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Voltammetric Tests on Different Carbon Nanotubes as Nanobiosensor Devices

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ABSTRACT

This paper addresses a recent advance in electrochemical pretreatment of carbon nanotube (CNT)-based nanobiosensors. The unique chemical and physical properties of CNTs have paved the way to new and improved sensing devices. CNTs which are produced by different processes, i.e. arc-discharge (ARC) in solution and/or gas and chemical vapor deposition (CVD), have different effects on sensors efficiency. Various samples of ARC-CNT and CVD-CNT were chosen herein and ARC-CNT anodic pretreatment resulted in a dramatic improvement in the electrochemical reactivity (cycle voltammetric tests in the range of 0.0 to 1.5 V). In contrast, CVD-CNT appeared to be resistant to the anodic activation based on their structure as well as purification. However, in a separate experiment, different samples of multi-and single-wall CVD-CNTs were compared. The high purity multi-walled CNT synthesized by ARC showed the best outcome on the electrochemical behavior of glassy carbon electrode when compared to the other samples. The generic application of CNT and the effect of its structure and purity as a nano biosensor for electrochemical responses are widely discussed.

Keywords: arc discharge, carbon nanotube, chemical vapor deposition, cyclic voltammetry, electrochemical pretreatment, nanobiosensor
Abbreviations: CNT, carbon nanotube

INTRODUCTION

The number of publications on carbon nanotubes (CNTs) and CNT-reinforced composite materials has grown very quickly since CNTs were discovered by Iijima (Jahanshahi *et al*. 2007a) about 17 years ago. CNTs are a form of carbon with a long, tubular structure and a graphitic lattice (Iijima 1991). Due to the unique behavior of CNTs, including their remarkable electrical, chemical, mechanical and structural properties they have been the subject of intense study since their discovery (Rao *et al*. 2001). Three typical synthesis methods have been developed for the production of CNTs, namely the conventional arc discharge in an inert gas (argon, helium) atmosphere (or hydrogen), laser vaporization and chemical vapor deposition (CVD) (Molavi *et al*. 2009). CNTs can be divided into single-wall carbon-nanotubes (SWCNT) and multi-wall carbon- nanotubes (MWCNT). SWCNT possess a cylindrical nanostructure (with a huge aspect ratio), formed by rolling up a single graphite sheet into a tube. MWCNT comprise of several layers of grapheme cylinders that are concentrically nested like rings of a tree trunk (with an interlayer spacing of 3.4 A) (Iijima and Ichihashi 1993). The unique properties of carbon nanotubes make them extremely attractive for the task of chemical sensors, in general and electrochemical detection, in particular (Jahanshahi *et al*. 2006b). It has long been recognized that the electrochemical pretreatment of carbon electrodes can have a dramatic effect on the electron-transfer properties of the redox systems. The origins of these effects have been attributed to several factors. Engstrom attributed the lowering of the over potential at glassy-carbon (GC) electrodes to the introduction of quinine functionalities upon the carbon surface (Engstrom 1982; Jahanshahi *et al*. 2007b) and later to the possible removal of impurities form the electrode surface. CNT is an attractive material for the development of biosensors because of its capability to provide strong electrocatalytic activity and minimize surface fouling of the sensors. However, it has been shown that mode of fabrication of the CNT, either by chemical vapor deposition (CVD) or the ARC discharge process, affects the electrochemical reactivity of the CNT (Jahanshahi *et al*. 2006a). The single-walled carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs) have become the focus of considerable interest on the basis of their large specific area, their unique architecture, remarkable mechanical and electrical properties (Kangbing *et al*. 2006). The larger specific area could produce higher sensitivity because of its great adsorption capability to organic molecules. CNTs contain plenty of carboxyl or other oxygenic groups at their terminus. These probably so-called quinone-like groups as those at the glassy carbon electrode (GCE) surface could result in an increase in the effective electrochemically active surface area of CNTs towards electrochemical reaction. Combined with high electronic conductivity, better biocompatibility and useful mechanical properties all qualities of CNTs could promote electron transfer between reactant molecules and electrode surface (He *et al*. 2006; Chen *et al*. 2007). However, it has been shown that preparation techniques of the CNT may affect the electrochemical reactivity of the CNT.

In this study, electrochemical behavior of uric acid on modified CNT electrode are investigated and compared with naked electrode. In this regards, the single wall and multi wall CVD-CNTs as well as ARC-CNTs are tested in these experiments and the effects of their purity along with structure upon voltammetric responses are studied.

MATERIALS AND METHODS

Materials

Uric acid (Sigma, Sweden), sodium phosphate (Aldrich, UK) and alumina powder were purchased as materials for this part of experiment. All chemicals were of analytical grade. All solutions were daily prepared, using doubly distilled water. In all cases a standard three electrode configuration and a typical cell volume of 10 cm^3

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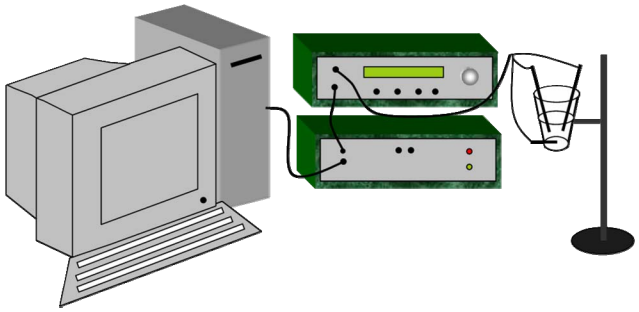

Fig. 1 The computer set up system; Potentostat/Galvanostat; model 263A, EG&G.

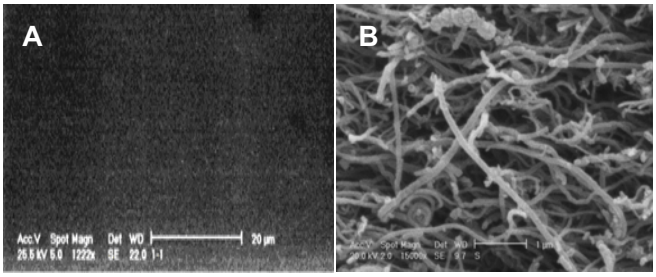

Fig. 2 SEM image of electrode without (A) and with (B) CVD MWCNT coating as an example.

was maintained. Different types of CVD and gas arc discharge synthesized CNTs were prepared. Experiments were performed in a three electrode cell. The electrode chemical experiments were carried out and a platinum wire was used as an auxiliary electrode; double junction Ag-AgCl-KCl saturated electrode was also used as the reference electrode and modified CNT GCE (BAS, 3 mm) was served as the working electrode. CNTs was supplied from Oil and Gas Industry Research center of Iran, custom assembled in home and purchased from material limited (NM, USA) and Bucky (TX, USA).

Electrochemical pretreatment

Two-electrode super-capacitor cells with a surface of 4 cm^2 were assembled in a glove box. 2 M HNO_3 was applied for pre-acid treatment of CNTs for 20 hrs. After drying the CNTs in room temperature, they were sonicated with dispersing agent, dimethyl formamide (DMF), for 1 hr. The electrode was polished with alumina powder and then 25 µl of DMF/CNT solution (2 mg CNT/2 ml DMF) was dropped on to the surface of GCE. About 1 mM uric acid (UA) in a 0.3 M phosphate buffer solution pH 7 was prepared as an analyte solution for all experiments. Cyclic volta metric measurements were conducted using an Auto Lab computer-controlled potentiostat. **Fig. 1** shows the computer setup system. Volta metric measurements were performed at different constant current density (20–800 mA) between 0 and 1.5 V and the results analyzed by M398 software. **Table 1** shows the different system set ups selected for various CNTs produced by various methods.

RESULTS AND DISCUSSION

The effect of CNT fabrication method on electrochemical pretreatment

Nanomaterials or matrices with at least one of their dimensions ranging from 1 to 100 nm, display unique physical and chemical features and could be affected differently on the sensors. **Fig. 2** shows the SEM images of the modified CNT and naked electrodes. As the figure shows all the surfaces of GC electrode are covered by CNTs. Cyclic voltammograms for uric acid obtained at the multi-walled ARC-CNT modified GC electrode before and after the electrochemical pretreatment. The corresponding peaks are shown in **Fig. 3**. When the potential scan is repeated, the peak current decreases rapidly and the electrode regenerates, indicating that the accumulated UA can be removed. The voltammograms of uric acid for 2 set up at the surface of GC electrode covered by ARC-MWCNT fabricated in the solution, ARC-MWCNT in gas and CVD-MWCNT are shown in **Figs. 4** and **5**. The presented results reveal that the electrochemical pretreatment effects on CVD-CNT and ARC-CNT modified electrode respond differently. While the CVD-CNT appears to be resistant to anodic activation due to the impurities; the ARC-CNT following such pretreatment, displays a great enhanced electro analytic behavior. It follows from **Table 2** that UA can cause a largest anodic peak at the ARC (gas)-MWCNTs/GC. CVD-MWCNTs and ARC-MWCNTs fabricated in the solution showed high electro catalytic activity toward oxidation of UA. It is clear from the results that there is no big difference in voltametric characterization of ARC-CNTs produced in gas or liquid. Therefore the ARC-CNTs fabricated in gas could be substituted by the ones which synthesized in liquid.

The effect of CNT structure on electrochemical pretreatment

For the next step three different single, double and multi wall CVD-CNT were chosen for comparing in their category. The cyclic voltammograms of each of them are illustrated in **Fig. 6**. **Table 3** reveals that the oxidation of UA occurs at considerably the lowest potential at the CVD-MWCNT modified electrode. As it was expected the MWCNT displayed a greatly enhanced electrochemical reactivity following such treatment since it comprise of several layers of grapheme cylindrical that are concentrically nested like rings of a tree trunk. It should be noted that the purity of CNTs affected their electrochemical characteristics and properties. The oxidation peaks appeared in the cyclic voltammograms could be related to impurities deposited onto the surface of CNTs. These impurities included different metal catalysts, carbon nanostructure, etc; in which metal catalysts played the most important role. The more efficient method for purification of produced CNT subsequently leads to better results.

Table 1 The selected different system setups for electrochemical experiments on uric acid.

	Scan rate (mV/s)	Step time (s)	No. of Points	Elec. Area (cm^2)	Initial pot. (V)	Vertex1 pot. (V)	Final pot. (V)
Setup 1	100	$20*10^{-3}$	2001	1.00	1.00	-1.00	1.00
Setup 2	50	$40*10^{-3}$	1001	1.00	1.00	0.00	1.00
Setup 3	100	$20*10^{-3}$	1001	1.00	1.00	0.00	1.00

Table 2 The amounts of oxidation-reduction of CVD-CNT modified GC electrodes.

Synthesis method	Type of CNTs	Set up	Y ($mV.sec^{-1}$)	E_P^{ox} (mV)	I_P^{ox} (µA)	E_P^{R} (mV)	I_P^{R} (µA)
	Bare electrode	1	100	500	80	-	-
		2	50	500	31	-	-
		3	100	500	40	-	-
CVD	MWCNTs	1	100	445	115	420	35
		2	50	440	105	416	20
	SWCNTs	1	100	460	95	430	18
		2	50	450	50	420	5

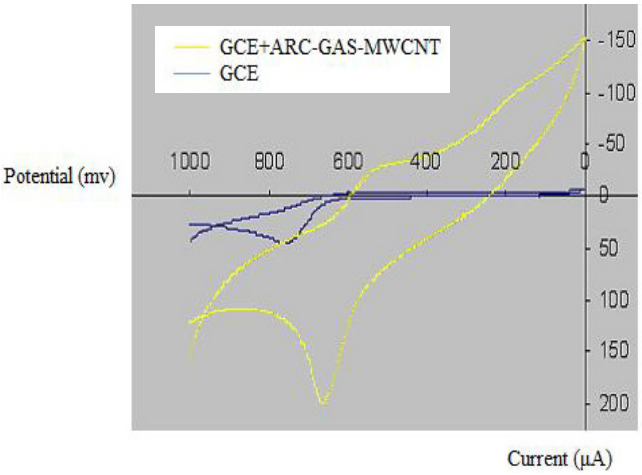

Fig. 3 Voltammograms of 5 mM UA with ARC-GAS-MWCNT modified electrodes, set-up 2.

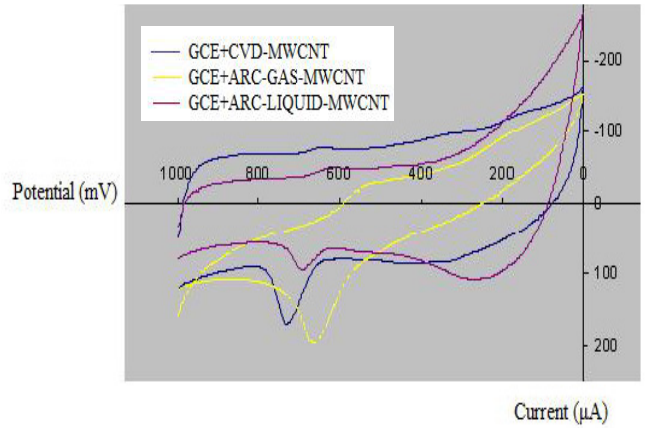

Fig. 4 Voltammograms of 5 mM UA with different MWCNT modified electrodes, set-up 2.

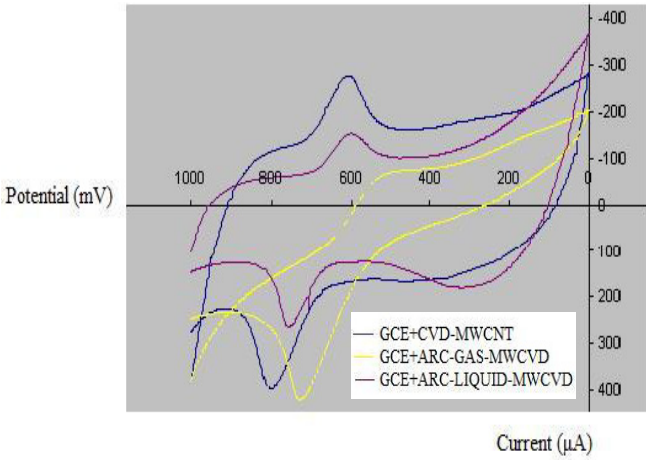

Fig. 5 Voltammograms of 5 mM UA with different MWCNT modified electrodes, set-up 3.

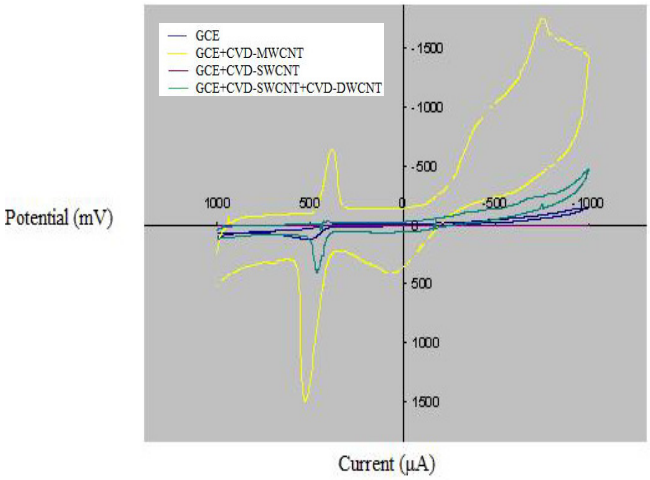

Fig. 6 Voltammograms of 5 mM UA with SW/DW/MW CVD-CNT modified electrodes, set-up 1.

CONCLUSION

The glassy carbon electrode was modified by different type of CNTs. The results presented above reveal a fact that the electrochemical pretreatment produces significantly different effects on the CVD-CNT and ARC-CNT modified electrodes. While the CVD-CNT appears to be resistive to the anodic activation that is due to the impurities and its structure; the ARC-CNT displays a greatly enhanced electrochemical reactivity because of such pretreatment. Recent data have shown the electro catalytic behavior of ARC-prepared CNT is due to the presence of edge plane defects at the open ends of the CNT rather than that on the corresponding side walls. This has been supported by the evidence that ARC-grown CNT, exhibit a higher catalytic activity than CVD-CNT, since the latter has close ends and resemble that of basal plane graphite. In addition, the MWCNTs have shown a better electrochemical behavior than SWCNTs based on their structure.

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REFERENCES

Engstrom RC (1982) Electrochemical pretreatment of glassy carbon electrodes. *Annals of Chemistry* **54**, 2310

Iijima S (1991) Helical microtubules of graphitic carbon. *Nature* **354**, 56-58

Iijima S, Ichihashi T (1993) Single carbon nanotube of 1-nm diameter. *Nature* **363**, 603-605

Jahanshahi M, Raoof J, Hajizadeh S, Jabari Seresht R (2007a) Application of Taguchi method in optimization of ARC-carbon canotubes fabrications. In: *Nanotechnology and its Application*, American Institute of Physics, pp 77-81

Jahanshahi M, Raoof J, Hajizadeh S, Jabari Seresht R (2007b) Synthesis of liquid arc discharge carbon nanotubes for applying in nano (bio)sensors, *Proceedings of an International Conference on Nanoscience and Nanotechnology*, 2007, Sweden

Jahanshahi M, Rostami AA, Hajizadeh S, Toubi F (2006b) Improvment of nanobio-sensors ability by multi walled carbon nano-tubes. *Proceedings of*

Table 3 The amounts of oxidation-reduction of ARC-CNT modified GC electrodes.

Synthesis method	Type of CNTs	Set up	Y (mV.sec^{-1})	E_P^{ox} (mV)	I_P^{ox} (µA)	E_P^{R} (mV)	I_P^{R} (µA)
ARC discharge in gas	MWCNTs	1	100	640	160	560	50
		2	50	650	130	570	35
	SWCNTs	1	100	680	100	570	30
		2	50	685	60	580	15
ARC discharge in liquid	MWCNTs	1	100	670	130	550	40
		2	50	675	110	550	35

First International Congress on Nanoscience and Nanotechnology, 2006, Tehran, Iran

Jahanshahi M, Rostami AA, Toubi F, Hajizadeh S (2006a) Carbon-nanotubes based, nanobiosensors: Voltammtric test and Fe^{3+} detection in clinical usage. *Nanobio Europe Conference*, 2006, Grenoble, France

He JL, Yang Y, Yang X, Liu YL, Liu ZH, Shen GL, Yu RQ (2006) β-Cyclodextrin incorporated carbon nanotube-modified electrode as an electrochemical sensor for rutin, *Sensors and Actuators B* **11**, 94-100

Chen J, Lin Z, Chen G (2007) Enhancement of electro chemiluminesence of lucigenin by ascorbic acid at single-wall carbon nanotube film-modified glassy carbon electrode. *Electro Chemica Acta* **52**, 4457-4462

Kangbing W, Wang H, Chen F, Hu S (2006) Electrochemistry and voltammetry of procaine using a carbon nanotube film coated electrode. *Bioelectrochemistry* **68**, 144-149

Molavi H, Shariaty-Niasar M, Jahanshahi M (2009) The synthesis of carbon nanotubes by arc discharge method in liquid media. *Journal of Faculty of Engineering, Tehran University*, in press

Rao CN, Satishkumar BC, Govindaraj A, Nath M (2001) Nanotubes. *ChemphysChem* **2**, 78-105