

Arc-discharge Carbon Nanotube Fabrication in Solution: Electrochemistry and Voltametric Tests

¹Mohsen Jahanshahi, ²Mojtaba Shariaty-Niassar, ³Abbas Ali Rostami, ²Hoda Molavi,
¹Forough Toubi

¹Nanobiotechnology Research Lab., Faculty of Chemical Engineering, Babol University of
Technology, Babol, Iran.

²Transport Phenomena & Nanotechnology Research Lab., Faculty of Chemical Engineering,
University of Tehran, Tehran, Iran.

³Electrochemistry Research Lab., Faculty of Chemistry, University of Mazandaran, Babolsar, Iran

Abstract: Arc discharge in a solution was applied to fabricate Carbon Nanotubes, CNTs. The products were then applied to electrochemical nano biosensors. The result of such application was compared with other synthesized CNTs, produced by using other methods. The high purity multi walled CNT synthesized by Arc discharge has shown the best outcome on the electrochemical behavior of glassy carbon electrode; comparing to other samples. The performance leads to a better understanding of its electrochemical reactivity. The results also showed a noticeable influence of CNT characteristics on nanobiosensor. Finally the generic application of CNT and the effect of its structure as well as the purity as a preliminary step toward the application in nano(bio)sensor are discussed.

Key words: Carbon Nanotube, Arc discharge, Fabrication, Electrochemical behavior, Nanosensor

INTRODUCTION

Carbon nanotubes (CNTs) are a form of carbon with a long, tubular structure and a graphitic lattice, which were identified by Iijima (Iijima, S., 1991). CNTs can either be single-walled (SWCNT) or multi-walled (MWCNT). The later of which is made of concentric SWCNTs (Baddour, E. and C. Briens, 2005). Although CNTs can be synthesized by a variety of techniques; but Arc Discharge in a gas media, Chemical Vapor Deposition (CVD) and Laser Ablation are the most common methods for commercial and bulk production (Merkoc, A., 2005; Harrison, S. and A. Atala, 2007).

High vacuum requirements, complex instrumentation and high cost for synthesis of CNTs; have made these methods inaccessible to the majority of researchers across the world (Shariaty-Niassar, M., 2006). Recently, arc discharge in the liquid phase has attracted considerable attention. That is due to its simplicity, low cost and the fact that a vacuum media is not required. Carbon nanostructures can be synthesized with such technique (Yao, Y., 2004; Bera, D., 2006).

However the traditional arc-plasma growth method for CNTs necessitates complex gas handling equipment: a sealed reaction chamber, a liquid-cooled system and time-consuming purge cycles. The extraction of the nanotube product is complicated too. In comparison, arc-plasma in solution calls for simple operation and equipment, which has made this method attractive for the production of CNTs (Bera, D., 2006; Bera, D., 2004).

A number of investigations on the arc discharge in solution showed its promising potential for the synthesis of various carbon nanostructures (Jahanshahi, M., 2009). Although the method is highly efficient for bulk production, a full-fledged instrumentation is not yet reported. However, automation of arc discharge in vacuum is given in literature (Shariaty-Niassar, M., 2007). CNTs have been the subject of numerous investigations in chemical and physical areas. That is due to their novel structural, mechanical, electrical and chemical properties (Yan, X.X., 2004; Yan, Q., 2006; Wu, K., 2004). Depending on their atomic structure, CNTs behave electrically as a metal or as a semiconductor. The subtle electronic properties suggest that CNTs have the ability to promote electron-transfer when used as an electrode in chemical reactions (Jahanshahi, M., 2006). Recent studies demonstrated that a modified CNT electrode can impart strong electrocatalytic activity

Corresponding Author: Mojtaba Shariaty-Niassar, Transport Phenomena & Nanotechnology Research Lab., Faculty of Chemical Engineering, University of Tehran, Tehran, Iran.
E-mail: mshariat@ut.ac.ir

to some important biomolecules, including cytochrome c, NADH, hydrogen peroxide, and catecholamines such as dopamine, epinephrine, and ascorbic acid (Lin, I. and Y. Li, 2006; Wu, K., 2006).

It has been reported that modified CNT electrodes were successfully applied to study and determine many biological and organic molecules (Jahanshahi, M., 2006; Wang, M., 2005; He, J.L., 2006; Chen, J., 2007). However, the comparison between the behavior of electrodes made of synthesized CNT (by Arc discharge or CVD) has not yet been reported.

In this study, the carbon nanostructures are synthesized with a simple Arc discharge technique in NaCl and LiCl solution which avoids costly vacuum equipment. The technique is highly efficient for bulk production and systematic parametric study which is not yet reported. The paper has also focused on the electrochemical behavior of uric acid on synthesized modified CNT electrode and compared with other similar types.

2. Experimental:

2.1 Carbon Nanotube Fabrication:

2.1.1 Materials:

All chemicals were of analytical grade and aqueous solutions were prepared with doubly distilled water. Salts such as NaCl (Fluka, Sweden) and catalysts such as Ni 99.5% (Merck, Germany), Mo 95% and Co 99% (Sigma, UK), graphite and gelatin powder, as well as two German graphite electrodes; anode (6 mm diameter) and cathode (12 mm diameter), with high purity were purchased. A direct current DC arc discharge was generated in solution between the two carbon electrodes. A Pyrex beaker (12×15×32 cm) was used as a container.

2.1.2 Synthesis:

A 5mm diameter hole was drilled at the open end of the anode and filled with a mixture of graphite and metallic catalysts powder. The electrodes submerged in 0.25M NaCl solution and aligned horizontally with 1mm gap. In order to strike the electric arc, electrodes brought into contact. The performed arc lasted for 60 seconds. The discharge current and voltage for all experiments sustained at 25V and 100A respectively during which the arc showed to be quite stable. Evaporation of the solution during the arc discharge is considered to be negligible. Experiments performed by using different metallic and bimetallic catalysts: the mixture of graphite and 5 at% Fe, 2 at% Ni and 2 at% Co as catalyst and Ni-Mo 2:1 at% and Co-Mo 2:1 at% as bimetallic catalysts. The products mainly had sunk to the bottom of the vessel with little floatation at the surface of the liquid. A schematic plan of the system is shown in Figure 1. The area between the electrodes is called; the plasma region. The plasma can also be seen to surround the anode, indicating the direction of plasma expansion.

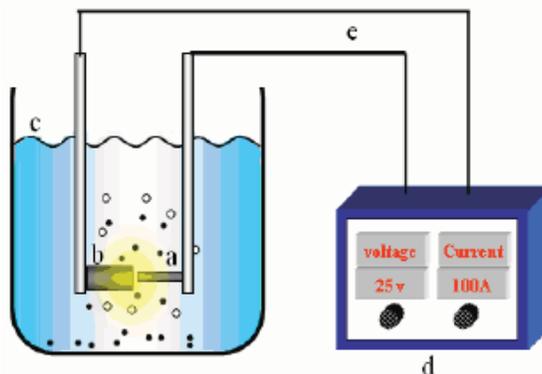


Fig. 1: The schematic feature of the arc discharge setup a) anode b) cathode c) media surface d) power Supplier e) wires

No deposit was observed on the cathode surface. That is mainly due to the solution agitation. The product was then collected by filter and subsequently purified. The nanostructure morphology of the deposits were further characterized and analyzed by scanning electron microscope (SEM), transmission electron microscope (TEM) and later approved by Raman spectroscopy.

2.1.3 Purification:

In order to purify the deposit; a sonicating process was used for 0.5 g as-prepared deposit in 12 N HCl for 30 minutes then the resulting solution was left to stand overnight. Then it was refluxed in 6 N HCl for 6 hours. After treating the deposit with acid, the solution was diluted with distilled water and centrifuged. Subsequently, the supernatant solution was decanted and the residue was transferred onto a Millipore filter paper. The residue on the filter paper was washed with distilled water (4–5 times) to remove the acid. The residue was dried in an oven at $C 80 -100$ for 5 hours. Then the carbon nanotubes were weighted and kept in desiccators.

2.2 Electrochemical Experiments:

2.2.1 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 cm³ was maintained. Different types of CVD and gas arc discharge synthesized CNTs were prepared.

In general, a comparison was made between the SWCNTs and MWCNTs synthesized by arc discharge in gas and CVD with those synthesized by this research using arc discharge in liquid.

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 CNT modified glassy carbon electrode, MGCE (BAS, 3mm) was served as the working electrode.

2.2.2. Electrochemical Pretreatment:

Two-electrode super-capacitor cells with a surface of 4 cm² were assembled in a glove box. 2M HNO₃ was applied for pre-acid treatment of CNTs for 20 hours. After drying the CNTs in room temperature, they were sonicated with dispersing agent, Dimethyl Formamide (DMF), for 1 hour. The electrode was polished with Alumina powder and then 25 micro liter of DMF/CNT solution (2mg CNT/2ml DMF) was dropped on to the surface of GCE. About 1mM 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. 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 two different system setups selected for CNTs produced by various methods.

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

	Unit	Setup 1	Setup 2
Scan Rate	mv/s	100	50
Step Time	s	20×10^{-3}	40×10^{-3}
No. of Points		2001	1001
Working Elec		Solid	Solid
Elec. Area	cm ²	1.00	1.00
Initial Pot	V	1.00	1.00
Vertex 1 Pot	V	-1.00	0.00
Final Pot	V	1.00	1.00

RESULTS AND DISCUSSION

3.1. Structures of Produced CNTs:

In order to consider the best conditions for fabricating CNTs, the effect of different parameters such as voltage and catalyst were taken into consideration. During arc-discharge in solution, clusters of CNTs were found to be floating on water surface. NaCl (0.25 M) solution was prepared as a liquid media for arc discharge. Some amount of 5 at% of Fe, gelatine and graphite powders were applied as catalyst, a binder and a filler, respectively. With a potential of 15 or 20 V, a stable and uniform plasma region could not be performed and hence an undesired product was obtained. These were composed of CNTs together with other carbonaceous materials such as dislodged graphene sheets, carbon NanoParticles, amorphous carbon and carbon fibers. Whereas by applying a voltage of 25V and a constant current of 100A a stable plasma was performed and fabricated CNTs of about 50 nm diameter were produced. Figure 2 shows these products without purification.

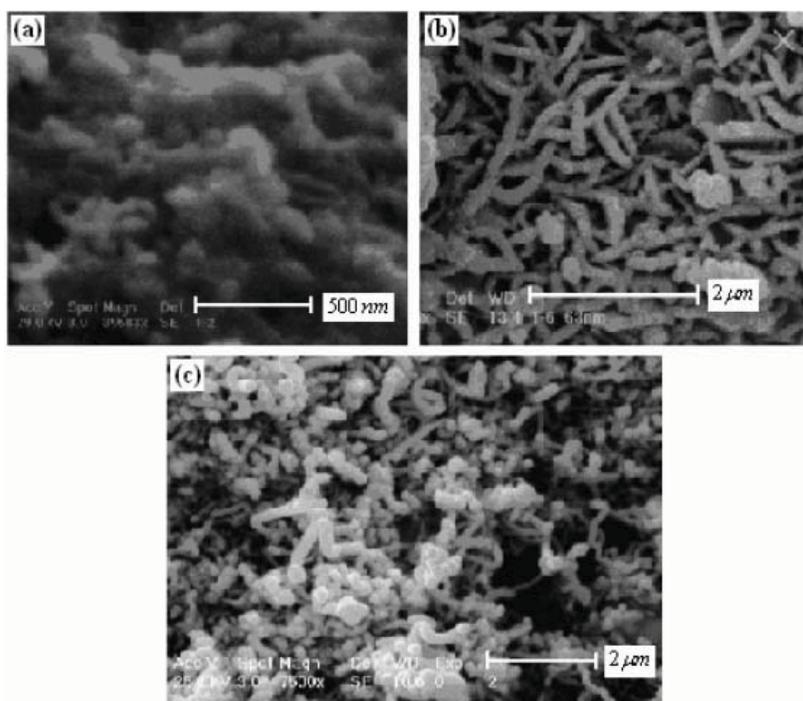


Fig. 2: SEM images of fabricated unpurified samples under different voltage a) 15 V, no CNT produced because of unstable plasma region; b) 20 V, carbon nanostructure were fabricated; c) 25 V, CNTs and nanofibers.

Two different bi-catalysts of Ni-Mo and Co-Mo with the ratio of 2:1 at%, were used to evaluate their effects on CNTs growth. As it is shown in Figure 3, CNTs' growth by using Ni-Mo catalyst have better structure than those with Co-Mo. Figure 4, however shows SEM and TEM images of the produced CNTs as well as TEM image of purified CNT, at the above electrical condition, using 1:1 at% Ni:Mo bi-catalyst. TEM image of as-synthesized CNT shows a CNT which has a catalyst on its end. On the other hand, TEM image of purified samples presents open-ended CNTs.

Figure 5 shows the Raman spectrum of produced CNTs after purification stage in an optimum condition (25V, 100A and 2:1 at% Ni:Mo bi-catalyst). The ratio of $I_{G/D}$ in this spectrum is about 3.7 indicating the low amount of disorder structures compared to crystalline ones (IG and ID correspond to the disorder (D) and graphite (G) bands, respectively).

In both solutions (NaCl and LiCl), the ratio of 2:1 at% of Ni:Mo lead to a better result. However, Figure 6 shows the comparison of purified synthesized CNT in two separate solutions of NaCl and LiCl.

3.2 Electrochemical Analysis:

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. Figure 7 shows the SEM images of the bare electrode and the modified CNT electrode. As the figure shows all the surfaces of GCE are covered by CNTs. However the outcome of different CNTs used herein were illustrated in Table 2.

The voltammogram of uric acid for two setups is shown in Figure 8. When the potential scan is repeated, the peak current decreases rapidly and the electrode regenerates, indicating that the accumulated UA can be removed. For comparison, a MWCNTs/MGCE (Modified GCE) was tested.

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.

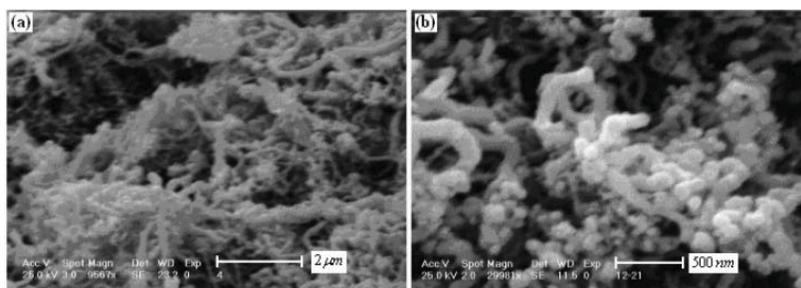


Fig. 3: The effect of different catalysts on the structure of as-synthesized CNTs under 25 V, 0.25 M NaCl solution, 2:1 at% catalyst ratio a) Ni-Mo; b) Co-Mo

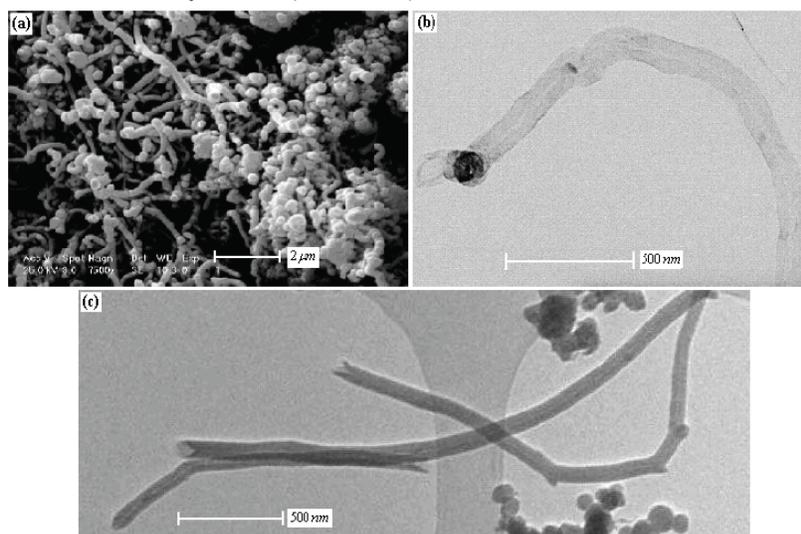


Fig. 4: a) SEM, b) TEM image of as-produced CNT, c) TEM image of purified CNTs synthesized by using 1:1 at% Ni:Mo bicatalyst

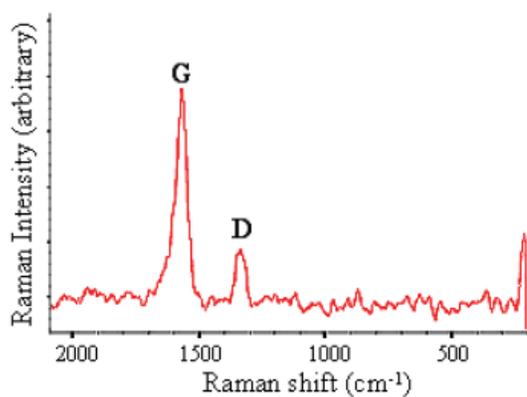


Fig. 5: Raman spectrum of CNTs prepared by DC arc discharge under: 0.25 M NaCl solution, 25 V, 100 A, Ni-Mo catalyst, 1:2 catalyst ratio

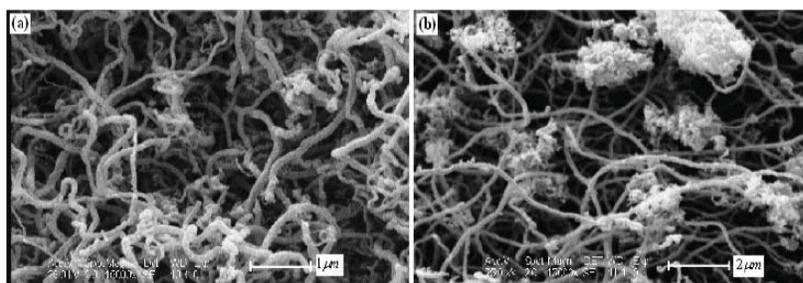


Fig. 6: SEM images of purified CNTs synthesized in 0.25 M a) NaCl b) LiCl solutions

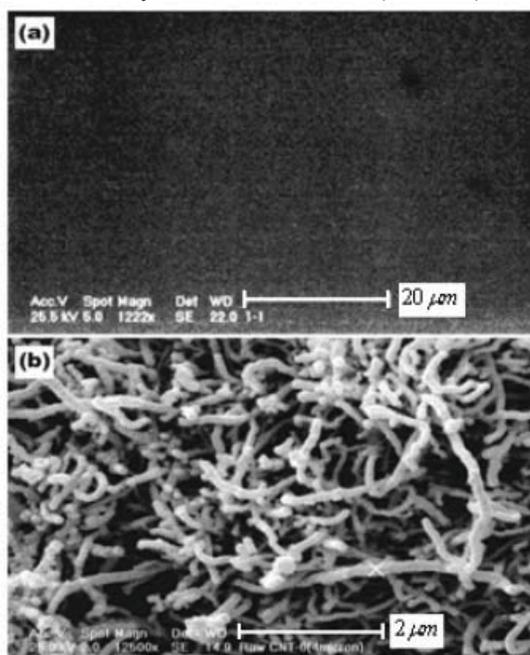


Fig. 7: The SEM image of Electrode (a) without (b) With CVD MWCNT coating as an example.

Table 2: The amounts of oxidation-reduction of different modified GC electrodes with various kinds of CNTs

Methods	CNTs	setup	Initial pot (V)	Vertex Pot (V)	v (mV.sec ⁻¹)	E_p^{OX} (mv)	I_p^{OX} (A)	E_p^R (mv)	I_p^R (A)
	Electrode	1	1	-1	100	50	90	-	-
		2	1	0	50	500	31	-	-
	MWCNTs	1	1	-1	100	44	115	420	35
		2	1	0	50	440	105	415	20
CVD	SWCNTs	1	1	-1	100	460	95	430	18
		2	1	0	50	450	50	420	5
ARC discharge in Gas	MWCNTs	1	1	-1	100	64	160	560	50
		2	1	0	50	650	130	570	35
	SWCNTs	1	1	-1	100	680	100	570	30
		2	1	0	50	685	60	580	15
ARC discharge in liquid	MWCNTs	1	1	-1	100	670	130	550	40
		2	1	0	50	675	110	550	35

E_p^{OX} : Potential of oxidation,
 I_p^{OX} : Current of oxidation,
 E_p^R : Potential of reduction ,
 I_p^R : Current of reduction, i : Scan rate

From Figure 8; it follows that UA can cause a largest anodic peak at the CVD-MWCNTs/GC. Part of this can be described as for the difference between CNTs structures and their purity. Meanwhile, the ratio of peak current to the background current is also much larger than the other modified electrodes.

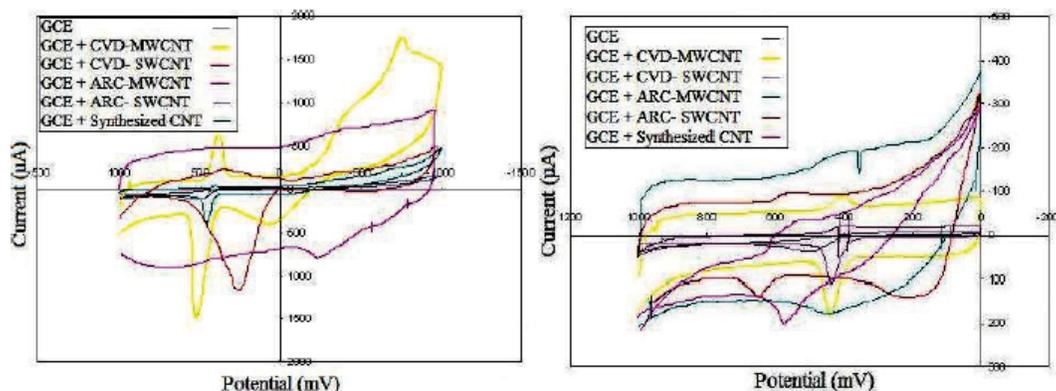


Fig. 8: Voltammograms of 5 mM UA with different modified electrodes a) setup 1; b) setup 2

ARC-MWCNTs produced in the gas and fabricated in the solution showed high electro catalytic activity toward oxidation of UA. ARC-SWCNTs in gas, CVD-MWCNT and CVD-SWCNT stand on third, fourth and fifth place, respectively. Another catalytic property of the synthesis in liquid is the *edge plane defect* that is due to the open ended structure of ARC-CNTs. It is clear from the table that there is no big difference in voltametric characterization of ARC-CNTs produced in gas or liquid. Therefore, the fabricated ones in gas, could be substituted by those synthesized in liquid.

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.

Conclusions:

In this study MWCNTs were successfully synthesized, by using arc discharge in NaCl solution in the presence of the bi-catalyst of 2:1 at% Ni-Mo and purified with acid treatment. SEM and TEM images together with Raman spectroscopy, indicate that the best results are achieved under the condition of 25V, 100A current in a 0.25M NaCl medium. However, the results have also depicted that the amount of amorphous carbon was minimal when bimetallic catalyst was used. In order to evaluate the fabricated CNT; the glassy carbon electrode was modified by produced CNT and hence subjected to electrochemical comparison with the performance of other types of CNT. 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. Current research data have shown the electro catalytic behavior of ARCCNT that 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. Because, 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.

ACKNOWLEDGMENTS

The Authors gratefully acknowledge and appreciates the supports given by Nanobiotechnology Research Laboratory of Babol University of Technology, I.R. Iran; the Transport Phenomena & Nanotechnology Research Laboratory, Faculty of Chemical Engineering, Tehran University and the Electrochemistry Research Laboratory of Mazandaran University.

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