Electrochemical Pretreatment of Single and Multiwall CNT-based biosensors

Hamad Al-Mobarak *, Sabah Al-Rafat

Department of Chemistry, Qatar University, Qatar

Received: 24 March 2020  Accepted: 04 May 2020  Published: 01 June 2020

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 ARC-CNT 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 Voltamogram; 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 graphene cylinders that are concentrically nested like rings of a tree trunk (with an interlayer spacing of 3.4 Å) [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
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 quinone functionalities upon the carbon surface and later to the possible removal of impurities from 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<sup>3</sup> 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/AgCl 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 voltammograms for ascorbic acid (a), NADH (b) and hydrogen peroxide (150mVs<sup>-1</sup>), obtained at the CVD-CNT (A) and the
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)

<table>
<thead>
<tr>
<th>Analyte</th>
<th>CVD-CNT No treatment</th>
<th>CVD-CNT Treatment at +1.50V</th>
<th>ARC-CNT No treatment</th>
<th>ARC-CNT Treatment at +1.50V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ascorbic acid</td>
<td>+0.50</td>
<td>+0.50</td>
<td>+0.42</td>
<td>+0.13</td>
</tr>
<tr>
<td>NADH</td>
<td>+0.18</td>
<td>+0.18</td>
<td>+0.58</td>
<td>+0.45</td>
</tr>
<tr>
<td>H₂O₂</td>
<td>+0.59</td>
<td>+0.59</td>
<td>+0.89</td>
<td>+0.65</td>
</tr>
</tbody>
</table>

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 than 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. ARC-CNT 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) CVD-CNT Lagers.
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 pretreatmen
t 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