

Induced NH₂ bonding of carbon nanotubes using NH₃ plasma-enhanced chemical vapor deposition

Ai-Huei Chiou · Yu-Ming Chang · Wen-Fa Wu ·
Chang-Ping Chou · Chun-Yao Hsu

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Abstract Plasma-enhanced chemical vapor deposition was used to modify the multiwall carbon nanotubes (MWCNTs) using ammonia (NH₃) plasma. For various durations of NH₃ plasma treatment, a scanning electron microscope, X-ray, Raman spectroscopy and contact angle measurement were used to ascertain several characteristics of the MWCNTs. The experimental results show that: (1) the length of the MWCNTs is reduced, if the duration of the plasma treatment is increased; (2) the NH₃ plasma treatment can incorporate amine (NH₂⁻) or amino (NH⁻) functional groups onto the MWCNT surface; (3) the plasma treated carbon nanotubes become more hydrophilic.

1 Introduction

Carbon nanotubes (CNTs) are widely used for electronic components, chemical and biological sensors, scanning probe microscopy, field emission tips, high-strength composites, hydrogen and ion storage components [1] because of their physical and chemical properties and their

excellent mechanical properties [2]. Although CNTs have many advantages, their surface contains many impurities, including amorphous carbon, carbon oxides and other chemical compounds, which hinder the application of CNTs, in practical systems. For use in biology and medicinal chemistry, CNTs must be purified and dissolved in physiological media. If the CNT surface is to be modified, to alleviate these problems, more precise control of chemical functionalization and an understanding of the related structures are needed.

In recent years, several post treatment techniques, such as chemical processes [3], electron irradiation, plasma treatment and laser exposure [4], have been developed. Each of these techniques has proven to be an effective method of cleaning CNTs, but some techniques can damage the structure and properties of the CNT. For example, acid treatment is often used to introduce -COOH and -OH groups, to modify CNTs and increase their aqueous solubility [5]. This can damage the structure of the CNT [6], decrease its stability [7] and even sever the CNT into short pieces [8]. In addition, most chemicals have disadvantages such as toxicity, instability and the possibility of environmental pollution.

Of these approaches, plasma treatment is the most widely used purification method, because it reduces amorphous carbon and induces bonding onto the CNT surface. The interface between the materials and their environment usually plays a decisive role in many applications, such as biology, or drug delivery systems [9]. Therefore, the surface modification of materials has become an important topic for study, because the properties of the material can be maintained, even if the surface structure is changed [10].

Plasma-enhanced chemical vapor deposition (PECVD) is a special type of CVD process that utilizes plasma to

A.-H. Chiou · C.-P. Chou
Department of Mechanical Engineering, National Chiao Tung University, Hsinchu, Taiwan, ROC

Y.-M. Chang
Institute of Nuclear Energy Research, Atomic Energy Council, Executive Yuan, Taoyuan, Taiwan, ROC

W.-F. Wu
National Nano Device Laboratories, Hsinchu, Taiwan, ROC

C.-Y. Hsu (✉)
Department of Mechanical Engineering, Loughwa University of Science and Technology, Kueishan, Taiwan, ROC
e-mail: cyhsu@mail.lhu.edu.tw

enhance the chemical reaction rates of precursors. The process uses radio frequency-generated plasma to assist the deposition reaction at lower temperatures [11]. PECVD has many benefits, in that it requires a lower temperature than conventional CVD, it reduces the thermal stress induced by small fabrication defects and it can also be used to improve printability, wettability, bondability, surface hardness and surface heat resistance. It also provides a method of cleaning surfaces, without the need for solvents and introduces cross-linking, at the surface.

Few studies have considered the effect of amino plasma treatment on CNTs. This investigates using PECVD system with amino-related functional groups for MWCNTs. There are three major sections: (1) the induction of amine (NH_2) bonding in MWCNTs, using PECVD; (2) characterization of the difference between the morphologies and structure of MWCNTs, before and after amino (NH_3) plasma treatment, using PECVD and (3) an investigation of the effect of changing the duration of NH_3 plasma treatment on the deposition of nitrogen-containing groups onto the surfaces of MWCNTs.

2 Experimental procedures

2.1 Synthesis and functionalization of MWCNTs

The substrate used in this study was a 6-inch, p-type (100) silicon wafer, with resistivity of 15–25 $\Omega\text{-cm}$. Firstly, in order to remove chemical impurities and particles, the wafer was cleaned, using a standard Radio Corporation of American cleaning process. Mattel PVD was used to deposit a 20 nm thick titanium nitride buffer layer and then a 7 nm thick transition metals (nickel) layer on the wafer substrates. Secondly, MWCNTs were synthesized, using thermal chemical vapor deposition (AT-CVD) [12]. The base pressure of the system was 760 Torr. The AT-CVD was performed at 550 $^\circ\text{C}$, with $\text{H}_2:\text{CH}_4 = 5:2$ sccm for 1 min.

It has been reported that the structure of CNTs depended on the synthesis parameter, such as reaction temperature, catalyst composition and reaction gas [13]. In order to investigate the influence of the Ni catalyst layers (7 nm) transformed into nanoparticles, after different H_2 gas flows rate (100 and 500 sccm) during pre-treatment are presented in Fig. 1. It is shown that, with higher H_2 gas flow rate during pre-treatment, lead to denser Ni catalyst nanoparticles and smaller RMS surface roughness (Fig. 1b). This is also similar to the results of Jian et al. [14]. Figure 2 shows the influences of H_2 flow rate pre-treatment on the morphology of MWCNTs synthesized at 550 $^\circ\text{C}$, with $\text{H}_2:\text{CH}_4 = 5:2$ sccm for 1 min. By applying higher H_2 gas flow rate during pre-treatment (Fig. 2b), the amorphous

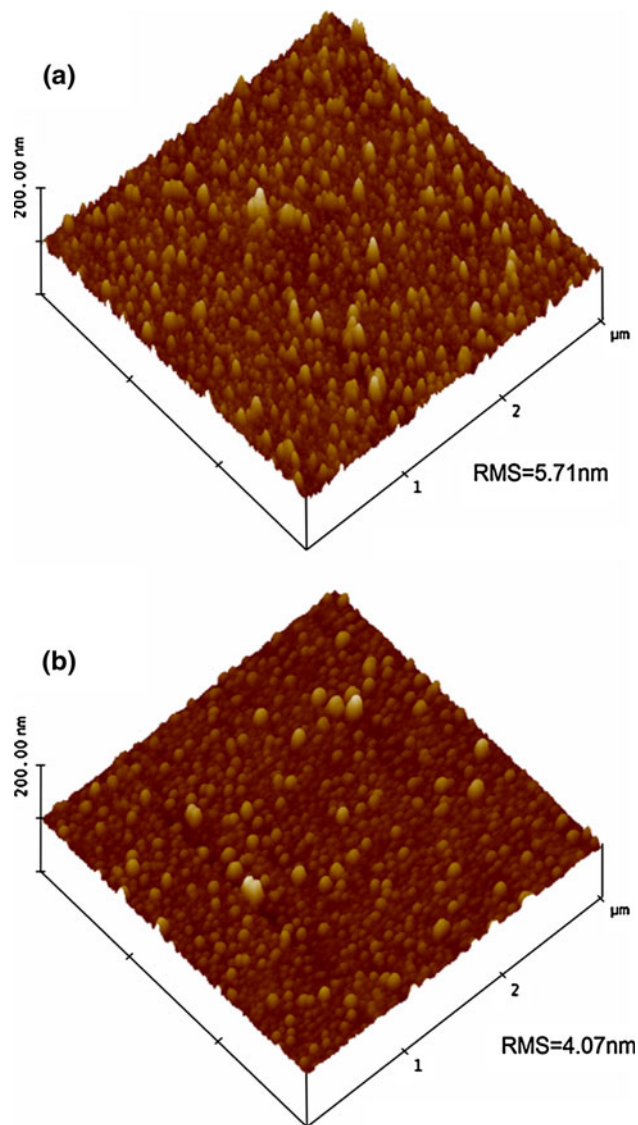


Fig. 1 AFM images and RMS surface roughness of Ni catalyst nanoparticles by different H_2 gas flow rate during pretreatment at **a** 100 and **b** 500 sccm

carbon and carbonaceous particles were decreased, and the MWCNTs yield increases apparently.

Finally, the MWCNTs were modified, using PECVD. For the post treatment, the microwave power was 300 W and the NH_3 gas flow rate was 700 sccm. In order to study the effect of varying the duration of the NH_3 plasma treatment, the ammonia plasma post-treatments were functionalized at 300 $^\circ\text{C}$, for 1, 3, 5 and 10 min, using PECVD (listed in Table 1).

2.2 Characterization of the morphologies and structures

A scanning electron microscope (SEM, Hitachi S-4000) was used to observe the lengths, density, morphologies and

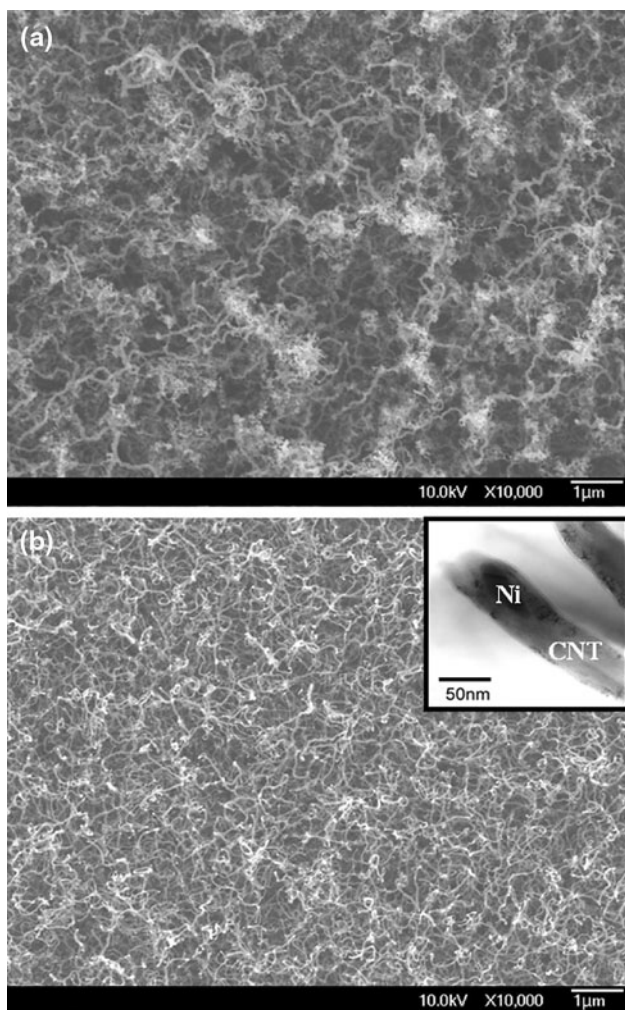


Fig. 2 SEM images of CNTs by different H₂ gas flow rate during pretreatment at **a** 100 and **b** 500 sccm

Table 1 Symbols representing MWCNTs samples with different plasma treatment times

System	PECVD			
Exp. parameters	C-NH ₃ -1	C-NH ₃ -3	C-NH ₃ -5	C-NH ₃ -10
Plasma type	NH ₃	NH ₃	NH ₃	NH ₃
Process temp. (°C)	300	300	300	300
Aux temp. (°C)	250	250	250	250
Flow rate (sccm)	700	700	700	700
Power (Watt)	100	100	100	100
Treatment time (min)	1	3	5	10

functionalized of the MWCNTs, and the functionalized MWCNTs. Fourier transform infrared spectroscopy (FTIR, AStEX PDS-17) was used to analyse the chemical compositions. X-ray Photoelectron Spectroscopy (XPS, VG Microlab 310F) was used to investigate the functional

groups and the chemical elements. Raman spectroscopy (Raman, Renishaw 2000) was used to examine the region between the crystallization and atom bands of the MWCNTs. A Contact Angle system (CA, KRÜSS GmbH GH-100) was also used to analyze the hydrophilic and the hydrophobic nature of the MWCNTs, and the functionalized MWCNTs.

3 Results and discussion

3.1 Morphological analysis

The effects of varying the duration of NH₃ plasma treatment time, on the surface morphologies of untreated and treated samples of MWCNTs are presented in Figs. 3, 4,

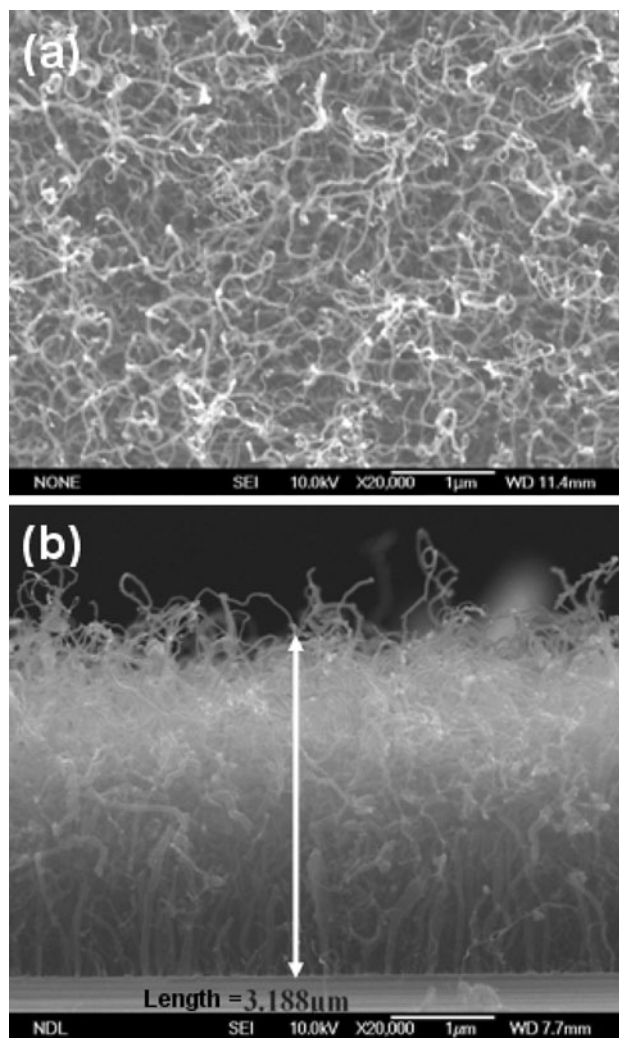


Fig. 3 SEM images of MWCNTs, using AT-CVD, at 550 °C, for 1 min, with an H₂/CH₄ mixture, a gas flow rate of 5:2 sccm and a base pressure of 760 Torr, **a** top view and **b** side view

Fig. 4 Top-view SEM images of MWCNTs, after plasma treatment with an NH₃ gas flow rate of 700 sccm, microwave power of 100 W and process temperature of 300 °C, for **a** 1 min, **b** 3 min, **c** 5 min and **d** 10 min

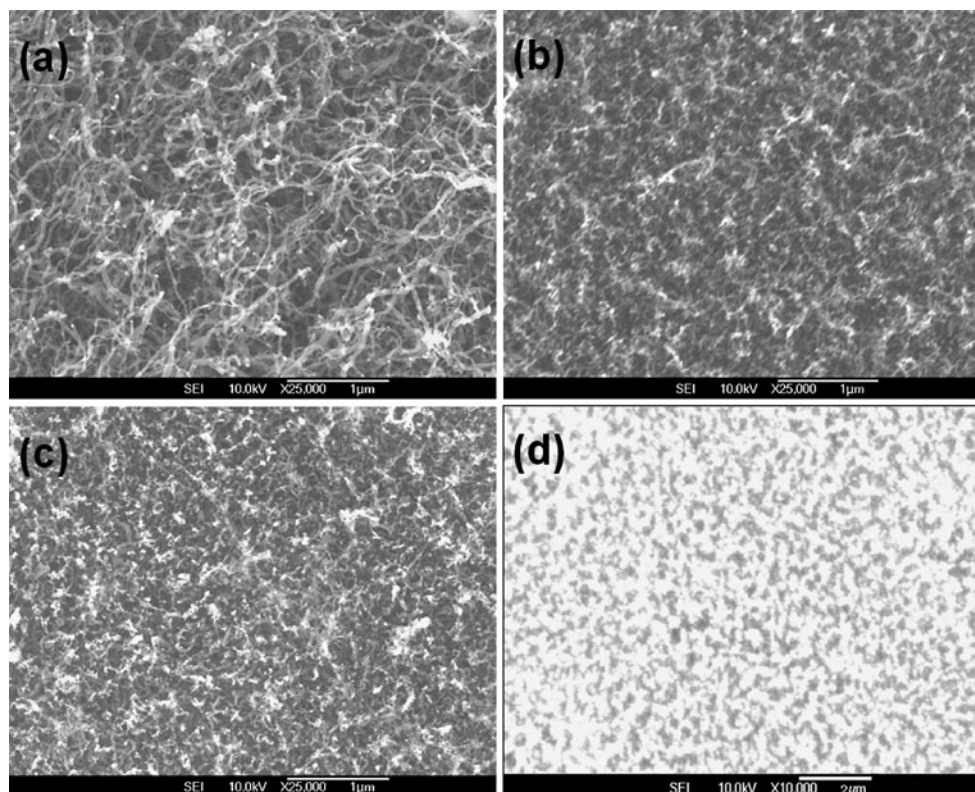
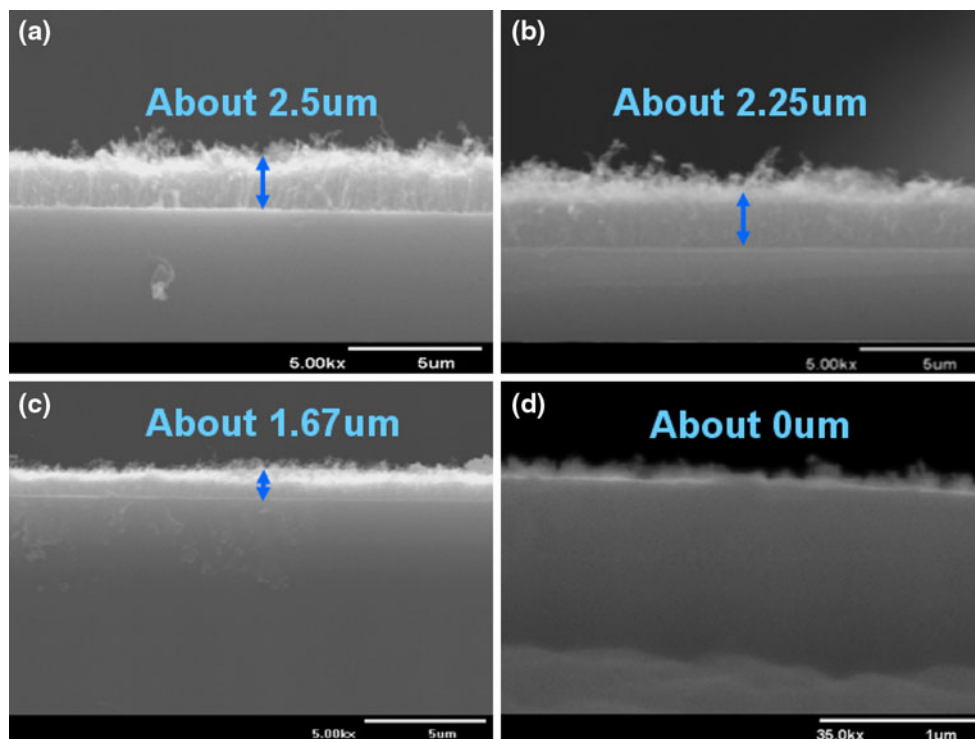


Fig. 5 Side-view SEM images of MWCNTs after plasma treatment with an NH₃ gas flow rate of 700 sccm, microwave power of 100 W and process temperature of 300 °C, for **a** 1 min, **b** 3 min, **c** 5 min and **d** 10 min



and 5. Figure 3 shows the morphology of the as synthesized MWCNTs, on a silicon wafer. The length of the MWCNTs is observed to be approximately 3.188 µm, as

shown in Fig. 3 (b). Figures 4 and 5 show the treated MWCNTs, for different durations of NH₃ plasma treatment.

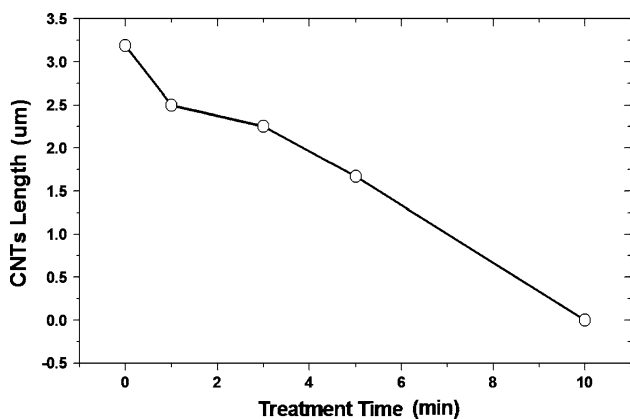


Fig. 6 Effect of the duration of plasma treatment on the length of MWCNT, for an NH₃ gas flow rate of 700 sccm, microwave power of 100 W and process temperature of 300 °C

The surface morphology of MWCNTs with no NH₃ plasma treatment is very rough. However, the surface morphology of MWCNTs becomes smooth, after NH₃ plasma treatment. In addition, the length of MWCNTs decreases, as the duration of the plasma treatment increases, as shown in Fig. 6. It can be seen that NH₃ plasma treatment performs an effective etching and cleaning process on MWCNTs [15], which can be established by Raman analysis. This method may cause interconnection in MWCNTs, which gives better surface roughness.

3.2 Graphite analysis

Raman spectroscopy is widely used to analyze the structure of MWCNTs [16]. This technique is highly sensitive to the disorder on the surfaces, because of the optical skin depth [17]. Figure 7 shows Raman spectra of MWCNTs before and after the NH₃ plasma treatment, as a function of different treatment time. These Raman spectra exhibit two distinct peaks, at 1,300–1,380 cm⁻¹ (D band) and 1,550–1,600 cm⁻¹ (G band). The D band peak is generally caused by defects in the curved graphite sheet, sp³ carbon, or other impurities and the G band shows the presence of crystalline, graphitic carbon in MWCNTs associated with the motion of two neighboring carbon atoms in a graphite sheet, in the reverse direction [18]. The ratio of the intensities of the D and G band peaks can be used to evaluate the comparative extent of structural defects. It has been confirmed [19] that the I_D/I_G ratio can be effectively determined by crystal space interaction. When I_D/I_G ratio decreases, the quality of MWCNTs improves.

Analysis of the results shows that the value of the I_D/I_G ratio, for MWCNTs with no modification, is 1.180. This value decreases, after 1, 3, and 5 min of NH₃ plasma treatment, as shown in Fig. 7. The decrease in I_D/I_G values probably occurs because of increased nitrogen content and

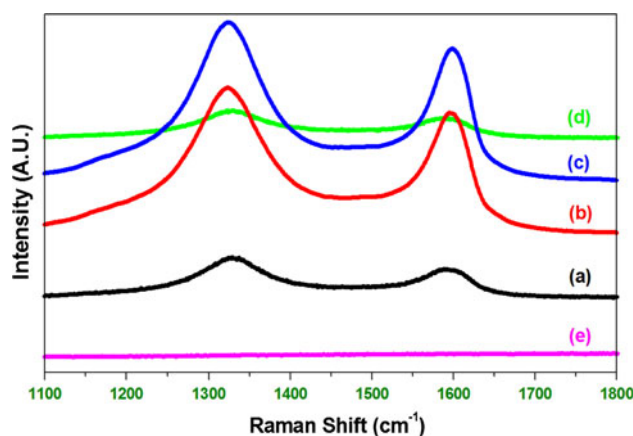


Fig. 7 Raman analysis of MWCNTs after plasma treatment, with an NH₃ gas flow rate of 700 sccm, microwave power of 100 W and process temperature of 300 °C, for **a** 0 min, **b** 1 min, **c** 3 min, **d** 5 min and **e** 10 min

the etching effect, which reduces surface impurities, as presented in Table 2. However, the I_D/I_G ratio increases, for the sample with 10-min NH₃ plasma treatment. The increase in I_D/I_G ratio for the plasma modified MWCNTs is probably due to over etching of the MWCNTs by NH₃ plasma treatment, which is consistent with SEM observations.

3.3 Hydrophobic properties

Water contact angle (WCA) introduced by Thomas Young [20] as a way of investigating wetting behavior and surface tension, now have many fields of application in the measurement of the characteristics of single, or multi-layer surface treatment techniques [21], such as the aging characteristics of modified surfaces and the migration of hydrophobic and hydrophilic functional groups, in aqueous and nonaqueous environments [22]. Contact angle analysis is sensitive to the chemical composition of the top molecular layer and is a relatively simple, inexpensive and popular technique for the characterization of material

Table 2 Values of peaks at the D band and G band in the Raman spectra for the MWCNTs before and after different durations (1, 3, 5 and 10 min) of plasma treatment

Sample	D-peak	G-peak	I _D /I _G
CNTs	1,328	1,588	1.180
C-NH ₃ -1	1,322	1,595	1.174
C-NH ₃ -3	1,324	1,598	1.144
C-NH ₃ -5	1,330	1,593	1.177
C-NH ₃ -10	–	–	–

Fig. 8 WCA observation of **a** original MWCNTs samples and after plasma modification **b** 1 min, **c** 3 min, **d** 5 min and **e** 10 min, with an NH_3 gas flow rate of 700 sccm, microwave power of 100 W and process temperature of 300 °C, using a CCD

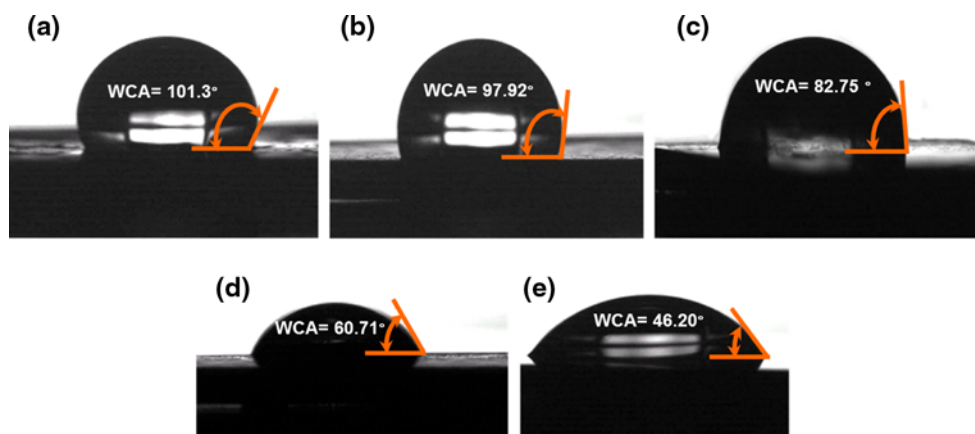


Table 3 Measured water contact angle (WCA) for MWCNTs, with different durations of plasma treatment (1, 3, 5 and 10 min)

Parameter	CNTs	C-NH ₃ -1	C-NH ₃ -3	C-NH ₃ -5	C-NH ₃ -10
WCA (°)	101.3	97.92	82.75	60.71	46.20

surfaces. After plasma treatment, the bulk surface can induce hydrophobic functional groups.

Figure 8 shows the WCA testing of MWCNTs, without and with modification by NH_3 plasma treatments. The unmodified MWCNTs have hydrophobic features, with a contact angle of 101.3°. The different contact angles, after various NH_3 plasma treatments, are shown in Table 3. This result indicates that the treated MWCNTs become hydrophilic. It also presents evidence of the functionalization of the MWCNT surface. This occurs because of the formation of nitrogen-containing functional groups at the MWCNTs surface, through the reactions between the active species from the NH_3 plasma and the surface atoms. The NH_3 plasma increases the surface energy of MWCNTs surface.

Figure 8 shows that the number of hydrophilic ions increases, with the duration of NH_3 plasma treatment. This phenomenon has also been observed by several researchers [23, 24]. Ammonia is considered to be an effective precursor to the introduction of amine functionalities to carbon nanotubes [23] and other materials [24], enhancing their hydrophilicity and biocompatibility. The use of NH_3 , with PECVD may induce nitrogen-containing functional groups onto the MWCNT surface, which can be confirmed by XPS and FTIR analysis. WCA analysis shows a correlation between ammonia and hydrophilicity.

3.4 Elemental analysis

In order to evaluate the functional groups formed by the NH_3 plasma treatment and to discover the reason for the reduction in contact angle, the chemical bonds on MWCNT surface treated by NH_3 plasma were determined, using

FTIR and XPS analysis. Figure 9 shows the results of FTIR analysis of the MWCNT chemical bonds, for various durations of modification. The peak, at 2,800–2,950 cm^{-1} , is attributed to C–H stretching vibration. N–H stretching vibration bands, at 3,200–3,400 cm^{-1} , can be observed. These provide further information concerning the effects of NH_3 plasma on the surface of MWCNTs, as shown in Fig. 9. The results show that the peak at 3,100–3,500 cm^{-1} is caused by NH_2 groups [25]. These results agree with those reported by Yook et al. [26].

XPS analysis was used to investigate the effect of NH_3 plasma treatment of MWCNTs. XPS analysis determines the difference between the untreated MWCNT and the modified MWCNT, through the elemental chemical shifts. Figure 10 shows the results of XPS analysis for MWCNT chemical bonds, for various durations of modification. Before modification, the full spectrum appears to be composed of graphitic carbon (284.8 eV), as shown in Fig. 10. The modification of MWCNTs by NH_3 plasma treatment does not cause a large change in the C1 s and

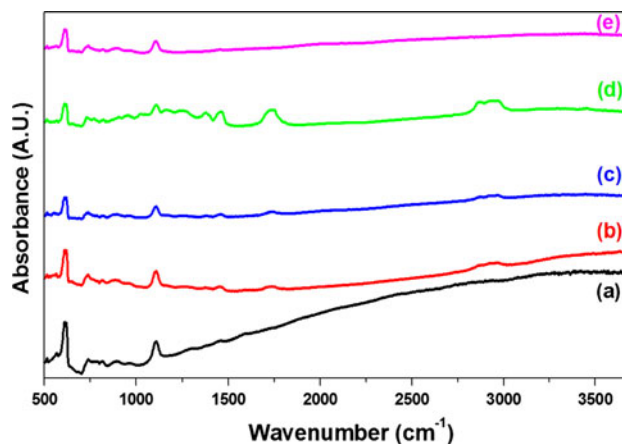


Fig. 9 Comparison of FTIR spectra for **a** original MWCNTs samples and after NH_3 plasma treatment **b** 1, **c** 3, **d** 5 and **e** 10 min, with an NH_3 gas flow rate of 700 sccm, microwave power of 100 W and process temperature of 300 °C

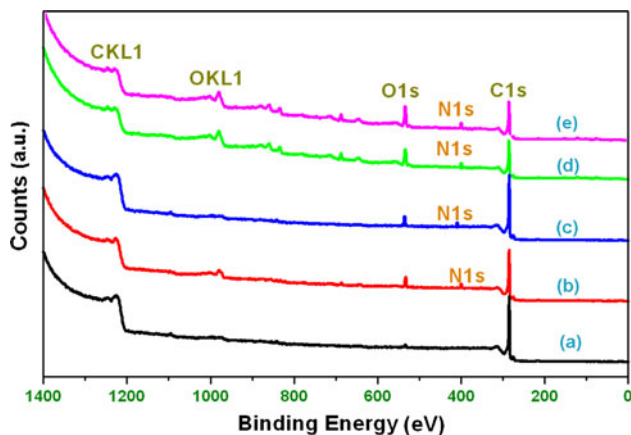


Fig. 10 The XPS wide scan spectra for MWCNTs samples, with an NH₃ gas flow rate of 700 sccm, microwave power of 100 W and process temperature of 300 °C, with plasma modification for **a** 0 min, **b** 1 min, **c** 3 min, **d** 5 min and **e** 10 min

Table 4 Atomic concentration of C, N, and O, in MWCNTs with different surface modification times

Element contain (%)			
Samples (treatment time)	C1 s (%)	N1 s (%)	O1 s (%)
Untreated MWCNTs	97.13	–	2.87
C-NH ₃ -1 (1 min)	86.69	2.5	7.81
C-NH ₃ -3 (3 min)	82.43	2.99	14.58
C-NH ₃ -5 (5 min)	76.17	3.66	20.17

O1 s spectra, but there is an observable change in the N1 s spectra. The atomic compositions of untreated MWCNTs are 97.13% C and 2.87% O. After modification, N content increases linearly, with duration of NH₃ plasma treatment, as shown in Table 4. Detailed examination of the C1 s, O1 s and N1 s spectra allowed the acquisition of more information about the bonding structure of the MWCNTs.

Figure 11 shows the intensity of the N1 s spectrum. There are no observable peaks for the untreated MWCNTs, but peaks appear for the NH₃ plasma modified MWCNTs. The N1 s spectrum may consist of more than one element, for example, -C ≡ N (from 398.3 to 399.2 eV), C–NH₂ (from 398.3 to 399.2 eV), N = C (from 399.0 to 400.1 eV), -NH- (from 399.7 to 400.0 eV), -C–NH₃ (from 399.7 to 400.0 eV), C–N (from 399.7 to 400.0 eV) and O = C–NH₂ (at 400.4 eV) [27]. This is caused by the decomposition of the ammonia that bonded the surface of MWCNTs, to free radicals (NH₂ or NH) [28]. Figure 12 shows the typical high-resolution C1 s spectrum, for MWCNTs, with and without NH₃ plasma treatment. The findings suggest that: (1) sp²-hybridized graphite-like carbon atom (C = C) is at 284.1 ± 0.2 eV; (2) the sp³

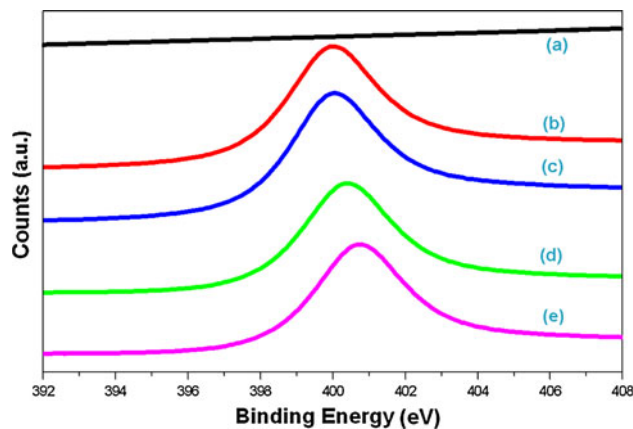


Fig. 11 N1 s spectra for MWCNTs samples, with an NH₃ gas flow rate of 700 sccm, microwave power of 100 W and process temperature of 300 °C, with plasma modification for **a** 0 min, **b** 1 min, **c** 3 min, **d** 5 min and **e** 10 min

hybridized carbon atom (C–C) is at 285.1 ± 0.2 eV; (3) peaks at 286.0 ± 0.2 eV are considered to be C–O and C–N groups; (4) peaks at 287.2 ± 0.2 eV and at 288.7 ± 0.2 eV are considered to be C = O group and O–C = O group, respectively [29, 30].

Table 5 indicates that N/C ratios increase, from 0 to 0.048, and O/C ratios increase, from 0.030 to 0.265, if the duration of NH₃ plasma treatment is increased. This occurs because of the formation of some nitrogen groups on the MWCNT surfaces, due to NH₃ plasma treatment. Therefore, the ammonia plasma post-treatments can introduce functional groups, such as C–NH₂ and C–N. These results demonstrate that PEVCD treatment is a reliable and effective method, which can expediently endow MWCNTs with various new functional groups, while maintaining their original bulk structures.

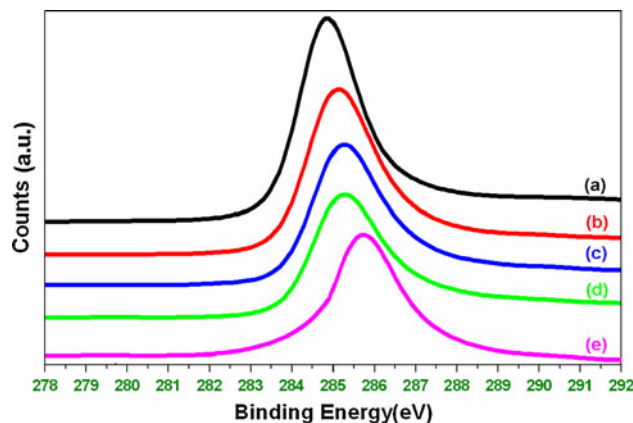


Fig. 12 C1 s spectra for MWCNTs samples, with an NH₃ gas flow rate of 700 sccm, microwave power of 100 W and process temperature of 300 °C, with plasma modification for **a** 0 min, **b** 1 min, **c** 3 min, **d** 5 min and **e** 10 min

Table 5 N/C and O/C ratios, for MWCNTs samples with different durations of treatment

Samples	N/C	O/C
Untreated MWCNTs	0	0.030
C-NH ₃ -1 (1 min)	0.029	0.090
C-NH ₃ -3 (3 min)	0.036	0.177
C-NH ₃ -5 (5 min)	0.048	0.265

4 Conclusion

In this study, the induction of amino groups onto an MWCNT surface, using a PECVD system, was investigated. After NH₃ plasma treatment, the surface roughness of the MWCNT improved but the quality (I_D/I_G ratio) of the MWCNT decrease, after plasma treatment for a longer period (5 and 10 min). NH₃ plasma treatment shortened the length of the MWCNTs grown on the blanket.

The results of XPS and Raman spectra analysis indicate that treatment time affects the atomic composition and structural properties of MWCNTs. The approach taken is an efficient method for the introduction of amino groups onto MWCNTs surfaces. NH₃ plasma treatment was confirmed to be an effective precursor to the introduction of amine functionalities onto the MWCNT surface, to enhance their hydrophilicity and biocompatibility. These results demonstrate that the induction of amino groups onto an MWCNT surface, using a PECVD system, is an effective and reliable method.

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