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Fabrication of bottom-up multiwalled carbon nanotube electrode for sensitive electrochemical detection

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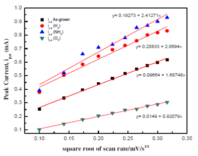
GRAPICAL ABSTRACT



ABSTRACT

Preliminary study of the growth of multiwalled carbon nanotube (MWCNT) was done using plasma enhanced chemical vapour deposition (PECVD) technique. Post treatment of MWCNT using different kinds of plasma atmosphere including oxygen, hydrogen and nitrogen were applied to introduce defects on the surface of MWCNTs and nitrogen plasma gives the most significant arises on the peak current compared to the bare electrode with increment from ~0.33 mA to ~0.42 mA with increased of effective area from ~0.32 cm^2 to ~0.49 cm^2. The study was extended into fabrication of screen-printed electrode system using photolithography methods and the MWCNTs working electrodes were modified under nitrogen plasma to enhance the surface sensitivity.

Keywords: Bottom-up, Multiwalled carbon nanotube, plasma-enhanced chemical vapour deposition, plasma-treatment, cyclic voltammetry

1. INTRODUCTION

Since the discovery in the early 1991s by S. Ijima, carbon nanotubes (CNTs) have inspired prevalent investigations amongst researchers [1]. The outstanding electrical, mechanical and thermal properties of CNTs have making them potentially applicable in nanotechnology science [2]. In the pristine state, carbon nanotubes have inert nature which easily forms aggregation between them leading to potential negative impact for adsorption and dispersion therefore restrict their real life applications. Surface enhancement of the nanotubes is required in order to improve their dispersion in the organic matrices through the defects applied.

The nanofabrication method involves CVD technique is called “bottom–up” methods in which the processes elaborate in creating nanoscale structures [3]. Bottom–up approaches seek to obligate molecular or atomic components built up into more complex nanoscale assemblies or directed self-assembly founded on complex mechanisms and technologies. This methodology has the potential of generating functional multi-component devices by the controlled assembly of atoms and molecules, without waste or the need for making or eliminating parts of the final system. Vapour phase deposition via CVD involves the process of detachment of molecules of the gaseous reactants, which consequently react chemically to form innumerable structures once activated by heat, light, or plasma discharge. Mostly solid-state, stable products are formed as a result of the chemical reactions [4-6].

Various modification on the surface of CNTs have been developed and become commercially available in recent years such as air oxidation [7], ozone oxidation [8], wet chemical oxidation [9] and plasma treatment [10-12]. The employment of these treatments is to graft the functional groups on the surface of the nanotubes individually without changing the bulk properties of the nanotubes. Unfortunately, the treatments involved harsh conditions leading to network destructive, damage the sidewalls and cutting the nanotubes structure which disrupt the unique properties of CNTs [13]. However, amongst these treatments, plasma modification has been the most attractive method due to its advantages such as of nonpolluting method, shorter treatment time and creating various functional groups depending on the plasma atmospheres. Therefore, many efforts on plasma surface treatments studies have been focused by researchers.

Plasma surface treatment employs gases, such as oxygen, nitrogen, hydrogen, and ammonia. When exposed to the plasma, the excited species, radicals, electrons, ions, and UV light within plasma strongly interact with the surface of the nanotubes leading to the breaking of sp2- hybridized graphite-like carbon (C=C) bonds within the CNT lattice creating the defects (so-called the active sites). Hence, the binding of functional groups occurred at the active sites which then interact with the plasma-generated surface-bound radicals forming the dangling bonds [14]. P. Mishra et.al [15] reported enhanced sensitivity of CNTs by increasing the oxygen contents on the surface of the nanotubes through longer processing time. Modification by nitrogen plasma done by Hussain et.al [16] demonstrates the presence of pyridinic and pyrrolic functionalities on CNTs surface leading to improvement of reversibility of the electron transfer process.

The development of plasma modifications on the surface of carbon nanotubes was studied extensively to improve the electrochemical signal by introducing various functional groups. However, from our investigations, there is lack of comparison study using different kinds of plasma atmospheres applied on CNTs have been done. In this study, the grown MWCNTs by PECVD were modified under different plasma atmospheres including nitrogen, hydrogen and oxygen to create defects on the surface of the nanotubes with the aim to enhance the electrochemical performance of the MWCNTs.

2. MATERIALS AND METHODS

2.1 Materials

Silver, titanium, cobalt, acetone, potassium ferricyanide, potassium chloride and distilled water.

2.2 Methods

Firstly, by using magnetron sputtering, Ti thin film as the conducting layer and then Co thin film as catalyst for growing CNTs were deposited with a thickness of about 10nm and 6.6 nm on Si (100) substrate at a base chamber pressure of ~10-3 mbar and temperature of 42 °C. MWCNTs were then synthesized by using PECVD in an Oxford Instruments Nanofab-700 system at ambient pressure. Prior to CNTs growth the catalyst films were undergone annealing process to promote the formation of catalyst nanoparticles. The process took place in vacuum at 700 °C for 10 min in hydrogen (100 sccm), with an applied plasma power of 200 W. MWCNTs growth was performed in the same furnace chamber with 50 sccm of acetylene (C2H2) at a pressure of 1,000 mTorr at 700 °C for 10 min. The plasma treatment was performed as tabulated in Table 1.

2.3 Characterization

The surface morphology of all the pristine and modified carbon nanotubes was characterized using a field emission scanning electron microscopy system (JEOL JSM- 7500F). The quality of the CNTs was evaluated by Raman spectroscopy system (NT-MDT NTEGRA Spectra). A 473 nm air-cooled laser was focused on a diffraction limited resolution of 250 nm, and the acquisition time was accumulated up to 5 min. The electrochemical characterizations of the electrodes were investigated by using potentiostatic system of cyclic voltammetry (CV). Electrochemical behavior of the Fe^{2+}/Fe^{3+} redox reactions at the surface of CNTs was studied in 0.1 M KCl solution containing 0.01M potassium ferricyanide at various scan rates of 10 to 100 mV s^{-1}. All experiments were carried out at 25 °C in a screen-printed electrode. The working and counter electrode was either the bare or plasma treated MWCNTs while the reference electrode was the silver (Ag) respectively. The geometrical area of the working electrode was set to a constant value of 0.36 cm^2.

3. RESULTS AND DISCUSSION

3.1 *Field Emission Scanning Electron Microscopy (FESEM)*

Figure 1 shows the surface morphology of as grown multi-walled carbon nanotubes film before and after exposing to ammonia, hydrogen and oxygen plasma. From Fig. 1, slight differences of the surface morphology between the untreated (Fig 1a) and plasma modified (Fig. 1b, c, d) samples are observed.

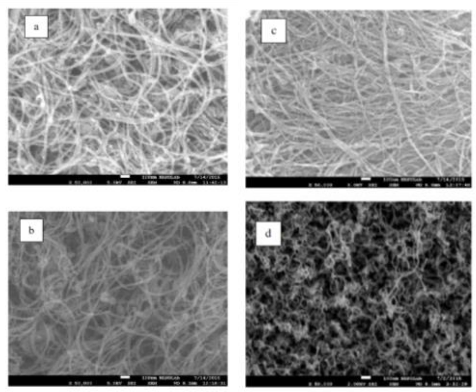


Fig. 1 Top-view FESEM images of **a)** as-grown MWCNT **b)** NH3- plasma treated MWCNT **c)** H2- plasma treated MWCNT and **d)** O2- plasma treated MWCNT

3.2 Raman Spectroscopy Analysis

Raman spectroscopy was performed to investigate the quality of nanotubes. Raman spectra of carbon nanotubes are usually observed in two peaks near 1360 cm^{-1} and 1580 cm^{-1} associated to the D and G bands, respectively. The D band is due to presence of defects or amorphous-phase carbon, and the G band is due to graphite or ordered-phase carbon representing that plasma treatment the modified structure of the carbon nanotube by plasma. Fig 2 shows the Raman spectra of untreated and plasma treated CNTs. Analysis of the ratio between D and G band intensities (ID/IG) gives us information on the degree of perfection of CNTs. Larger ratio indicates reduction in the degree of perfection due to increase of structural defects introduced by plasma treatment. I band is attributed to incorporation of functional groups in CNTs and impurities in the graphite lattice. D″ band appearance is related to stacking defects in MWCNTs layer.

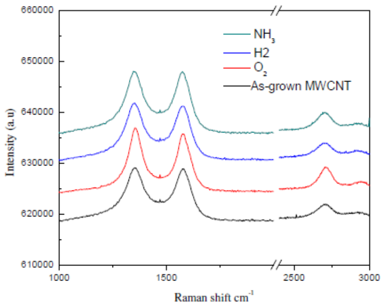


Fig. 2 Raman spectra of **a)** as-grown MWCNT **b)** NH_3-plasma treated MWCNT **c)** H_2-plasma treated MWCNT and **d)** O_2-plasma treated MWCNT

Table 1 Raman spectra of bare and different plasma atmosphere

Type of MWCNT	I_D/I_G ratio
As-Grown	0.998
CNT-NH_3	1.034
CNT-H_2	1.017
CNT-0_2	1.089

In the Figure 2, bare MWCNT shows lowest ratio followed by hydrogen, ammonia and oxygen. Oxygen plasma treatment has the largest defects which designate the supplementary oxygen functionalities have been successfully integrated in the lattice of the nanotubes. The low ratio of as-grown CNTs is due to no functionalities was introduced.

3.3 Electrochemical Characterizations

Figure 3a shows cyclic voltammograms (CVs) of the bare MWCNT, NH_3-MWCNT, H_2-MWCNT and O_2-MWCNT in a 0.10 M KCl containing 0.01 M ferricyanide (Fe(CN)$6^{3-/4-}$) solution at scan rates of 20 mVs^{-1}. Corresponding to the well-defined and quasi-reversible redox peaks shown in the CVs, the redox reactions occur directly between the electrode and electrolytes [17]. The oxygen-plasma MWCNT has lower redox peak current with reduction of ~0.190 mA compared to the unmodified MWCNT. For hydrogen and nitrogen plasma treatments, there were significant enhancement of redox peak currents as compared to unmodified MWCNT with the increments of 0.169 mA and 0.187 mA for anodic peak current (ipa). While the cathodic peak current (ipc) shows increments of -0.183 mA and 0.202 mA respectively. The improvement of the current signals is correlated to the increment of the rate ofdiffusion of potassium ferricyanide and larger effective surface area that improved sensitivity of the electrode.

The influence of scan rates on the redox reactions was investigated and the responded peak currents (ip) against square root of scan rates ($mVs^{½}$) are illustrated in Fig 3b. The plots show linear relationship of ip towards $mVs^{½}$. The results obtained are used to calculate the electroactive surface area (cm^2) by using Randles-Sevcik equation (1) as tabulated in Table 1.

$$i_p = 2.69 \text{ x } 10^5 n^{3/2} A D^{1/2} C v^{1/2} \qquad (1)$$

From equation (1), n is the number of electrons in the redox reactions, A is the electroactive surface area of the electrode (cm^2), D is the diffusion coefficient of the molecules in solution (cm^2/s), C is the concentration of molecule in bulk solution (mol/ml), v is the square root of scan rates (mVs½) and ip is the peak current (mA). According to equation (1), electroactive surface area of electrode is directly proportional to peak current. The peak current of NH_3-MWCNT gives highest signal followed by H_2-MWCNT, bare MWCNT and O_2-MWCNT. Therefore, the electroactive surface areas of the electrodes followed the same order as the electrochemical response.

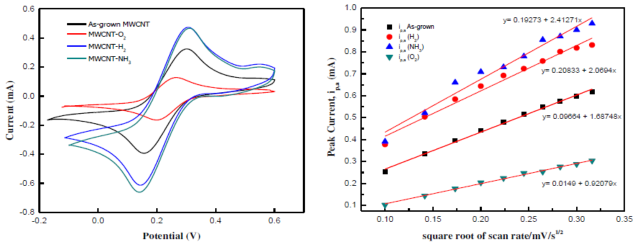


Fig. 3 (a) Comparison between the cyclic voltammograms of untreated and plasma treated CNTs at a scan rate of 20 mVs^{-1} (b) Plots of peak current against square root of scan rate of untreated and plasma treated MWCNT MWCNT 0.10 M KCl containing 0.01 M ferricyanide (Fe(CN)$6^{3-/4-}$) solution

Table 1 Electroactive surface areas of bare and plasma-treated MWCNTs

Type of MWCNT	Corellation coeffecient (R)	Effective surface area (cm²)
As-Grown	0.99561	0.319312
CNT-NH_3	0.99516	0.497333
CNT-H_2	0.97808	0.480494
CNT-0_2	0.9702	0.137296

The peak separation was then calculated as in Table 2. Smaller peak separation for oxygen treatmen indicates reversible reaction was take place with faster electron transfer rate in the redox reaction. Meanwhile, greater peak separation in in ammonia treated MWCNT specifies quarsireversible reaction.

Table 2 Peak current and potential of bare and plasma-treated MWCNTs

Type of MWCNT	i_{pa}	i_{pc}	i_{pa}/i_{pc}	E_{pa}(mV)	E_{pc}(mV)	ΔP(mV)
As-Grown	0.335	-0.334	1.003175	298	158.84	139.16
CNT-NH_3	0.522	-0.536	0.972281	305.33	144.2	161.13
CNT-H_2	0.504	-0.517	0.973777	300.45	153.81	146.64
CNT-0_2	0.144	-0.140	1.027913	278.47	183.26	95.21

4. CONCLUSION

Multiwalled carbon nanotubes have been successfully grown on silicon substrate via catalytic CVD techniques. Modification strategies of MWCNTs plasma treatment using different atmospheres proved ammonia plasma significantly improved the sensitivity of the electrodes up to 0. 4800 mV/s with increased of effective area of working electrode (~0.497333 cm^2) as compared to the bare electrode. Ammonia treated MWCNTs electrodes will be further modified for electrochemical application in biosensor with highly sensitive and rapid detection.

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