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A comparison of effects of plasma and acid functionalizations on structure and electrical property of multi-wall carbon nanotubes

Fathollah Pourfayaz[a,*], Yadollah Mortazavi[b], Abbas-ali Khodadadi[c], Seyed Hassan Jafari[d], Shahab Boroun[c], Masoud Vesali Naseh[c]

[a] Department of Renewable Energies and Environment, Faculty of New Sciences and Technologies, University of Tehran, Tehran, Iran
[b] Nanoelectronics Centre of Excellence, University of Tehran, P.O. Box 11155-4563, Tehran, Iran
[c] Catalysis and Nanostructured Materials Research Laboratory, School of Chemical Engineering, University of Tehran, Tehran, Iran
[d] School of Chemical Engineering, University of Tehran, P.O. Box 11155-4563, Tehran, Iran

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ABSTRACT

Multi-wall carbon nanotubes were functionalized by dielectric barrier discharge plasma in air, CO_2 and He (followed by exposure to NH_3) and also by refluxing in concentrated nitric acid for 2 and 4 h. The influence of these treatments on structural and electrical properties of the carbon nanotubes was investigated. Fourier transform infrared technique was used to identify functional groups on surface of the carbon nanotubes. The graphitic structure of carbon nanotubes was characterized by Raman spectroscopy and the specific surface areas were measured by Brunauer–Emmett–Teller technique. The results indicated that the nitric acid treatment significantly destroys the graphitic structure of the carbon nanotubes and shortens them while the plasma treatments have very little damaging effects on the structure. In order to study effects of the utilized treatments on electrical properties, buckypapers were prepared from the carbon nanotubes and their electrical surface resistivities were measured. The measurements showed that the acid treatment increases the electrical surface resistivity of the buckypapers while the plasma treatments do not change it considerably. Among all the studied treatment methods, the plasma treatment was found to be the most efficient approach for functionalization of carbon nanotubes.

1. Introduction

Unique properties of carbon nanotubes (CNTs) have attracted many interests from both academia and industries for their use in various fields such as nanoelectronics and renewable energies [1]. However, practical applications of CNTs are facing some challenges. CNTs are chemically inert and tend to form bundles due to strong van der Waals forces. This can reduce the efficiency of CNTs for most applications [2]. In order to increase interactions between CNTs and other materials and boost their performance, formation of proper functional groups on the surface of CNTs is suggested. However, functionalization of CNTs can considerably destroy graphitic structure of the CNTs and deteriorate its transport properties substantially. Hence, researchers try to develop functionalization methods which have minimal destructive effects on the structure and properties of the CNTs.

CNTs are functionalized covalently or noncovalently. The noncovalent functionalizations, such as molecular wrapping in which long molecules are wrapped around CNTs, do not have significant negative impact on CNTs intrinsic properties. However, using this technique, the interactions between the functional groups and CNTs are basically very weak.

CNTs are usually covalently functionalized by different methods such as wet chemistry and exposure to high temperature vapors [3]. Wet chemistry uses inorganic acids with various concentrations and is widely used to functionalize CNTs. It has been shown that this treatment not only destroys the graphitic structure of the CNTs but also cuts the CNTs and shortens their length [4–6]. The extent of damages depends on the treatment conditions such as acid concentration, duration and temperature of the treatment.

Structural damages induced by this method result in an increase in the electrical resistivity of CNTs which in turn reduce their performance for many applications such as synthesis of conductive polymer composites with nanosize component [7]. Plasma treatment is another procedure to functionalize CNTs covalently [8–10]. In this method the CNTs maintain their structural integrity to a large extent [11]. This is mainly due to the mild conditions applied in the course of functionalization. For instance, plasma treatment may be performed at room temperature with short treatment time. Depending on the plasma atmosphere used (oxygen, nitrogen, ammonia, etc.), different functional groups can be formed on the CNTs surface. The quantity of functional groups can also be

* Corresponding author. Tel.: +98 21 61118517.
E-mail address: Pourfayaz@ut.ac.ir (F. Pourfayaz).

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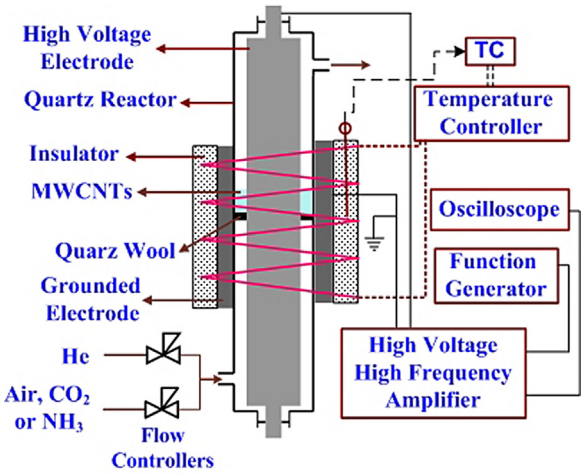

Fig. 1. Schematic of the set-up used to functionalize the CNTs.

controlled by plasma parameters such as voltage and duration of plasma exposure [8–10].

In this work, multi-wall CNTs are functionalized by different plasma gases namely air, CO_2 and $He + NH_3$ and also by a conventional nitric acid treatment. The effects of these various treatments on the structure and electrical properties of the CNTs are determined. A detailed comparison between these methods of functionalization is presented in order to introduce possibly the best treatment method as far as the properties of CNTs are concerned.

2. Experimental

2.1. Functionalization of CNTs

Multi-wall CNTs (purity: >95%) were purchased from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China). In order to remove most of the defects and functional groups, formed on the surface of the CNTs during synthesis and purification processes, the CNTs were pretreated prior to functionalization. They were annealed under He gas flow while heated to 1000 °C at a rate of 5.0 °C/min and then remained at 1000 °C for 30 min. The temperature was then reduced to room temperature under continuous He gas flow. The pretreated CNTs prepared as such are called annealed CNTs and hereafter designated as A-NT.

In plasma method, the annealed CNTs were functionalized by a dielectric barrier discharge (DBD) plasma. Air, He (followed by exposure to NH_3), and He plus CO_2 were used to functionalize the CNTs. Fig. 1 shows ~~the~~ schematic of the set-up used to functionalize the annealed CNTs by the DBD plasma. Details of the conditions and set-up have been described elsewhere [8–10]. The annealed CNTs functionalized by the air plasma under a power of 90 W (voltage = 9 kV and frequency = 2.5 kHz) and with a treatment time of 5 min, are called functionalized CNTs in air (denoted as F-NT-air). The annealed CNTs were also functionalized by He plus CO_2 plasma (hereafter referred to as F-NT-CO_2), under the following conditions: voltage = 9 kV, frequency = 2.6 kHz, duration = 20 s and He vol% = 60. The annealed CNTs treated by the He DBD plasma (voltage = 9 Kv, frequency = 2.6 kHz and duration = 6 min) followed by an exposure to NH_3 gas, are symbolized as F-NT-NH_3.

In order to functionalize the CNTs by acid treatment, the annealed CNTs were refluxed in a concentrated nitric acid for 2 or 4 h. They were then washed with deionized water and centrifuged for several times until the solution pH reached to about 7. The acid functionalized CNTs were finally dried overnight at about 90 °C. Hereafter, the acid treated CNTs for 2 and 4 h are designated as Acid-NT-2 h and Acid-NT-4 h, respectively.

2.2. Characterization of CNTs

Fourier transform infrared (FTIR) technique was used to detect the formation of functional groups on the surface of the CNTs. The FTIR spectra were obtained using a Bruker Vector22 spectrometer with a resolution of 5 cm^{-1}. Due to the large absorbance of CNTs, FTIR spectroscopy with diffuse reflectance (DRIFTS) accessory was utilized. Prior to DRIFTS-FTIR, the CNTs were purged with He gas at 100 °C for 30 min. Raman spectroscopy was also used to compare the extent of defect sites in the structure of CNTs formed during functionalization by different methods. Raman measurements were performed using an Almeg Thermo Nicolet Dispersive Raman Spectrometer by the second harmonic at 532 nm of an Nd:YLF laser. Specific surface areas of the CNTs were measured by nitrogen adsorption after degassing of the samples, using a Quantachrome CHEMBET-3000 apparatus. The error associated with the BET surface areas measurements was about ± 2 m^2/g.

In order to investigate the effects of different treatments on the electrical properties of the CNTs, the buckypapers were prepared through multiple steps of CNTs dispersion and suspension filtration (Fig. 2). For this purpose 100 mg of CNTs were dispersed in 20 ml of deionized water and were sonicated for 30 min. The suspension was then immediately filtered. In order to measure the surface electrical resistivity, the buckypapers were cut into rectangular pieces (10 × 3 mm). A two-point method was used with contacts formed by a silver paint. The surface electrical resistivity of each sample which is reported here is the average of three measurements. The experimental error of the surface electrical resistivity measurement was about ± 0.05 of Ω/sq.

3. Results and discussion

3.1. FTIR spectra of the CNTs

In Fig. 3, the FTIR spectra of the annealed and functionalized CNTs are presented. In the spectrum of A-NT sample, a weak peak at around 1530 cm^{-1} is observed. This peak, attributed to C=C stretching band of the CNTs, indicates the presence of small quantities of functional groups and defects on the CNTs surface even after annealing at 1000 °C. As is observed, functionalization of the

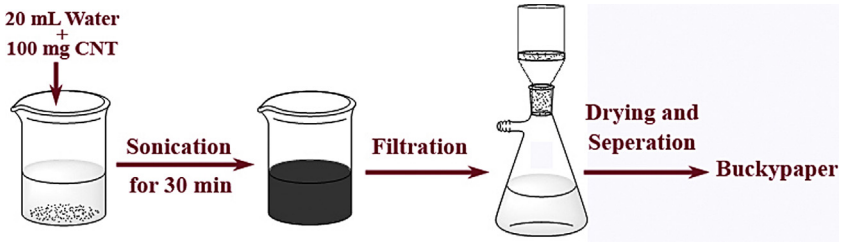

Fig. 2. Schematic of the steps of preparation of the buckypapers.