Research Paper

Electrochemical Pretreatment of Single and Multiwall CNT-based biosensors

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Abstract

This paper addresses recent advance in electrochemical pretreatment of Carbon-Nanotubes (CNT) based Nanobiosensors. CNT which has been produced by different processes, i.e. arc-discharge and chemical vapor deposition (CVD), subjected to the electrochemical activation. As for ARCCNT the anodic pretreatment resulted in a dramatic improvement in the electrochemical reactivity (cycle Voltammetric test in 1.5 V) while CVD-CNT appeared to be resistant to the anodic activation. Such a huge difference was illustrated through NADH, ascorbic acid hydrogen peroxide and hydrazine model redox systems. The influence of the pretreatment potential and time is examined. The results herein offer a better understanding of the electrochemical reactivity of CNT. Common design of CNT-based Nanobiosensors along with practical examples of such novel devices is strongly discussed.

Keywords: Electrochemical Pretreatment; Carbon Nanotube; Cycle Voltammogram; Nanobiosensor

1. Introduction

Carbon nanotubes (CNT) have become the subject of intense investigation since their discovery. Such considerable interest reflects the unique behavior of CNT, including their remarkable electrical, chemical, mechanical and structural properties. CNT can display metallic, semi-conducting and superconducting electron transport, possess a hollow core suitable for storing guest molecules and have the largest elastic modulus of any known material [1, 2] . CNT can be made by chemical vapor deposition, carbon arc methods, or laser evaporation and 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 (Figure 1). 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) [3-5] . The unique properties of carbon nanotubes make them extremely attractive for the task of chemical sensors, in general and electrochemical detection, in particular [5-7] .
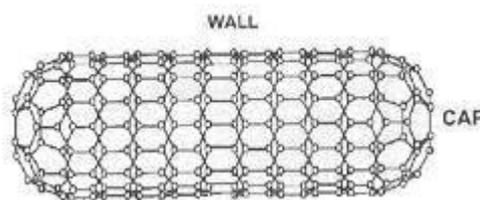

Figure 1. Structure of SWCNT

The purpose of the present study is to investigate the electrochemical pretreatment of CNT-modified electrodes and relates it to the nature of the electro catalytic response of CNT for nanobiosensor usage. It has long been recognized that the electrochemical pretreatment of carbon electrodes can have a

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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 and later to the possible removal of impurities form the electrode surface [8-10] .

In addition, CNT electrodes are particularly useful for the biosensing of important substrates as they offer an accelerated electron transfer of, for example NADH along with minimization of surface fouling. As indicated from figure 2, the CNT electrodes exhibit a substantial negative shift of the anodic peak potential and increased current signal. The catalytic activity is evident from the defined peaks [9-11] .
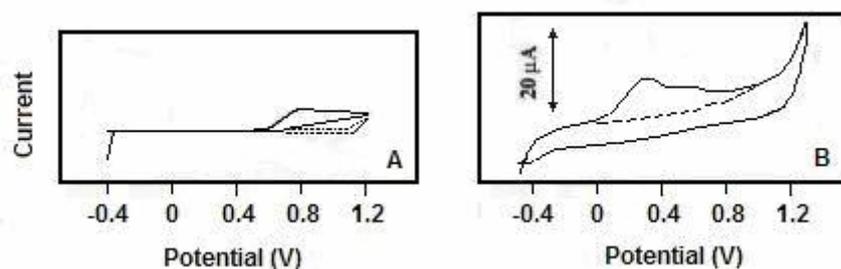
However, it has been shown that mode of production of the CNT, either by chemical vapor deposition (CVD) or the ARC discharge process, affects the electrochemical reactivity of the CNT, with the CVD displaying a higher electrocatalytic activity [9].This has been tentatively attributed to the higher density of edge plane defects observed at the CVD-CNT surface. These data have been substantiated recently by Banks et al. who have investigated the origin of the electrocatalytic response of the CNT. They found that CVD-produced CNT display remarkably similar behavior to that of an edge plane pyrolytic graphite electrode [1, 12-14] . Here we compare and discuss the electrochemical pretreatment of ARC-and CVD-prepared multi-walled CNT; and discuss various aspect of the work [8-11] .

Figure 2. Cyclic voltammograms for 5mM NADH at unmodified (A), MWCNT- modified (B) and SWCNT- modified

ARCCNT (B) modified GC electrodes before and after (light and dark lines, respectively) the electrochemical pretreatment.

The corresponding peak potentials (or the initial potential at which an oxidative current is observed), prior to and after the pretreatment, are detailed in Table 1. (In figure 3 hydrogen peroxide has not been shown). A comparison of the data detailed in figure 2 and Table 1 reveals that the oxidation of each analyte occurs at considerably lower potentials at the untreated CVD-CNT layer compared to the untreated ARC-CNT modified GC electrode (light lines). These findings are consistent with previous literature data and reflect in the CVD-CNT [9]. Overlaid in figure 3 are the voltammetric signals recorded after each electrode had undergone a 4 min electrochemical pretreatment at +1.5 V (dark line). The similarity of the peak potential at the CVD-CNT before and after the pretreatment indicates that they are not prone to surface activation. In contrast, the ARC-CNT layer (B) displays a marked lowering in the oxidative peak potential for all three analytes under these conditions. Furthermore, analysis of the peak heights for each analyte reveals that the CVD-CNT layer shows little variation in the peak intensity prior to and after the surface oxidation whilst the signals of the ARCCNT modified GC electrode increase following the anodic treatment.

2. Material and Methods

All reagents were obtained from Sigma and Aldrich. All solutions and subsequent dilutions were prepared daily, using doubly distilled water. Cyclic voltammetry measurements were conducted using an Auto Lab computer-controlled potentiostat. In all cases a standard three electrode configuration and a typical cell volume of 10 cm^3 was maintained. Multi-Wall CNT was supplied from industry oil and gas research center of Iran and purchased from Material Limited (NM, USA) and Bucky (TX, USA). A CNT glassy carbon (BAS, 3 mm diameter) served as the working electrode with platinum wire as the counter electrode and an Ag/AgC1 reference electrode.

2.1. Electrochemical pretreatment

The various CNT GC electrodes were electrochemically pretreated prior to voltammetric measurement by applying a fixed potential (+0.60 to +1.95V) to the working electrode for a selected time (0-180s) under stirring conditions.

3. Results and Discussions

Figure 3 details cyclic voltammogtams for ascorbic acid (a), NADH (b) and hydrogen peroxide

(150mVs⁻1), obtained at the CVD-CNT (A) and the

potential on their responses to 5 mM ascorbic acid (data not shown).

To further demonstrate this apparent different activation effects on ARC-and CVD-CNT electrodes, we examined the influence of the pretreatment

Table 1. A summary of the cyclic voltammetric peak potentials obtained for different analytes at the CVD-CNT and ARC-CNT layers before and after anodic pretreatment. (Based on the cyclic voltammetric data of figure 3)

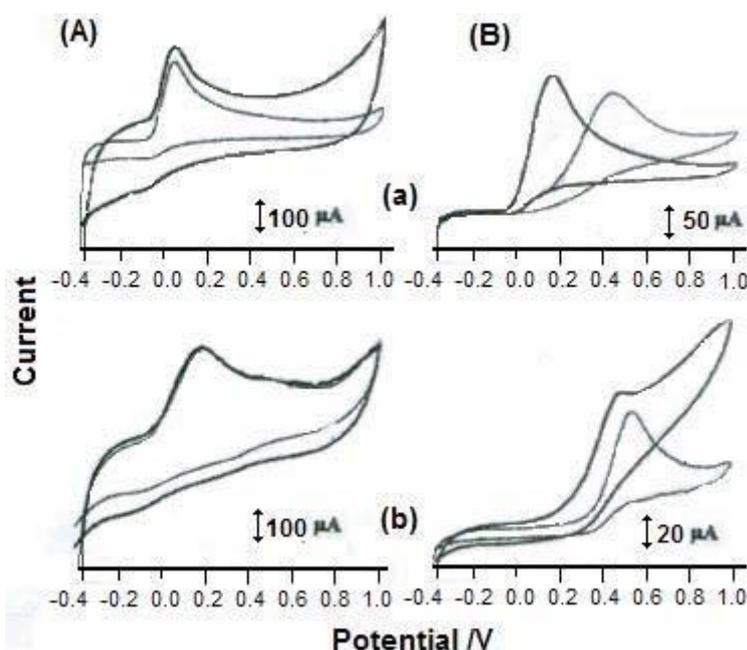| Analyte	CVD-CNT		ARC-CNT	
	No treatment	Treatment at +1.50V	No treatment	Treatment at+1.50V
Ascorbic acid	+0.50	+0.50	+0.42	+0.13
NADH	+0.18	+0.18	+0.58	+0.45
H_2O_2	+0.59	+0.59	+0.89	+0.65

Figure 3. Cyclic voltammograms obtained at the CVD-CNT (A) and ARC-CNT (B) modified GC electrodes in the presence of (a) 5 mM ascorbic acid, (b) 5 mM NADH

4. Conclusions

The results presented above reveal that the electrochemical pretreatment produces significantly different effects on the CVD-CNT and ARC-CNT modified electrodes. While the CVD-CNT appears to be resistant to the anodic activation, the ARC-CNT displays a greatly enhanced electrochemical reactivity following such pretreatment.

Recent data have shown the electrocatalytic behavior of CVD-prepared CNT is due to the presence of edge plane defects at the open ends of the CNT rather that on their side walls .This has been supported by evidence that CVD-grown CNT exhibit a higher catalytic activity than ARC-CNT as the latter have closed ends and resemble that of basal plane graphite. CVD-CNT prepared at elevated

temperatures [12] may possess a larger fraction of exposed edge planes compared to "hollow-tube" CVD-CNT. It has been previously reported that the oxidation of the basal plane can result in fragmentation of the surface to expose edge plane defects, producing faster electron transfer rates at the electrode surface. ARCCNT are largely inactive until edge plane are created. It can be though that the anodization of the ARC-CNT layer produces stress on the CNT which then effectively "breaks" their end caps, exposing new edge plane carbon, and leading to the electrocatalytic behavior. This is supported by the results obtained for the oxidation of ascorbic acid detailed in figure 4. Figure 4 details the corresponding plots of the anodic peak potential against the pretreatment potential for the oxidation of NADH (A) and hydrazine (B) at the (a) ARC-CNT and (b) CVDCNT Lagers.
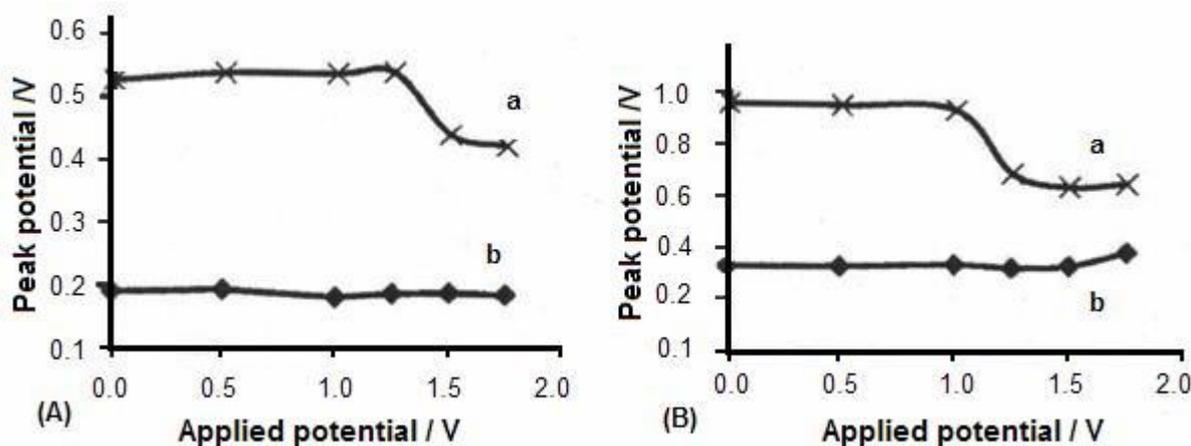
Figure 4. Dependence of the cyclic voltammetric oxidation peak potential upon the pretreatment potential for oxidation of 5 mM (A) NADH and (B) hydrazine at (a) the ARCCNT and (b) CVD-CNT layers. Other conditions as in figure 3.

This process is known to both shorten and carboxylate the CNT. The resulting voltammogram for 5 mM ascorbic acid displayed an oxidative wave at +0.06V (not shown), analogous to that of the untreated CVD-CNT electrode. The extent to which the anodic pretreatment affects the electrochemical behavior will depend on the mechanism of the specific redox process begin studied as outlined by the three systems detailed above.

Better control of the chemical and physical properties of CNT and should lead to more efficient electrical sensing devices. Further spectroscopic and voltammetric studies have been carried out and the results will be reported in our future publication.

References

1. Santharaman P, Venkatesh KA, Vairamani K, Benjamin AR, Sethy NK, Bhargava K, et al. 2017. ARM-microcontroller based portable nitrite electrochemical analyzer using cytochrome c reductase biofunctionalized onto screen printed carbon electrode. *Biosensors and Bioelectronics* 90: 410-417.

2. Torres-Martínez CL, Nguyen L, Kho R, Bae W, Bozhilov K, Klimov V, et al. 1999. Biomolecularly capped uniformly sized nanocrystalline materials: glutathione-capped ZnS nanocrystals. *Nanotechnology* 10(3): 340-354.

3. Kar S, Biswas S, Chaudhuri S. 2005. Catalytic growth and photoluminescence properties of ZnS nanowires. *Nanotechnology* 16(6): 737-740.

4. Soltantabar Shahabedini A, Alinezhad Chamazketi M, Yaghoubi Nezhad A, Mostafavi SM. 2020. Electrophoretic removal of sodium dodecyl sulphate from peptide solution through a hydrogel-micropipette system. *Eurasian Chemical Communications*. en.

5. Rossetti R, Hull R, Gibson JM, Brus LE. 1985. Excited electronic states and optical spectra of ZnS and CdS crystallites in the ≅15 to 50 Å size range: Evolution from molecular to bulk semiconducting properties. *The Journal of Chemical Physics* 82(1): 552-559.

6. Hu J, Bando Y, Zhan J, Golberg D. 2005. Growth of Wurtzite ZnS Micrometer-Sized Diskettes and Nanoribbon Arrays with Improved Luminescence. *Advanced Functional Materials* 15(5): 757-762.

7. Jiang Y, Meng X-M, Liu J, Xie Z-Y, Lee C-S, Lee S-T. 2003. Hydrogen-Assisted Thermal Evaporation Synthesis of ZnS Nanoribbons on a Large Scale. *Advanced Materials* 15(4): 323-327.

8. Zhang H, Ji Y, Ma X, Xu J, Yang D. 2003. Long Bi2S3nanowires prepared by a simple hydrothermal method. *Nanotechnology* 14(9): 974-977.

9. Wang Z, Daemen LL, Zhao Y, Zha CS, Downs RT, Wang X, et al. 2005. Morphology-tuned wurtzite-type ZnS nanobelts. *Nature Materials* 4(12): 922-927.

10. Haddad R, Cosnier S, Maaref A, Holzinger M. 2009. Non-covalent biofunctionalization of single-walled carbon nanotubesviabiotin attachment by π-stacking interactions and pyrrole polymerization. *Analyst* 134(12): 2412-2418.

11. Paul KB, Singh V, Vanjari SRK, Singh SG. 2017. One step biofunctionalized electrospun multiwalled carbon nanotubes embedded zinc oxide nanowire interface for highly sensitive detection of carcinoma antigen-125. *Biosensors and Bioelectronics* 88: 144-152.

12. Dong L, Chu Y, Zhang Y, Liu Y, Yang F. 2007. Surfactant-assistant and facile synthesis of hollow ZnS nanospheres. *Journal of Colloid and Interface Science* 308(1): 258-264.

13. Ferreira GMD, Ferreira GMD, Almeida GWR, Soares NFF, Pires ACS, Silva LHM. 2019. Thermodynamics of multi-walled carbon nanotube biofunctionalization using nisin: The effect of peptide structure. *Colloids and Surfaces A:*

Physicochemical and Engineering Aspects 578: 123611.

14. Le Goff A, Gorgy K, Holzinger M, Haddad R, Zimmerman M, Cosnier S. 2011. Tris(bispyrene-bipyridine)iron(II): A Supramolecular Bridge for the Biofunctionalization of Carbon Nanotubes via π-Stacking and Pyrene/β-Cyclodextrin Host–Guest Interactions. *Chemistry – A European Journal* 17(37): 10216-10221.