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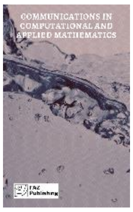

Tuning of the Structure and Electrical Properties of MWCNTs by Dielectric Barrier Discharge (DBD) Plasma Treatment

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Abstract: This paper aims to investigate the effect of oxygen and nitrogen dielectric barrier discharge (DBD) plasma treatment at different voltages on the structure and electrical properties of metallic multi-walled carbon nanotubes (MWCNTs). The surface structure and electrical properties changes before and after treatments were studied by using Transmission Electron Microscopy (TEM), Fourier Transform Infra-Red (FTIR) and hall effect measurement. The degree of defect was observed increased along with increasing applied voltage of plasma, obviously demonstrated from TEM measurements. For the MWCNTs-O_2, the FTIR exhibited formation of oxygen-containing groups such as C=O and COOH on the MWCNTs and the addition of N-H vibration bending for the MWCNTs-N_2. The highest hall mobility (172.9 cm^2/Vs) was achieved when MWCNTs treated with nitrogen at 12kV which is slightly higher than mobility of SWCNT thin film (150 cm^2/Vs) reported by previous researcher. This showed that at higher intensity, the nitrogen-containing group can modify the metallic MWCNTs to semiconducting behavior.

Keywords: metallic MWCNTs, DBD plasma treatment, hall mobility.

1.0 Introduction

In recent years, carbon nanotubes (CNTs) have received much attention owing to their nanoscale dimension and superior materials characteristics [1]. However, as-produced CNTs have a variety of tube diameter and chiral angle that influence their metallic and semiconducting properties. Practically, single-walled carbon nanotubes (SWCNTs) that are produced by various synthesis methods contain one-third metallic properties and the remaining two-thirds act as semiconductors [2]. Meanwhile, multi-walled carbon nanotubes or bundles of CNT are prone to be metallic due to their large diameter and complex structure of each tube [3]. This recently inevitable structural intermixture of as-synthesized SWCNTs prohibits the widespread application of high performance transistors, sensors and diodes [4-6].

Currently, various efforts have been employed to separate or use selective growth of semiconducting and metallic SWCNTs [7-12]. To date, it is still a challenging work to control the production of semiconducting CNTs on a large scale. In addition, the generation of SWCNTs is very costly and complicated as compared to MWCNTs that can be produced on a vast scale with a reasonable price [13]. With regard to this issue, the modification of MWCNTs surface and electrical properties to ensure that they portray a semiconducting behavior needs further exploration. Previous work by Collin et al. [2] proposed the conversion of metallic MWCNTs into semiconducting one by burning or removing the outer carbon shells via electrical breakdown. However, this method remains uncontrolled and can cause cascade breakdown, thus, might destroy CNT devices.

Recent studies into defects and imperfections of MWCNTs could propose a possible route to modify their electronic nature. For example, v-CNT tips that were activated from MWCNTs doped with nitrogen can allow the tuning of their electronic properties [14]. Janas et al. exposed the CNT nanotube films to vapors from harsh chemicals in order to modify their electronic

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properties [15]. The structural and electrical properties of CNT can also be altered by the replacement of carbon atoms with boron dopants [16] and an oxidizing agent [17]. Various approaches have been stabilized to change the electrical and electronic peculiar of MWCNTs, like polymer wrapping [18, 19], electrochemical methods [20], fluorination [21] and plasma treatment [22]. Plasma treatment provides some valuable advantages, involving the requirement of short time treatment, the capability to be processed at room temperature and it is also an environmentally friendly process.

Different defect structures and functional groups can be formed on the CNT surface depending on the plasma parameters, such as applied voltage, plasma gas used, time treatment, and the power and frequency of the plasma. The C=C bond of CNT is bombarded by the excited molecules and it generates radicals during plasma discharge, thus, produces open ends and defect sites as the main sites for functionalization. Dielectric barrier discharge (DBD) plasma is the simplest and most flexible plasma amongst the different methods used to create a plasma. This method is characterized by the existence of at least one dielectric barrier in contact with the discharge between cylindrical or two planar electrodes connected to a high voltage power supply.

In this work, the MWCNT defects were produced by using atmospheric pressure oxygen and nitrogen DBD plasma treatment at 50 Hz. The frequency of 50 Hz for DBD is more practicable for industrial usage because it needs no impedance matching network compared to high frequency DBD. High frequency DBD has a very complicated impedance matching network and unnecessary power losses through dielectric barrier heating. The objective of the present work is to study the probability of altering the electronic properties of metallic MWCNT by DBD treatments by using two different gases at atmospheric pressure. Changes in the structural surface and electrical properties that appeared on the MWCNTs after the treatments were examined by using TEM, FTIR and hall effect measurement.

2.0 Experimental Procedure

2.1 Materials

The commercial MWCNTs powder was prepared via Combustion Chemical Vapour Deposition (CCVD) without purification. The length was about 10-30µm and the outer and inner diameters were between 20-30 nm and 5-10 nm, respectively.

2.2 DBD Apparatus

The experiments were performed in ambient air using the experimental set-up, as shown in Figure 1. Two gases which are oxygen and nitrogen were used separately as a buffer gas. Discharges were produced between two circular plane parallel copper electrodes, 60 mm in diameter. In the case of DBD, both electrodes were enclosed by a 2 mm thick glass material. The glass material serves as a dielectric barrier which permits the charge build up and maintains the plasma from micro discharge. An additional fine wire mesh (#325) was inserted between the electrode and the glass in order to obtain a stable glow discharge. In both cases, the gap distance and gas flow rate were kept constant at 2mm and 1lpm, respectively. A voltage between 1 to 20 kV at a frequency of 50 Hz was used as the voltage supply.

The voltage applied to the electrodes was measured through a high voltage probe (Tektronix P6015A, 1000x). The discharge current was measured by using a Pearson Rogowski current monitor through a 50 Ω resistor connected in series to the ground.
The waveform of the applied voltage and discharge current were recorded by using a PicoScope 5242A.

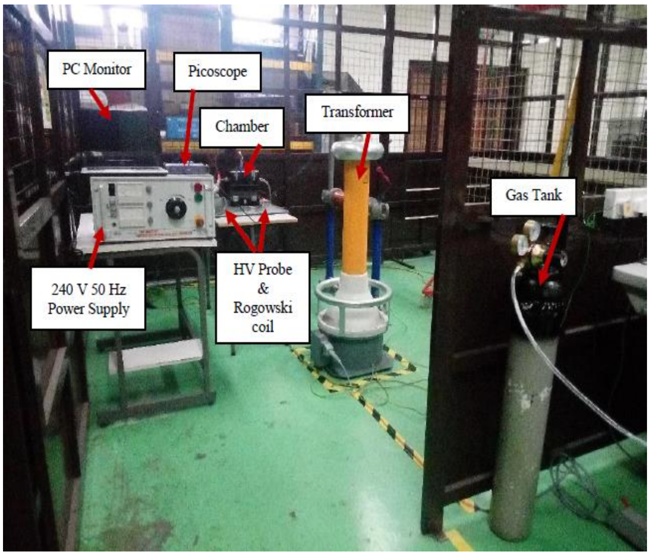


Fig. 1 - Apparatus setup for DBD plasma treatment

2.3 Thin Film Fabrication

The fabrication of MWCNTs thin film was done on glass substrate, by using drop casting method. 0.6 mg of treated and untreated MWCNTs powders at different gas sources and different plasma voltages, was dissolved in 60 mL DI water and left for 2 h in sonic bath and stirred for 6 h to get a uniform solution. Then, each MWCNTs solution was dropped on a cleaned glass substrate by using micropipette in the same volume so that a similar thickness of thin film for all samples can be obtained. Finally, all samples were baked at 100 ^{o}C to evaporate the DI water.

2.4 Materials Characterizations

Materials characterizations were carried out in two forms, which were in powder and thin film forms. The pristine and treated MWCNTs structures were characterized in powder form using FTIR Spectroscopy and Raman Spectroscopy. The MWCNTs solution forms were required to observe and analyze the internal and detail structure of the pristine and treated MWCNTs by using the Transmission Electron Microscopy (TEM). To analyze their electronic properties, thin films of pristine and treated MWCNTs deposited with two electrodes (Al and Au) by using thermal evaporation were analyzed by using the current voltage (IV) measurement.

2.4.1 Transmission Electron Microscopy (TEM)

TEM was accomplished by dipping a holey-carbon TEM grid into a suspension of the MWCNTs and shot by using a TEM Hitachi HT7700 field-emission gun. It operating voltage was set to 297 kV. The images were captured by a CCD camera mounted on a GIF 200 electron energy loss spectrometer.

2.4.2 Fourier Transform Infra Red (FTIR) Spectroscopy

The FTIR spectra were used to identify the functional group attached to the MWCNTs surface. The spectra were obtained and recorded by using a Perkin Elmer spectrophotometer by mixing 6mg of CNT powder with KBr and transformed into a pellet.

2.4.3 Raman Spectroscopy

The defect structure of the MWCNTs samples was investigated using a Raman Horiba Xplora Plus system with excitation line set to $\lambda = 532$ nm and magnification set to 40x. Detailed scans from 800 cm^{-1} to 2000 cm^{-1} were conducted on each MWCNT sample. Common peaks that appeared in the Raman Spectra for MWCNTs were D-band (1350 cm^{-1}) which represented as defect present in CNT and G-band (1580 cm^{-1}) that shows crystallinity of the tubes.

2.4.4 Hall Effect Measurement

Hall effect measurement was conducted using Ecopia HMS-300 Hall Effect Measurement system.The electrical contact was made by placing small silver conductive ink on the four corners of thin film. The sample then was mounted onto the Lakeshore sample holder.

3.0 Results and Discussions

3.1 Transmission Electron Microscopy (TEM)

The internal structure of the MWCNT before and after DBD plasma treatment was examined by using a Transmission Electron Microscopy (TEM). TEM image of MWCNT-p in Figure 2(a) shows well-aligned and concentric graphite walls. Only residual amorphous were infrequently observed on the MWCNTs surface before plasma treatment.

Basically, the MWCNTs surface morphology should be affected by charged ions and electrons generated during the plasma treatment; physically and chemically. In this work, the structural damages (e.g., sidewall damage and distortion) and surface modifications were induced by plasma treatment. Moreover, the defect degree was observed to be increased along with increasing applied voltage of plasma, obviously demonstrated from the TEM measurements. Figure 2(b), 2(c) and 2(d) show TEM images for MWCNTs treated with oxygen DBD plasma treatment (MWCNT-O_2). There was an increase in the defects on the MWCNT surfaces at 10kV, 12kV and 14kV, respectively as compared to the smooth surface of pristine MWCNTs. Through the lowest applied voltage (10kV) of plasma, the tube surface experienced some defects and structural distortions as indicated by the red arrow. The morphology of CNT was evidently changed with the increase in applied voltage of plasma treatment. When the applied voltage was increased to 12kV and 14kV, the tube surface distortion was increased and the structure of MWCNT was obviously disordered.

Compared to the MWCNT-O_2, the surface morphologies of MWCNTs treated with nitrogen plasma treatment (MWCNT-N_2) exhibited very distinct morphologies that were significantly different from the pristine MWCNTs. These tubes structures were divided into hollow sections isolated by one to a few graphitic layers and always referred to as bamboo-like structures as shown in Figure 2(e) and 2(f). At a higher applied voltage of nitrogen plasma treatment, the bamboo-like structures of the tubes were damaged and tended to become disordered as presented in Figure 2(g). This experiment suggested that, when the applied voltage was increased during plasma, the stable plasma will change to unstable or filamentary plasma. At a higher voltage, this filamentary plasma will cause more tubes to become damaged and disordered. Defect structures were created on the MWCNT graphite layers during plasma treatment due to the bombardment of high energetic ions from the plasma. Thus, this will cause other defects such as dangling bonds. They may experience sp^3 defects since these interlayers cross-linked, therefore, lead to bents or irregular graphitic structures. The interaction between the excited species, such as radicals, electrons, ions and UV light with the CNT surface can break the C-C bonds during plasma treatment.

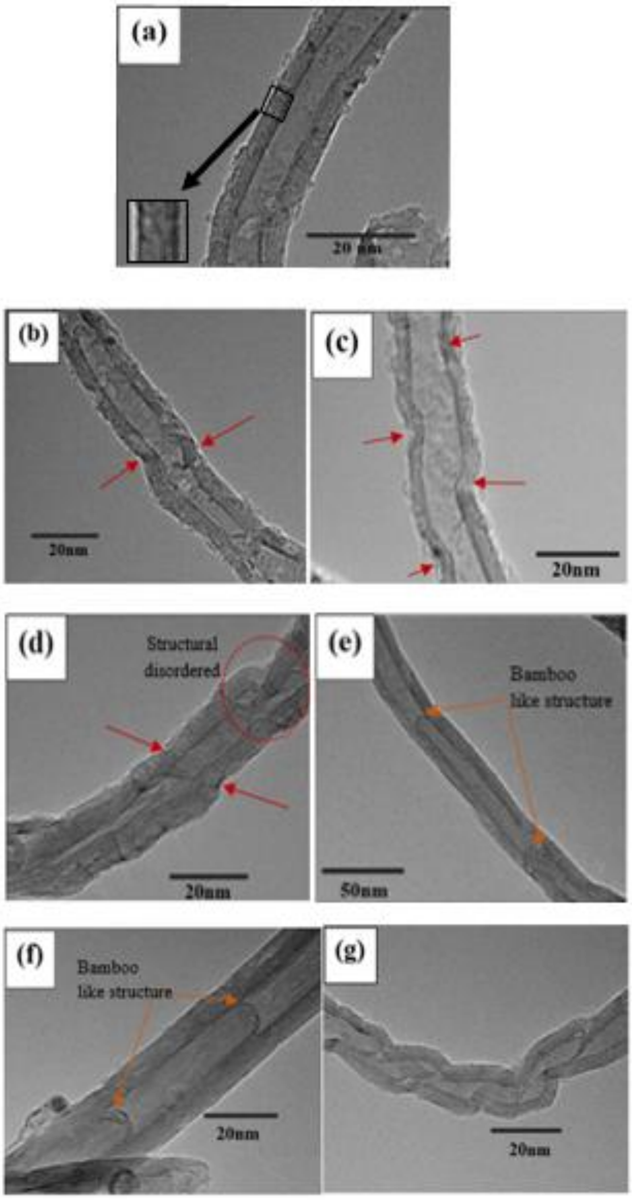
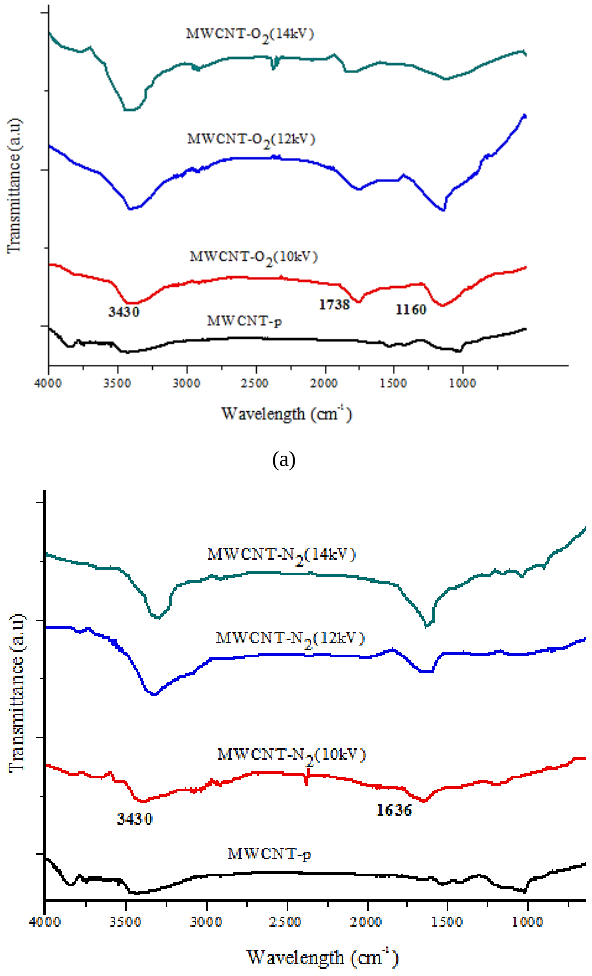


Fig. 2 - Transmission Electron Microscopy (TEM) images for (a) MWCNT-p, (b) MWCNT-O_2 at 10kV, (c) MWCNT-O_2 at 12kV, (d) MWCNT-O_2 at 14kV, (e) MWCNT-N_2 at 10kV, (f) MWCNT-N_2 at 12kV and (g) MWCNT-N_2 at 14kV.

3.2 Fourier Transform Infra Red (FTIR) Spectroscopy

The functional groups attached to the MWCNT surface resulting from plasma treatment by oxygen and nitrogen gases was identified using FTIR spectroscopy. Figure 3 shows the spectra of pristine MWCNT (MWCNT-p), MWCNT treated with oxygen (MWCNT-O_2) and MWCNTs treated with nitrogen (MWCNT-N_2). The dominant transmittance at 3430 cm^{-1} in all spectra was identified owing to the O-H stretching vibration, which could be due to water absorption from the surroundings, carboxylic or O-H groups on the CNT surfaces.



(a)

(b)

Fig. 3 - FTIR transmittance spectra for pristine MWCNTs and MWCNTs treated with (a) helium and (b) nitrogen DBD plasma.

The peak observed at 1160 cm-1 in the spectrum of the MWCNT-O2 were attributed to the C-O stretching, while the presence of the COOH group was confirmed by the presence of a small peak at 1738cm-1 which corresponded to the C=O bond. All reactive oxygen species that were incorporated into the MWCNTs were due to the oxygen atoms that originated from the gas supply present in the discharge chamber. As can be seen, the intensity of this peak intensified with increasing discharge voltage of the DBD plasma, but diminished at higher discharge voltage. This indicated that, within the plasma, the concentration of oxygen functional groups attached to the surface of MWCNT decreased with increasing plasma discharge voltage. The ion bombardment energy became higher at higher voltages and might cause the ions to bombard the surface of the MWCNT too strongly and break the C=C bond of the MWCNT rather than attached to the CNT surface.

In the case of MWCNT-N_2, the peaks at 1636 cm^{-1} were caused by the N-H bending vibration of amine or C=O stretching vibration of amides. The incorporation of amino groups on the MWCNTs surface after nitrogen DBD plasma treatment was clearly confirmed by the simultaneous existing of N-H bending vibration peak and N-H stretching vibration peak at 3430 cm^{-1}. From these spectra, the peaks at 1636 cm^{-1} became deeper at higher discharge voltage of plasma. This means that the incorporation of nitrogen atoms on the MWCNTs surface becomes intense when the discharge voltage of the plasma is increased.

3.3. Hall Effect Measurement

Hall effect measurement was conducted using Ecopia Hall Effect Measurement System HMS-3000 at low temperature to room temperature. The electrical contact was made by placing small silver conductive ink on the four corners of thin film. Hall effect measurements are important for characterization of semiconductor materials because it can obtain information especially mobility of material. Higher mobility is important in designing switching devices like diode and transistor.

Figure 4 and 5 show the variation of hall mobility of MWCNTs treated by O_2 and N_2 DBD plasma respectively. The mobility was taken from sample of MWCNTs that treated at different plasma applied voltage and different treatment time. From Figure 4.20, the highest mobility was achieved by MWCNTs treated at 8 kV applied voltage. It can be seen from all applied voltages and treatment time, the mobility of MWCNTs-O_2 were increased slightly but the mobility does not exceed 20 cm2/Vs. Compared to MWCNTs-N_2, the mobility was increased sharply for all applied voltages at 10 minutes time treatment and decreased gradually at 15 and 20 minutes time treatment. It is suggested that, in this experiment, the optimum voltage and time treatment for N_2 DBD plasma to modify the MWCNTs from metallic to semiconducting behaviour are at 12 kV and 10 minutes respectively.

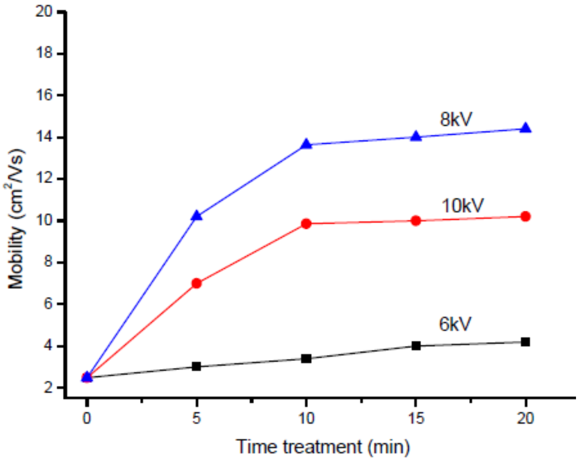


Fig. 4 - Variation of Hall Mobility of MWCNTs-O_2 at different applied voltage and treatment time.

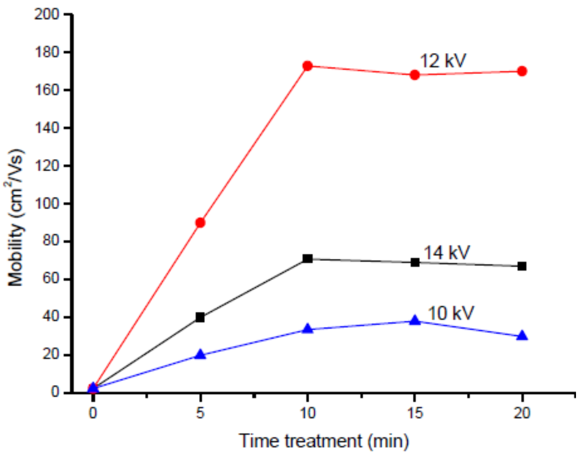


Fig. 5 - Variation of Hall Mobility of MWCNTs-N2 at different applied voltage and treatment time.

Even though the mobility of MWCNTs-O_2 increase slightly with applied voltage and time treatment, but the mobility achieved are too small and not capable to apply in switching devices. Figure 6 shows the hall mobility at room temperature of untreated MWCNTs and treated MWCNTs with respect to applied voltage of plasma treatment. It is interesting to observe that nitrogen atom in MWCNTs change significantly the hall mobility of undoped or pristine MWCNTs. The highest hall mobility (172.9 cm2/Vs) was achieved when MWCNTs treated with nitrogen at 12kV which is slightly higher than mobility of SWCNT thin film (150 cm2/Vs) reported by previous researcher [23]. This value than drop to 33.63 cm2/Vs when applied voltage of nitrogen DBD plasma is increased to 14kV. Thus, it is suggests that with moderation of nitrogen plasma applied voltage, bamboo-like structure of MWCNTs will be created. This structure could increase the mobility of metallic MWCNTs and tends to convert metallic MWCNT into semiconducting behaviour. It is well known that nitrogen has one additional electron at their valence band compared to carbon. Thus, the electronic properties of MWCNTs can be predicted if N atom is doped to the C atoms in the graphitic lattice. This extra electron is believed can carry current and generate n-type semiconductor.

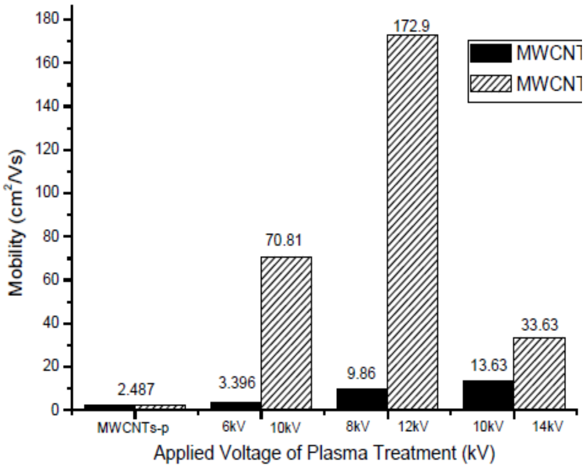


Fig. 6 - Hall mobility of MWCNT-p, MWCNT-O2 and MWCNT-N2 at optimum plasma applied voltage.

4.0 Conclusion

A low frequency (50 Hz), atmospheric pressure, oxygen and nitrogen DBD plasma was used to modify the surface of MWCNTs. It was demonstrated in this paper that the applied voltages of non-thermal plasma generated by oxygen and nitrogen at atmospheric pressure affected the surface and electrical properties of the MWCNTs after the modification process. After treatment, the oxygen-containing groups such as C=O and COOH were formed for the O_2 DBD plasma, in addition to the N-H vibration bending for the N_2 DBD plasma. The results of the electrical characteristics indicated that the Ohmic behaviour of pristine MWCNTs tended to change to Schottky behaviour after the DBD plasma treatment. It suggested that the metallic MWCNTs were prone to change to semiconducting properties after being exposed to plasma treatment by controlling the voltage of plasma or energy of ion bombardment. It was also found that the MWCNTs-N_2 bamboo-like structures had a higher mobility than that of the pristine one and also the potential to have a semiconducting behaviour.

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