C under helium. Functionalization process is carried out using two separate methods. One method is a chemical treatment which includes refluxing in HNO₃ for 4 hr and the other is done by dry treatment using DBD plasma under air atmosphere. DBD plasma reactor consists of cylindrical electrodes employs high voltage of 1-10 kV with an output frequency of 0.5-10 kHz and is provided with gas inlet and outlet system.

An ultrasonic homogenizer (Hielscher,250UL) is used to disperse CNTs in water. FTIR and BET were used to characterize surface of functionalized CNTs. For the quantitative analysis of the functional groups, TPD in helium was used with gas chromatography (GC) analysis.

III. RESULT AND DISCUSSION

Fig. 1 shows SEM image and TGA curve of pristine MWNTs. In this curve, two peaks at 492^oC and 520^oC characterize oxidation of amorphous carbon and CNTs respectively. Time and temperature of thermal oxidation process are chosen from this curve.

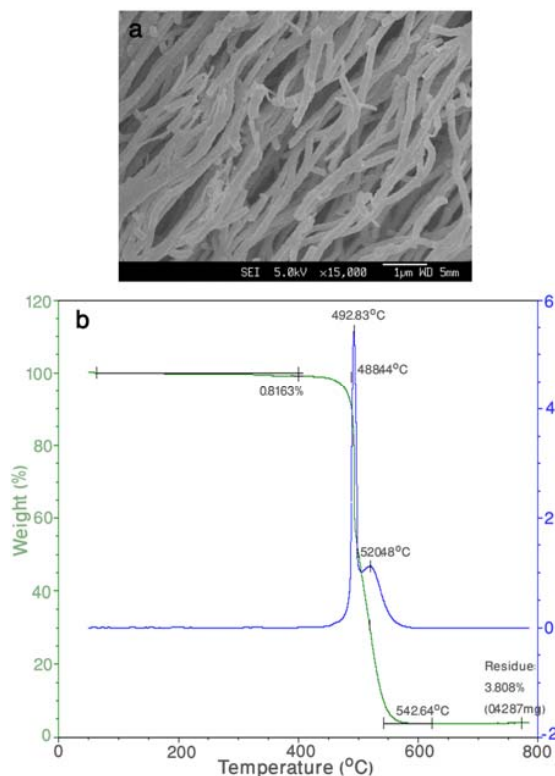


Fig. 1 (a) SEM image and (b) TGA curve of as-prepared MWNTs

Nanotubes due to their carbonic nature and also presence of van der Waals attraction between tubes are hydrophobic, So they exhibit low dispersibility in water and organic solvents[12] and irradiating them with ultrasonication, does not improve their dispersibility (Fig. 2a), However, chemical and plasma treated CNTs show hydrophilic behaviors. Acid washed MWNT (Fig. 2b) shows better dispersibility in comparison with air plasma treated one (Fig. 2c). This may be due to the OH groups formed in the acid washed case [13] that make hydrogen bonding with water molecules.

FTIR spectra of pristine and functionalized CNTs are shown in Fig. 3. The peaks which are identified at 1360, 1710 and 3402 cm^{-1} characterize C-O, C=O and O=H bonds in chemical modified nanotubes. Peaks at 1710 and 3450 cm^{-1} can be attributed to acidic groups like carboxyl, phenol and lactol. Peak at 1576 cm^{-1} assigns C=C bond in CNTs which is

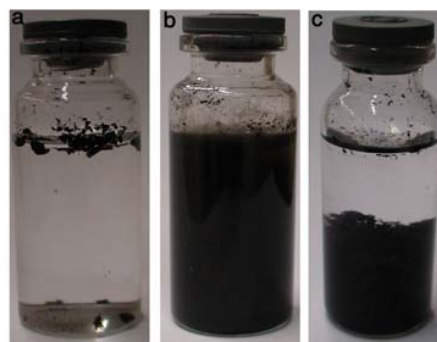


Fig. 2 Dispersibility behavior of (a) as-prepared (b) acid washed (c) air plasma treated CNTs after three weeks. The content of CNTs in each of the bottles is 0.5mg/mL and they are sonicated for 10 minutes.

appeared after disappearing of bond symmetry because of connection of oxygenated functional groups [13-15]. Since atmosphere of plasma is dry air and there is no hydrogen molecule, the band which assign O=H is vanished. In this case peaks at 1310 and 1710 cm^{-1} may be attributed to acidic groups such as lactone or basic groups such as ketones, chromene and pyrones[10].

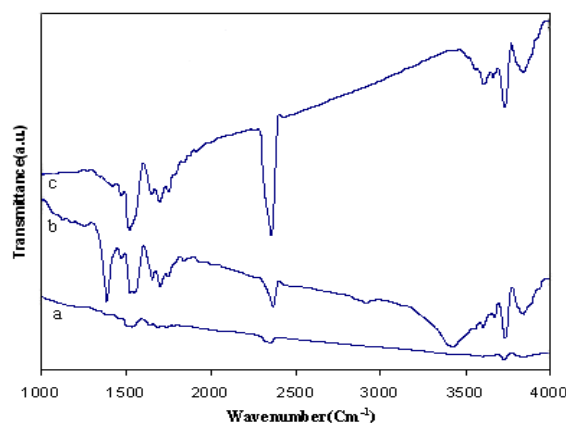


Fig. 3 FTIR spectra of (a) pristine (b) chemical treated (c) plasma treated CNTs.

TPD results with functionalized nanotubes are shown in Fig. 4. As seen in this figure, there are two peaks at 250^oC and 750^oC. It seems that at relatively low temperatures, lactone, lactol and carboxylic groups are decomposed. However, two adjacent carboxylic groups may be first dehydroxylated to the cyclic anhydride which decomposes at higher temperatures than that of free carboxylic groups [16]. It is generally accepted that evolution of CO₂ at low temperatures is mainly due to the decomposition of carboxylic acid, lactone and lactol groups, whereas CO is derived from the decomposition of, carbonyl and quinone. Diffusion of the evolved gases is rather slow in narrow pores, and CO molecules may react with surface-bound oxygen and oxidize to CO₂, or CO₂ molecules hitting the pore walls may form two CO molecules [7,16]. Table I shows the total amount of oxygen containing groups evolved as CO₂ and CO in the period of TPD process.

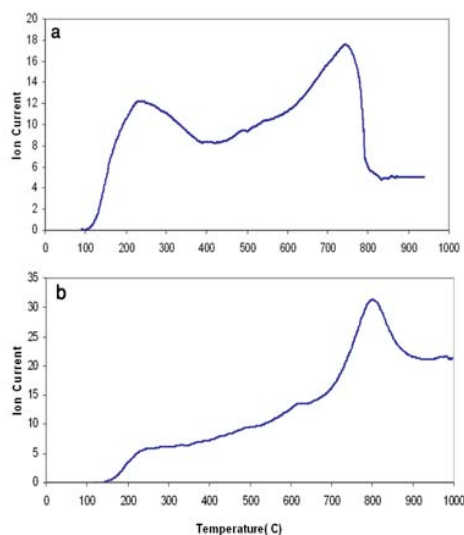


Fig. 4 TPD profile of (a) chemical treated CNTs (b) plasma treated CNTs

According to these results, chemical treatment in comparison with plasma treatment generates more functional groups. Results of BET analysis (Table II) indicate that both chemical and plasma functionalization increase the specific surface area of nanotubes. Functionalization causes opening up of tube ends [17] and generation of defects on the sidewall of nanotubes [18], therefore access into the cavity of the nanotubes can be achieved.

CNTs tend to form long bundles stabilized by numerous π - π interaction between the tubes. Formation of functional groups on the surface of nanotubes generates a repulsion force which leads to debundling of nanotubes and therefore causes surface area to increase [12].

TABLE I
TOTAL PERCENTAGE OF OXYGEN CONTAINING GROUP EVOLVED AS CO₂ AND CO

Symbol	Groups evolved as CO ₂ (%)	Groups evolved as CO (%)
Chemical treatment	1.5	1.6
Plasma treatment	0.52	0.7

TABLE II
BET SURFACE AREA OF PRISTINE AND FUNCTIONALIZED CNTs

Symbol	Oxidized nanotubes	Chemical treated nanotubes	Plasma treated nanotubes
Specific surface area (m ² /g)	94.45	248.8	236.45

IV. CONCLUSION

Purification process like thermal oxidation and acid washing produce oxygenated functional groups. Due to its strong oxidation feature and its lengthy process, functionalization using nitric acid could be more destructive in comparison with the plasma treatment. However plasma

treatment creates less functional groups than that of acid treatment. In other words, plasma treatment mainly functionalizes the surface of the material, whereas as far as chemical treatment is concerned, besides affected surface, some changes in the bulk of the material might occur.

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