Study of Nitroazobenzene Films Covalently Attached at the Surface of Carbon that Exhibit Conductance Switching

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(Received 3 December 2005; Accepted 10 April 2006; Published 19 April 2006)

The deposition of 4-nitroazobenzene (NAB) on carbon electrodes were achieved by the electrochemical reduction of 4-Nitro-4’-diazonium azobenzene tetrafluoroborate in anhydrous acetonitrile media using cyclic voltammetry technique at room temperature. The modified surfaces were examined as voltammetric electrodes for $\text{Fc/Fc}^+$, $\text{Ru(NH}_3)_6^{3+/2+}$, $\text{IrCl}_6^{2-/3-}$, $\text{Fc(COOH)}_2$, $\text{Fe(phen)}^{3+/2+}$ and $\text{Ru(bpy)}^{3+/2+}$. The modified electrodes exhibited very slow electron transfer in compare to unmodified surfaces, by factors that varied with the redox systems. However, after scanning the modified electrode in 0.1M n-tetrabutylammonium tetrafluoroborate ($\text{TBABF}_4$) in acetonitrile from +0.4 to $\sim$ −0.9 V versus Ag/Ag$^+$ for 25 cycles, the modified electrodes exhibited much faster electron transfer kinetics, for some redox systems approaching those observed on unmodified surfaces. The effect is attributed to an apparently irreversible structural change in the NAB monolayer, which increases the rate of electron tunnelling. The transition to the "ON" state is associated with electron injection into the monolayer. Once the monolayer is switched ON, it supports rapid electron exchange with redox systems, but not with dopamine, which requires adsorption to the electrode surfaces. A "switching" electrode may have the potential to impact the field of molecular electronics, which is one of the more popular areas of nanotechnology.

Keywords: nitroazobenzene; modified electrode; conductance switching; cyclic voltammetry

I. INTRODUCTION

The derivatization of surfaces is often required to improve the performance of many materials and change their surface properties and is often critical for some particular applications. Surface modification of carbon electrodes has been directed toward several goals, often involving electrode kinetics and chemical selectivity. In many cases, a surface-bound functional group can effect selectively by electrostatic repulsion or attraction, by providing a binding site for particular species, or by serving as a catalyst for certain electrochemical reactions [1–8].

The electrochemical grafting of specific organic molecules has become a method of choice since the deposition conditions can be easily controlled and adopted to the substrate. In this method, the substituted aryl groups by reduction of the corresponding diazonium salt are an attractive way to modify carbon-based surfaces [2, 3, 9–16]. Pinson and coworkers introduced this in the early 90’s [9]. Scheme 1 describes the two-step process of this reaction which involves (1) the electrochemical reduction of the diazonium function and the formation of phenyl radical and (2) the chemical grafting the radical at the surface of the electrode with the formation of a covalent bond between a surface atom of the substrate and the phenyl group.

Scheme 1

\[
\text{RC}_6\text{H}_4\text{N}_2^+ + e^- \rightarrow \text{N}_2 + \text{RC}_6\text{H}_4^* \\
\text{RC}_6\text{H}_4^* + \text{GC} \rightarrow \text{GC-C}_6\text{H}_4\text{R}.
\]

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The high reactivity of phenyl radicals produces densely packed monolayers on carbon, which often exhibit negligible observable pinholes. Examples of the electrochemical effects of diazonium modification include a complete inhibition of dopamine oxidation [4, 5]. Such modified carbon electrodes were characterized by a variety of electrochemical and spectroscopic techniques [2, 3, 17–20]. Most of the studies have demonstrated a strong bonding and dense packing of monolayers produced by diazonium reduction [10, 17, 21–23]. Kariuki and McDermott used scanning probe microscopy to demonstrate that reduction of diethyl aminophenyldiazonium ion can produce multilayers with thickness of $\sim 20$ nm under certain conditions, particularly high diazonium ion concentration and long reduction times [13, 14].

The purpose of this work was to study the deposition of 4-nitroazobenzene at the surface of glassy carbon (GC), ultraflat carbon films (UCFs), pyrolyzed photoresist films (PPF) [24, 25] by the reduction of 4-Nitro-4’-diazonium azobenzene tetrafluoroborate. The electrochemical reduction and film deposition was initially investigated by cyclic voltammetry. In addition, the current work also investigates conductance switching in an electrochemical context, in which a modified electrode with NAB is immersed in electrolyte solution containing a redox active analyte. When the monolayer is in its initial state, the carbon substrate is isolated from the solution, and redox reactions in solution require tunnelling through the monolayer. Once the monolayer is "switched" to a high conductance state, electron transfer may proceed through the monolayer, but the electrode/solution interface is defined by the monolayer rather than the substrate. The conducting NAB monolayer thus replaces the carbon substrate to form modified conducting surfaces.
II. EXPERIMENTAL

Diazonium reduction is very effective means to modify carbon surfaces [10, 17, 26], but care is required to successfully synthesize the reagents and modify the surface without multilayer formation. Problems occur when using "old" diazonium reagent, high reagent concentrations (> 1 mM) and long deposition times at excessive negative potentials [13, 14]. The following procedure is described in detail to avoid these difficulties.

Commercial glassy carbon (GC) electrodes (Bioanalytical Systems) were polished successively in 1 µm, 0.3 µm and 0.05 µm alumina slurries made from dry Buehler alumina and Barnstead Nanopure water (18 MΩ) on Buehler microcloth polishing cloth. Polished GC electrodes were sonicated in Nanopure water and then in a mixture of 50/50 (v/v) isopropanol (Mallinckrodt AR) / acetonitrile (Aldrich), combined with an equal volume of Norit A activated carbon, in both cases for 10 minutes [24]. Samples were rinsed with acetonitrile and then with Nanopure water, dried with an argon gas stream, and derivatized immediately. Derivatized electrodes were not sonicated, to reduce the possibility of damage to the monolayer. The procedure for preparing and cleaning Ultraflat carbon films (UCFs), pyrolyzed photoresist films (PPF) have been described elsewhere [24-26].

4-Nitro-4’-diazenium azobenzene tetrafluoroborate (NABDS) was prepared according to Dunker, et al [27]. Surface derivatization was performed using 1 mM solution of NABDS in acetonitrile containing 0.1 M n-tetraethylammonium tetrafluoroborate (TBABF4, Aldrich).

The following solutions were prepared as indicated: 1 mM potassium hexachlororidate(IV) (Aldrich Chemical Co.) in 1 M KCl; 1 mM hexamamineruthenium(III) chloride (Strem Chemicals) in 1 M KCl; 1 mM 1,1’-ferrocenedicarboxylic acid (Aldrich Chemical Co.) in pH 7 phosphate buffer +1 M KCl; 2 mM tris(1,10-phenanthroline)iron(II) (from 2 mM ferrous ammonium sulphate (reagent grade, J. T. Baker) and 6 mM 10 phenanthroline (Aldrich Chemical Co.)) in 1 M KCl; 1 mM tris(2,2’-bipyridyl) ruthenium(II) hexahydrate (Aldrich chemical Co.) in pH 7 phosphate buffer +1 M KCl; 1 mM Dopamine hydrochloride (DA, Sigma Chemical Co.) in 0.1 M H2SO4; 1 mM Ferrocene (Fc, Fluka) in acetonitrile(ACN) containing 0.1 M TBABF4. Phosphate buffer solutions were prepared from 0.1 M KH2PO4 (Matheso, Coleman and Bell) and additional NaOH (Mallinckrodt) to pH 7.0. Potassium chloride (Ana chemical), Sulphuric acid (GFS Chemicals), and other chemicals were used as received except water in acetonitrile was removed with 4 Å molecular sieves followed by fractional distillation at atmospheric pressure. All solutions were prepared daily and were purged with high purity nitrogen gas for 10-minute prior to use.

Cyclic voltammetric measurements were performed in a standard three-electrode cell. The surface area of working electrode was defined by an elastometric O-ring and electrochemically [28] determined to be 0.35 ± 0.01 cm². A platinum auxiliary electrode and Ag/AgCl (saturated KCl) or Ag/Ag+ as a reference electrode were used. For preparation of Ag/Ag+, 10 mM AgNO3 was dissolved in 0.1 M TBABF4, in acetonitrile. The cell was connected to a BAS 100 W potentiostat (Bioanalytical Systems Inc.) and data were recorded with PineChem (version 2.7.2) software.

III. RESULTS AND DISCUSSION

Derivatization of nitro-azobenzene (NAB) film on the GC surfaces was performed using cyclic voltammetry between +0.4 to −0.7 V with a scan rate of 200 mV/s. versus Ag/Ag+ in 1 mM 4-Nitro-4’-diazenium azobenzene tetrafluoroborate in 0.1 M TBABF4 in acetonitrile. Figure 1 presents a broad and irreversible cathodic wave, which has highest cathodic current at a potential of −0.19 V, disappeared completely on the second scan. Electrochemistry is a useful characterization method when a redox active modifier (most commonly the nitro-phenyl group) is attached to the surface, enabling the coverage of the electroactive groups to be determined by cyclic voltammetry. Following the derivatization NAB, the modified GC (referred to as “GC-NAB”) was cleaned in stirred acetonitrile for 10 min., then it was placed in acetonitrile containing 0.1 M TBABF4 and scanned from +0.4 to −1.3 V at a scan rate of 100 mV/s. ON electrode had been scanned for 25 cycles between +0.4 and −0.9 V versus Ag+/Ag at a scan rate of 20 mV/s. In the first case, the attachment of nitro azobenzene film on GC surfaces was proved by the reversible wave observed in the cyclic voltammetry of the modified electrode transferred in a pure electrolyte solution. The voltammogram of the GC-NAB surface in blank electrolyte is shown in Fig. 2A. The first wave was followed by the reversible cathodic wave at −1.2 V corresponding to the reduction of the nitro group to the radical anion [29]. The oxidation wave observed on the return sweep is attributed to the oxidation of the radical anion according to Scheme 2.
A. In 0.1 M TBABF$_4$ in acetonitrile, potential limit: +0.4 to −1.3. B. In 90:10 H$_2$O-EtOH + 0.1 M KCl.

**Scheme 2**

\[
\text{GC-Ar-N=N-Ar-NO}_2 \\ 
\Leftrightarrow \text{GC-Ar-N=N-Ar-NO}_2^* \]

Transformation of NO$_2$ group into NH$_2$ groups was carried out by the following method [30]: Cyclic voltammogram of GC-NAB in a protic solution (90:10 H$_2$O-EtOH +0.1 M KCl), shows an irreversible wave (see Fig. 2B) at potential of −0.61 V vs. Ag/AgCl, suggesting that the classical reduction of NO$_2$ to NH$_2$ occurs according to Scheme 3 within the grafted layer.

**Scheme 3**

\[
\text{GC-Ar-N=N-Ar-NO}_2 + 6e^- + 6H^+ \\ 
\rightarrow \text{GC-Ar-N=N-Ar-NH}_2 + 2H_2O. \]

The process of switching a NAB-GC electrode ON depends on the number of cycles and the range of applied potential. Dopamine (DA) oxidation in water provides a useful test for pinholes, should they be present in the initial modified electrodes or after switching ON. DA requires an adsorption site for rapid oxidation, and is electro-inactive on electrode surfaces completely covered by NAB monolayers [4, 5]. Therefore, DA response is an indication of the presence of bare electrode area, or might occur from pinhole formation. Voltammogram of 1 mM DA in 0.1 M H$_2$SO$_4$ (see Fig. 3A) on bare GC, at initial NAB-modified and NAB-modified after placing it in acetonitrile containing 0.1 M TBABF$_4$ and scanned from +0.4 to −0.9 V vs. Ag/Ag$^+$ for 25 cycles at a scan rate of 20 mV/s, show that no observable DA response is visible for GC modified with NAB radical. The last process will
be referred to as turning the electrode "ON". The cyclic voltammetry of DA indicated that, scanning GC-NAB in blank electrolyte at a potential of more negative than the reduction of NO$_2$ begins to occur, damaged the surface of modified carbon electrodes.

The phenomenon of conductance switching in an electrochemical cell was examined by several redox systems. Several redox systems, chosen because of their varying sensitivity to carbon surface structure, were used to probe electron transfer. Voltammogram of 1 mM ferrocene in acetonitrile containing 0.1 M TBABF$_4$ at scan rate of 100 mV/s on polished GC electrode, initial NAB-modified and NAB-modified after switching "ON" is shown in Fig. 3B. Figure 3B indicates that $\Delta E_p$ for $F_c/F_c^+$ (200 mV) on the bare GC electrode is much smaller than that on the initial modified NAB surface (630 mV). When NAB-GC electrode is placed in acetonitrile containing 0.1 M TBABF$_4$ and turned "ON" by 25 cycles at the scan rate of 20 mV/s, the peak current increased and the $\Delta E_p$ decreases significantly, approaching to that observed on unmodified surface (200 mV). For other examined redox system, the $\Delta E_p$ for 1 mM of Ru(NH$_3$)$_3^{3+/2+}$, IrCl$_6^{2-/3-}$, Fe(COOH)$_2$, Fe(phen)$_3^{3+/2+}$ and Ru(bpy)$_3^{3+/2+}$ solutions for modified glassy carbon surfaces turned "ON" 93, 127, 69, 88 and 79 mV compared to 66, 66, 59, 66, and 68 mV vs. Ag/AgCl reference electrode for unmodified electrode respectively. These redox systems exhibit very slow electron transfer for the initial NAB modified surfaces, and exhibit a major decrease in $\Delta E_p$ almost approaching those observed on unmodified surface following negative potential excursions. Figures 4 and 5 show a typ-
A. 1 mM Ru(NH$_3$)$_6^{3+/2+}$ in 1 M KCl. B. 1 mM Ferrocene in 0.1 M TBABF$_4$ in acetonitrile.

**FIG. 6**: Cyclic voltammetry results of two redox systems on PPF electrodes, unmodified, initial NAB-modified and NAB-modified after switching ON, 100 mV/s scan rate. A. 1 mM Ru(NH$_3$)$_6^{3+/2+}$ in 1 M KCl. B. 1 mM Ferrocene in 0.1 M TBABF$_4$ in acetonitrile.

A typical voltammogram of similar experiments on the surfaces of electrodes for 1 mM 1,1'-ferrocenedicarboxylic acid in pH 7 phosphate buffer +1 M KCl (Fig. 4A); 1 mM tris(2,2'-bipyridyl)ruthenium(II) chloride hexahydrate in pH 7 phosphate buffer +1 M KCl (Fig. 4B); and 1 mM hexaammineruthenium(III) chloride in 1 M KCl (Fig. 5A and B). The cyclic voltammograms of all examined redox systems clearly show that the electrochemical reaction of these redox systems is completely blocked when a carbon electrode is initially modified with NAB. In this case, the characteristic oxidation/reduction waves of the redox couples are not detected. The cyclic voltammograms of Fig. 6 are typical examples of the voltammetry of some redox system which show that, the similar results are obtained when ECFs or PPF used as working electrodes. Summary of data from cyclic voltammetry of the examined redox systems for NAB-modified electrodes are listed in Table I.

There is a possibility for the mechanism of rate enhancement (decrease of $\Delta E_p$ and increase rate constant) associated with a 25 cycles in a potential range of +0.4 to −0.9 V, and it will be considered in turn. The monolayer might be reductively desorbed to create pinholes or bare GC areas, which exhibit faster kinetics than the intact monolayer. However, such pinholes should be electroactive toward dopamine and should not the flat response (see Fig. 3). The lack of dopamine response rules out significant regions of uncovered carbon electrode.

Kinetic effects that may be responsible for the observed changes in electron transfer rate include electron tunnelling through the monolayer and activation effects associated with reorganization of the redox system during electron transfer at the solution/ monolayer interface. Both tunnelling and reorganization may be modified by changes in monolayer structure or orientation that accompany switching. Electron tunnelling through poly(phenylethynyl) monolayers has been studied using Au/thiol self-assembled monolayer system [31]. The carbon and chemisorbed NAB may be considered to be electronic system, and the electric field from the applied potential causes partial redistribution of the electrons within the systems. As the electrode potential becomes more negative, structural rearrangement occurs to form the quinoid structure, and complete transfer of 1e occurs from carbon to NAB. The covalent, conjugated bond between GC and NAB has the effect of softening the boundary between the graphitic conductor and chemisorbed NAB, thus making electron transfer a less discrete event.

**IV. CONCLUSION**

The deposition of 4-nitroazobenzene (NAB) on carbon electrodes were achieved by the electrochemical reduction of 4-Nitro-4'-diazonium azobenzene tetrafluoroborate in anhydrous acetonitrile media using cyclic voltammetry technique at room temperature. The modified surfaces were examined as voltammetric electrodes for Fc/Fc$^+$, Ru(NH$_3$)$_6^{3+/2+}$, IrCl$_2^{2-/3-}$, Fe(COOH)$_2$, Fe(phen)$_3^{3+/2+}$, and Ru(bpy)$_3^{3+/2+}$. The oxidation of 1 mM Dopamine hydrochloride in 0.1 M H$_2$SO$_4$ has been used to test for pinholes, should they be present in the initial modified electrodes or after switching ON. The modified electrodes exhibited very slow electron transfer in compare to unmodified surfaces, by factors that varied with the redox systems. However, after scanning the modified electrode in 0.1 M n-tetrabutylammonium tetrafluoroborate (TBABF$_4$) in acetonitrile from +0.4 to −0.9 V versus Ag/Ag$^+$ for 25 cycles, the modified electrodes exhibited much faster electron transfer kinetics, for some redox systems approaching those observed on unmodified surfaces. The effect is attributed to an apparently irreversible structural change in the NAB monolayer, which increases the
### Table I: Data from cyclic voltammetry of a variety of redox systems for NAB-Carbon Electrodes.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Redox Systems</th>
<th>Conditions</th>
<th>(E_{1/2}) (V vs Ag/AgCl)</th>
<th>Initial (\Delta E_P) (mV)</th>
<th>ON (\Delta E_P) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>Dopamine</td>
<td>unmodified</td>
<td>-</td>
<td>196</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe/Fe(^{+})</td>
<td>unmodified</td>
<td>0.53</td>
<td>200</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ru(NH(_3))(^{3+/2+})</td>
<td>unmodified</td>
<td>-0.10</td>
<td>66</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>IrC(_6)2/3(-)</td>
<td>unmodified</td>
<td>0.85</td>
<td>66</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe(COOH)(_2)</td>
<td>unmodified</td>
<td>0.52</td>
<td>not measurable</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>Fe(phen)(^{3+/2+})</td>
<td>unmodified</td>
<td>0.93</td>
<td>66</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ru(bpy)(^{3+/2+})</td>
<td>unmodified</td>
<td>1.11</td>
<td>68</td>
<td>-</td>
</tr>
<tr>
<td>ECF</td>
<td>Dopamine</td>
<td>unmodified</td>
<td>-</td>
<td>101</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe/Fe(^{+})</td>
<td>unmodified</td>
<td>0.58</td>
<td>200</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ru(NH(_3))(^{3+/2+})</td>
<td>unmodified</td>
<td>-0.06</td>
<td>67</td>
<td>-</td>
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<tr>
<td></td>
<td>IrC(_6)2/3(-)</td>
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<td>1.06</td>
<td>65</td>
<td>-</td>
</tr>
<tr>
<td>PPF</td>
<td>Dopamine</td>
<td>unmodified</td>
<td>-</td>
<td>197</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Fe/Fe(^{+})</td>
<td>unmodified</td>
<td>0.54</td>
<td>191</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ru(NH(_3))(^{3+/2+})</td>
<td>unmodified</td>
<td>-0.10</td>
<td>70</td>
<td>-</td>
</tr>
</tbody>
</table>

- \(\Delta E_P\) is the difference in peak potentials.
- ON \(\Delta E_P\) refers to the on-set peak potential.

Rate of electron tunnelling.
