1999

Role of covalent modification and adsorption on heterogeneous electron transfer at carbon electrodes: characterization and application

Yi Liu

Lehigh University

Follow this and additional works at: http://preserve.lehigh.edu/etd

Recommended Citation


This Thesis is brought to you for free and open access by Lehigh Preserve. It has been accepted for inclusion in Theses and Dissertations by an authorized administrator of Lehigh Preserve. For more information, please contact preserve@lehigh.edu.
Liu, Yi

Role of covalent modification and adsorption on hererogeneous electron transfer at carbon...

May 31, 1999
ROLE OF COVALENT MODIFICATION AND ADSORPTION ON HETEROGENEOUS ELECTRON TRANSFER AT CARBON ELECTRODES: CHARACTERIZATION AND APPLICATION

By

Yi Liu

A Thesis
Presented to the Graduate and Research Committee
of Lehigh University
in Candidacy for the Degree of
Master of Science

in
Chemistry

Lehigh University
May, 1999
This thesis is accepted and approved in partial fulfillment of the requirements for the Master of Science.

5/4/99
Date

Michael S. Freund
Assistant Professor of Chemistry

Keith J. Schryer
Professor of Chemistry
Head of Chemistry Department
ACKNOWLEDGMENTS

I would like to express my sincere gratitude and appreciation to my advisor, Dr. Michael S. Freund, for his guidance and assistance during my research and his advice, suggestions and help in the preparation of this thesis.

I sincerely appreciate Chemistry Department for financial support. I would also like to thank Chen-Chan Hsueh, Matthew Henry and two former graduate students, Helen Chan and Gang Liu, for their assistance and friendship.

I will always be indebted to my family for encouraging me to pursue my education. Without their love and unconditional support, I would never be able to finish this work.

Finally, I thank my wife, Jing Wang, and our son, Jimmy, for their patience in enduring my absence from them throughout the many hours I devoted to this thesis.
## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>1 INTRODUCTION</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Carbon Electrode Materials</td>
<td>2</td>
</tr>
<tr>
<td>1.1.1 Structural Properties of HOPG and Glassy Carbon</td>
<td>2</td>
</tr>
<tr>
<td>1.1.2 Role of Defects in Electron Transfer and Adsorption</td>
<td>4</td>
</tr>
<tr>
<td>1.1.3 Chemistry of Edge Defects</td>
<td>6</td>
</tr>
<tr>
<td>1.2 Modification of Carbon Materials with Aromatic Diazonium Salts</td>
<td>7</td>
</tr>
<tr>
<td>1.3 Adsorption of Acetonitrile on Hydrophobic Surfaces</td>
<td>12</td>
</tr>
<tr>
<td>1.4 Objectives of this Study</td>
<td>13</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2 EXPERIMENTAL</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Materials</td>
<td>14</td>
</tr>
<tr>
<td>2.2 Instrumentation</td>
<td>15</td>
</tr>
<tr>
<td>2.3 Experimental Procedures</td>
<td>15</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>2.3.1 Synthesis of Substituted Benzenediazonium Tetrafluoroborate</td>
<td>15</td>
</tr>
<tr>
<td>2.3.2 Electrode Preparation</td>
<td>17</td>
</tr>
<tr>
<td>2.3.3 Electrochemical Techniques</td>
<td>18</td>
</tr>
<tr>
<td>2.3.3.1 Cyclic Voltammetry</td>
<td>18</td>
</tr>
<tr>
<td>2.3.3.2 Chronocoulometry</td>
<td>19</td>
</tr>
<tr>
<td>2.3.4 Surface Derivatization with Diazonium Salts</td>
<td>19</td>
</tr>
<tr>
<td>2.3.5 Preparation of Solutions Containing Redox Species</td>
<td>20</td>
</tr>
<tr>
<td>3 PREPARATION AND CHARACTERIZATION OF MODIFIED CARBON ELECTRODES</td>
<td>21</td>
</tr>
<tr>
<td>3.1 Grafting in Aprotic Medium</td>
<td>21</td>
</tr>
<tr>
<td>3.2 Redox Behavior of 4-Nitrophenyl Modified Surfaces in Aqueous Medium</td>
<td>23</td>
</tr>
<tr>
<td>3.3 Electrochemical Control of Surface Coverage</td>
<td>25</td>
</tr>
<tr>
<td>3.4 STM/STS of Modified HOPG Surfaces</td>
<td>27</td>
</tr>
<tr>
<td>4 BLOCKING OF ELECTRON TRANSFER AT MODIFIED HOPG</td>
<td>32</td>
</tr>
<tr>
<td>4.1 Blocking Effect of Surface Functional Groups</td>
<td>32</td>
</tr>
<tr>
<td>4.2 The Role of Acetonitrile in Blocking Electron Transfer</td>
<td>35</td>
</tr>
<tr>
<td>4.2.1 Effect of Acetonitrile Exposure</td>
<td>35</td>
</tr>
<tr>
<td>4.2.2 Effect of Acetonitrile in Aqueous Solution</td>
<td>39</td>
</tr>
<tr>
<td>4.2.3 Effect of Electrochemical Pretreatment</td>
<td>42</td>
</tr>
</tbody>
</table>
4.2.4 Effect on Adsorption of AQDS ........................................... 43
4.2.5 Conclusions ........................................................................ 46

5 APPLICATION OF MODIFIED CARBON ELECTRODES IN SENSOR

DESIGN ......................................................................................... 47

5.1 Background ........................................................................... 47

5.2 Influence of Surface Chemistry on Electrode Responses .......... 49

REFERENCES .................................................................................. 54

BIOGRAPHICAL SKETCH ................................................................. 59
LIST OF TABLES

Table 1.1 Properties of HOPG ..................................................4

Table 1.2 Electron Transfer Kinetics for Fe(CN)$_6^{3-}$ in 1 M KCl on Carbon Surfaces ....6

Table 1.3 Reduction Half-Wave Potentials (vs. SCE) of 4-Substituted Benzenediazonium Ions (R-C$_6$H$_4$-N$_2$$^+$) ..............................................................8

Table 3.1 Average Distance (Å) between Bright Spots on HOPG surfaces .................28
LIST OF FIGURES

Figure 1.1 HOPG structure. $L_a$ is the mean size of the graphitic microcrystallite along the a-axis. $L_c$ is the distance along the c-axis perpendicular to the graphite planes. Basal plane is an exposed hexagonal surface that is perpendicular to the c-axis. Edge plane is a cut surface that is paralleled to the c-axis.

Figure 1.2 STM images of a HOPG electrode after grafting of 4-nitro- (a) and 4-bromo (b) -phenyl groups by reduction of 2 mM nitrobenzene and bromobenzene diazonium salts respectively in CH$_3$CN+ 0.1 M Bu$_4$NBF$_4$ at $-250$ mV vs. SCE. STM current: 2 nA, bias voltage: 20 mV.

Figure 1.3 Bi- and tridimensional 10 x 10 nm STM images of HOPG surfaces. From top to bottom: clean surface, surface derivatized by oxidation of 1-naphthylmethyl carboxylate (at a potential of 1.10 V vs. SCE during 15 min in a 2 mM solution), surface derivatized by oxidation of 9-(10-methylanthyl)methyl carboxylate (at a potential of 0.65 V vs. SCE during 30 min in a 1 mM solution). Bias voltage: 17, 43, and 37 mV, respectively.

Figure 2.1 Schemes of two typical methods for the preparation of aromatic diazonium tetrafluoroborate salts. Method 1 is suitable for diazotization of aromatic amines that are soluble in aqueous mineral acid. Method 2 can be used to diazotize aromatic amines that are soluble in organic solvents.

Figure 3.1 Cyclic voltammograms of HOPG basal plane in a 5 mM solution of 4-nitrobenzenediazonium tetrafluoroborate in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$. Scan rate: 200 mV-s$^{-1}$ (A), 20 mV-s$^{-1}$ (B).

Figure 3.2 Cyclic voltammograms of a 4-nitrophenyl modified HOPG electrode in 0.5 M H$_2$SO$_4$ at 25 °C. The modified electrode surface was obtained by electrolysis of 5 mM 4-nitrobenzenediazonium tetrafluoroborate in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$ at $-600$ mV vs. AgQRE for 10 min. First scan: (-----); second scan: (----). Scan rate: 20 mV-s$^{-1}$.
Figure 3.3 Relationship between the scan rate and peak current at 410 mV of a 4-nitrophenyl modified HOPG electrode in a 0.5 M H$_2$SO$_4$ solution at 25 °C (R=0.987). .........................................................25

Figure 3.4 Electrochemical control of surface coverage of nitrophenyl groups on GC surface. Electrolysis of 5 mM 4-nitrobenzenediazonium tetrafluoroborate in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$ at 250 mV vs. AgQRE for various periods of time (o). Electrolysis at 0 mV vs. AgQRE for 8 min (■). .............................................................................27

Figure 3.5 5 nm x 5 nm Images of HOPG surfaces under low (left) and high (right) bias conditions. From top to bottom: unmodified surface, surface derivatized by reduction of bromobenzene diazonium salts (at a potential of −0.2 V vs. AgQRE for 2 min in a 5 mM solution), surface derivatized by reduction of hexadecylbenzene diazonium salts (at a potential of −0.4 V vs. AgQRE for 2 min in a 5 mM solution). Bias potential: 100 mV for low, and 1000 mV for high. Setpoint (from top to bottom): 1 nA, 0.65 nA, and 2 nA respectively .........................30

Figure 3.6 STS curves of bare HOPG basal plane and modified HOPG basal plane. The tip-sample separation is defined by a sample bias of 50 mV and setpoint current of 650 pA. ................................................................................31

Figure 4.1 Cyclic voltammograms of 1 mM K$_3$Fe(CN)$_6$ in 1 M KCl on bare HOPG basal plane (—), acetonitrile treated HOPG basal plane (—), and nitrophenyl modified HOPG basal plane (——). Scan rate = 200 mV-s$^{-1}$ ...........................................................................................33

Figure 4.2 Cyclic voltammograms of 1 mM ferrocene in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$ on bare HOPG basal plane (—), nitrophenyl modified HOPG basal plane (—), and methylphenyl modified HOPG basal plane (——). Scan rate = 200 mV-s$^{-1}$ ...........................................................................................33

Figure 4.3 The ΔE_p of 1 mM K$_3$Fe(CN)$_6$ in 1 M KCl and 1 mM ferrocene in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$ after exposing HOPG in various organic solvents followed by blowing dry with nitrogen. Error bars indicate one standard deviation (n = 3) ........................................................................36

Figure 4.4 Cyclic voltammograms of 1 mM K$_3$Fe(CN)$_6$ in 1 M KCl on HOPG basal plane. Freshly cleaved HOPG (——); after acetonitrile exposure (——); after electrochemical treatment (——). Scan rate = 200 mV-s$^{-1}$ ..........37
Figure 4.5 ΔE_p values of 1 mM Ru(NH₃)₆Cl₃ and K₃Fe(CN)₆ in 1 M KCl at HOPG basal plane as a function of time. Ru(NH₃)₆Cl₃ on freshly cleaved HOPG (○); Ru(NH₃)₆Cl₃ on HOPG after acetonitrile exposure (●). K₃Fe(CN)₆ on HOPG after acetonitrile exposure (V). Scan rate = 200 mV-s⁻¹

Figure 4.6 ΔE_p value of 1 mM K₃Fe(CN)₆ in 1 M KCl at HOPG basal plane as a function of mole fraction of acetonitrile. Scan rate = 200 mV-s⁻¹

Figure 4.7 Cyclic voltammograms of 1 mM K₃Fe(CN)₆ in 1 M KCl on Pt (A) and GC (C) electrodes. 1 mM K₃Fe(CN)₆ in 1 M KCl + 20% v/v CH₃CN on Pt (B) and GC (D) electrodes. Scan rate = 200 mV-s⁻¹

Figure 4.8 Cyclic voltammograms of 1 mM K₃Fe(CN)₆ in 1 M KCl on ECP treated HOPG (A, B) and GC (C, D) electrodes before (A, C) and after (B, D) CH₃CN exposure. Scan rate = 200 mV-s⁻¹

Figure 4.9 Cyclic voltammograms of 10 μM AQDS in 0.1 M HClO₄ at basal plane HOPG before (—), and after (---) acetonitrile exposure. Scan rate = 200 mV-s⁻¹

Figure 4.10 Cyclic voltammograms of 10 μM AQDS in 0.1 M HClO₄ on HOPG. Bare HOPG (——); rinsed with water (---); rinsed with H₂O/CH₃CN (1:1) mixture (·····)...

Figure 4.11 Cyclic voltammograms of 10 μM AQDS in 0.1 M HClO₄ at electrochemically treated HOPG before (—), and after (---) acetonitrile exposure. Scan rate = 200 mV-s⁻¹

Figure 5.1 Surface functional groups covalently modified on GC electrodes (A) and analytes detected with the array in aqueous solutions (B). Charges on molecules reflect state at pH 7.

Figure 5.2 Cyclic voltammograms of 5 mM analyte in 0.1 M, pH 7 phosphate buffer, on various modified electrodes. Scan rate = 100 mV-s⁻¹. Analytes and monolayers are indicated in Figure.
### SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>area</td>
<td>cm²</td>
</tr>
<tr>
<td>$D_j$</td>
<td>diffusion coefficient of species j</td>
<td>cm²·s⁻¹</td>
</tr>
<tr>
<td>E</td>
<td>potential of an electrode versus an reference electrode</td>
<td>V</td>
</tr>
<tr>
<td>$\Delta E_p$</td>
<td>$</td>
<td>E_{p,a} - E_{p,c}</td>
</tr>
<tr>
<td>$E_{p,a}$</td>
<td>anodic peak potential in CV</td>
<td>V</td>
</tr>
<tr>
<td>$E_{p,c}$</td>
<td>cathodic peak potential in CV</td>
<td>V</td>
</tr>
<tr>
<td>$F$</td>
<td>faraday; charge of one mole of electrons</td>
<td>C</td>
</tr>
<tr>
<td>$i$</td>
<td>current</td>
<td>A</td>
</tr>
<tr>
<td>$i_p$</td>
<td>peak current</td>
<td>A</td>
</tr>
<tr>
<td>$k^o$</td>
<td>standard heterogeneous rate constant</td>
<td>cm·s⁻¹</td>
</tr>
<tr>
<td>$L_a$</td>
<td>mean size of the graphitic microcrystallite along the a-axis</td>
<td>nm</td>
</tr>
<tr>
<td>$L_c$</td>
<td>distance along the axis perpendicular to the graphite planes</td>
<td>nm</td>
</tr>
<tr>
<td>$O_x$</td>
<td>oxidized form of a redox couple</td>
<td>none</td>
</tr>
<tr>
<td>$Q$</td>
<td>total charge passed</td>
<td>C</td>
</tr>
<tr>
<td>$Q_{ads}$</td>
<td>Charge due to adsorbed material</td>
<td>C</td>
</tr>
<tr>
<td>$Q_{dl}$</td>
<td>Charge due to double-layer capacitance</td>
<td>C</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant (8.31441)</td>
<td>J·mol⁻¹·K⁻¹</td>
</tr>
<tr>
<td>$Red$</td>
<td>reduced form of a redox couple</td>
<td>none</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>cathodic transfer coefficient</td>
<td>none</td>
</tr>
<tr>
<td>$\Gamma_j$</td>
<td>surface excess of species j at equilibrium</td>
<td>mol·cm⁻²</td>
</tr>
<tr>
<td>$\Gamma_j$</td>
<td>Initial surface excess of species j at equilibrium</td>
<td>mol·cm⁻²</td>
</tr>
<tr>
<td>$v$</td>
<td>scan rate in CV</td>
<td>V·s⁻¹</td>
</tr>
<tr>
<td>$\psi$</td>
<td>dimensionless rate parameter in CV</td>
<td>none</td>
</tr>
</tbody>
</table>
The objective of this study was to explore the effect of surface modification of carbon electrode by electrochemically reducing aromatic diazonium salts on the electrochemical response of HOPG and glassy carbon electrodes. The modified surfaces were studied by electrochemical methods and STM, and the surface coverage was controlled electrochemically to provide various degrees of modification. The effect of organic solvent (primarily acetonitrile) on the blocking of electron transfer and adsorption at HOPG electrode has been studied. The electron transfer of Fe(CN)₆³⁻/⁴⁻ and adsorption of anthraquinonedisulfonate (AQDS) on clean HOPG basal plane was significantly blocked by acetonitrile exposure. The blocking effect is related to surface chemistry of HOPG basal plane. Application of modified carbon electrodes in sensor design was also explored. It was possible to use a carbon electrode array with various surface interfaces to differentiate structurally similar compounds such as substituted hydroquinones.
CHAPTER 1
INTRODUCTION

1.1 Carbon Electrode Materials

Carbon is a widely used and extensively studied electrode material for electrochemical applications due to its low cost, low reactivity, and availability (Kinoshita, 1988). Commonly used materials for carbon electrodes are pyrolytic graphite, glassy carbon (GC), carbon fiber, carbon black and highly orientated pyrolytic graphite (HOPG). Carbon materials are often used in electrosynthesis or fuel cells, but analytical applications of carbon electrodes are limited due mainly to difficulties in preparing and characterizing well-defined carbon surfaces. In recent years, there have been many investigations aimed at understanding the relationship between carbon electrode structure and electroanalytical performance (Kuo and McCreery, 1999; Chen and McCreery, 1996; Chen et al., 1995; Cline et al., 1994; McCreery, 1991). It has been demonstrated that the principal factors that can influence carbon electrode performance include surface history, exposed microstructure, carbon-oxygen functionalities, hydrophobicity, and electronic properties. In this report experiments were performed almost exclusively on HOPG and GC electrodes.

1.1.1 Structural Properties of HOPG and Glassy Carbon

The structure of HOPG is shown in Figure 1.1. An exposed hexagonal surface that is perpendicular to the c-axis is known as a basal plane, while a cut surface that is
parallel to the c-axis is referred to as edge plane. HOPG is made by annealing pyrolytic graphite at high temperature under high compression force along the c-axis. Several grades are available based upon the line width of the d_{002} x-ray diffraction peak, with a greater line width corresponding to smaller microcrystallite size along the a-axis (i.e., along the basal plane). Grades are as follows: ZYA, 0.4°± 0.1°; ZYB, 0.8° ± 0.2°; ZYD, 1.2° ± 0.2°; ZYH, 3.5° ± 1.5°. The highest commercial grade (ZYA) HOPG has L_a and L_c values of 2 µm and 10 µm respectively. Properties of HOPG are summarized in Table 1.1, from which one can see that most are quite anisotropic. For example, the electronic and thermal conduction along the a-axis is much greater than the c-axis. HOPG basal plane also has very low double layer capacitance.

**Figure 1.1** HOPG structure. L_a is the mean size of the graphitic microcrystallite along the a-axis. L_c is the distance along the c-axis perpendicular to the graphite planes. Basal plane is an exposed hexagonal surface that is perpendicular to the c-axis. Edge plane is a cut surface that is paralleled to the c-axis.
Table 1.1 Properties of HOPG

<table>
<thead>
<tr>
<th>Property</th>
<th>HOPG, a-axis</th>
<th>HOPG, c-axis</th>
</tr>
</thead>
<tbody>
<tr>
<td>d_{002} (nm)</td>
<td>0.3354</td>
<td></td>
</tr>
<tr>
<td>ρ (Ω-cm)</td>
<td>4 × 10⁻⁵</td>
<td>0.17</td>
</tr>
<tr>
<td>L_a (nm)</td>
<td>&gt;1,000</td>
<td></td>
</tr>
<tr>
<td>L_c (nm)</td>
<td></td>
<td>&gt;10,000</td>
</tr>
<tr>
<td>Double layer capacitance (μF-cm⁻²)</td>
<td>1.9</td>
<td>60</td>
</tr>
<tr>
<td>Thermal conductivity (W·cm⁻¹·s⁻¹·K⁻¹)</td>
<td>24</td>
<td>0.10</td>
</tr>
<tr>
<td>Thermal expansion (10⁻⁶·°C⁻¹)</td>
<td>-1/2</td>
<td>27</td>
</tr>
<tr>
<td>Young's modulus (MPa × 10⁵)</td>
<td>10.3</td>
<td>0.3</td>
</tr>
</tbody>
</table>


GC is made from a different synthetic route to graphite. It has a complex structure of interwoven, randomly oriented graphitic ribbons, with L_a typically 5.0 nm and L_c 1.5 nm. The ordered layers occurring in the individual ribbons (or crystallites) are reported to be similar to the structure of pyrolytic graphite (McCreery, 1991). Due to the complex structure, GC is mechanically hard and yields reasonable isotropic electrical conductivity. It has been suggested that GC has more surface defects than HOPG (McCreery, 1991).

1.1.2 Role of Defects in Electron Transfer and Adsorption

Defects play an important role in electrochemistry of carbon electrodes. Primary defects on HOPG include exposed edge planes, atomic vacancies, ridges, and cracks. HOPG basal plane is atomically smooth and almost inert toward adsorption of impurities. Its well-defined layered structure makes it an ideal material for examining kinetics of electron transfer (ET) at carbon electrodes. However, it is almost impossible to prepare a defect-free basal plane surface. Removal of graphite layers parallel to basal plane with
scotch tape or a razor blade inevitably causes the formation of some edge-type defects. Increasing density of exposed edge plane has been correlated with faster heterogeneous ET kinetics (Wightman et al., 1984). For example, the standard heterogeneous rate constants ($k^0$) for many redox species have been reported to be several orders of magnitude faster at the exposed edge plane of HOPG than the basal plane (Bowling et al., 1989; Kneten and McCreery, 1992; Cline et al., 1994). Therefore, even a few percent of edge defects will have a significant impact on the electrochemical performance of carbon electrode.

Various methods have been used to activate carbon electrodes, among which laser activation (LA) and electrochemical pretreatment (ECP) are most commonly employed. Several $k^0$ values for Fe(CN)$_6^{3/4-}$ are listed in Table 1.2. Despite the uncertainties due to variations in surface preparation and cleanliness, certain valuable information can be deduced from Table 1.2. First, ET rate at HOPG edge plane is much faster than at basal plane. Second, LA and ECP dramatically improves ET kinetics for Fe(CN)$_6^{3/4-}$ at HOPG and GC electrodes. The enhancement has been explained in term of increase of LA or ECP-induced edge sites (McCreery, 1991). Evidence from STM and Raman spectroscopy of LA and ECP treated HOPG and GC surfaces have supported this explanation (Robinson et al., 1991). Third, surface oxides have little effect on observed kinetics. Large improvement of ET kinetics has been observed for both laser activated (less surface oxides) and electrochemically treated (more surface oxides) HOPG basal plane (McCreery, 1991).
Table 1.2  Electron Transfer Kinetics for Fe(CN)$_6^{3-/4-}$ in 1 M KCl on Carbon Surfaces.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$\Delta Ep$, mV</th>
<th>$k^0$, cm$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOPG, basal</td>
<td>&gt;1200</td>
<td>$&lt;10^{-9}$</td>
<td>Bowling et al., 1989</td>
</tr>
<tr>
<td>HOPG, edge</td>
<td>~ 70</td>
<td>0.06 – 0.1</td>
<td>Rice and McCreery, 1989</td>
</tr>
<tr>
<td>HOPG$^a$, LA, 50 MW-cm$^{-2}$</td>
<td>105</td>
<td>0.0063</td>
<td>Bowling et al., 1989</td>
</tr>
<tr>
<td>HOPG, ECP$^b$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GC, polished</td>
<td></td>
<td>0.14</td>
<td>Hu et al., 1985</td>
</tr>
<tr>
<td>GC, LA, 25 MW-cm$^{-2}$</td>
<td>75</td>
<td>&gt;0.5</td>
<td>Rice et al., 1990</td>
</tr>
<tr>
<td>Pt</td>
<td></td>
<td>0.24</td>
<td>McCreery, 1991</td>
</tr>
</tbody>
</table>

$^a$All entries for HOPG refer to basal plane unless noted otherwise. $^b$ECP 1.9 V vs. SCE, 2 min in 0.1 M KNO$_3$.

Numerous studies have shown that edge sites on HOPG are more reactive toward adsorption than the undisturbed basal plane. Zoval et al. (1996) have reported that at low coverage Ag particles are formed preferentially along step edges of thermally etched HOPG basal plane after electrochemical deposition. It has also been demonstrated that polar molecules such as anthraquinone-2,6-disulfonate (AQDS) adsorbs much more strongly on edge plane than basal plane of HOPG (Xu et al., 1998; McDermott et al., 1992). Ray and McCreery (1997) have shown that physisorption of Rhodamine 6G (R6G) was localized on defects of HOPG and chemisorbed nitroazobenzene (NAB) was found mainly at edge planes when the electrochemical reduction of NAB diazonium salt was conducted for a short period of time.

The above examples clearly indicate that the control of surface defects is of great importance for the reproducibility of electrochemical performances of HOPG basal plane.

1.1.3 Chemistry of Edge Defects

Surface oxides are believed to form spontaneously upon exposure of carbon to air.

Several oxygen containing functional groups reported to be present at carbon surfaces...
include phenol, carbonyl, carboxylic acid, quinone and lactone (McCreery, 1991). It has been shown that oxidation mainly occurs on edge plane of HOPG (Goss et al., 1993; Chang and Bard, 1991). Surface carbonyl (C=O) groups have been probed by selectively reacting with dinitrophenylhydrazine (DNPH) to form a Raman active adduct (Fryling et al., 1995). The reaction is schematically represented in the following:

\[
\text{NO}_2\text{C} = \text{NHNH}_2 + \text{O} \rightarrow \text{NO}_2\text{C} = \text{NNNH}^+ \rightarrow \text{NO}_2\text{C} = \text{NNNH}^+ \\
\]

It was found that polished GC surfaces have 1-5% coverage of carbonyl groups. The coverage increased to ~10% with electrochemical oxidation. DNPH treatment of HOPG surface also confirmed that C=O groups can form only on edges (Ray and McCreery, 1997).

McCreery and coworkers have concluded that adsorption of AQDS depends on electronic disturbances and partial charges near the edge plane defects rather than a specific chemical functionality (McDermott and McCreery, 1994). However, Swain and coworker have demonstrated that carbon-oxygen functional groups at the defects play an important role during the adsorption of AQDS by providing strong dipole-dipole and ion-dipole interactions (Xu et al., 1998).

1.2 Modification of Carbon Material with Aromatic Diazonium Salts

Pioneering work in Saveant's group has provided a new method of covalent modification of carbon surfaces using functionalized aryl radicals generated
electrochemically by the reduction of their corresponding diazonium salts (Delamar et al., 1992, 1997; Allongue et al., 1997). The basis of this approach is the addition of radicals to double bonds present in graphitic structures. The controlled formation of these radicals is induced via reductively induced homolytic dediazonium reactions.

\[
\text{ArN}_2^+ + e^- \rightarrow \text{Ar}^- + \text{N}_2
\]

Table 1.3 shows the half-wave potentials of a number of substituted benzenediazonium salts which have been shown to undergo reductively induced homolytic dediazonium reactions resulting in the corresponding substituted aryl radical (Elofson and Gadallah, 1969; Galli, 1988).

### Table 1.3 Reduction Half-Wave Potentials (vs. SCE) of 4-Substituted Benzenediazonium Ions (R-C_6H_4-N_2^+).

<table>
<thead>
<tr>
<th>R</th>
<th>NO_2</th>
<th>CN</th>
<th>Br</th>
<th>Cl</th>
<th>COOH</th>
<th>H</th>
<th>CH_3</th>
<th>OCH_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>E_{1/2} (V)</td>
<td>0.450</td>
<td>0.433</td>
<td>0.383</td>
<td>0.350</td>
<td>0.328</td>
<td>0.295</td>
<td>0.250</td>
<td>0.140</td>
</tr>
</tbody>
</table>

The surface modification procedure is represented schematically by the following reaction:

![Reaction Diagram]

The coatings thus grafted have been characterized by x-ray photoelectron spectroscopy (XPS) (Delamar et al., 1992), electrochemical methods (Allongue et al., 1997), and Raman spectroscopy (Liu and McCreery, 1995). In the case of 4-nitrophenyl grafted carbon surfaces, the main XPS signal appears at 406 eV, corresponding to the -NO_2 group (Allongue et al., 1997; Liu and McCreery, 1995), however, the origin of a small signal at 400 eV is not clear (Saby et al., 1997). The XPS experiments have also
indicated that close to a monolayer of substituted phenyl groups can be produced at the surface of a GC electrode (Liu and McCreery, 1995). The surface Raman spectra of modified GC, basal HOPG and edge HOPG are very similar despite the wide range of their edge plane densities (Liu and McCreery, 1995). This indicates that the aryl radical is aggressive enough to bind to both edge and basal sites, as suggested initially by Saveant and coworkers (Delamar et al., 1992).

The modified surfaces are very stable and can only be removed by abrasion methods. Due to the electrochemical nature of the modification reaction, it is possible to control the surface coverage through the concentration of the diazonium salts and the electrolysis time (Delamar et al., 1992; Allongue et al., 1997). Applications of this modification method include attachment of glucose oxidase on carbon surface (Bourdillon et al., 1992), electrochemical differentiation between dopamine and ascorbic acid (Downard et al., 1995), enhancement of the binding of epoxy groups with GC plates (Allongue et al., 1997) and carbon fiber (Delamar et al., 1997). Work in our lab has shown that polyaniline films can be modified via nucleophilic substitution reactions using substituted benzenediazonium ions (Liu and Freund, 1996).

Although scanning tunneling microscopy (STM) has been widely used to study HOPG surface, there are surprisingly few reports of STM studies on covalently modified HOPG surfaces with aromatic diazonium salts. Saveant and coworkers have reported two 100 x 100 nm images of modified HOPG basal plane (Figure 1.2) and used them as supports of the homogeneous distribution of phenyl groups (Allongue et al., 1997). For comparison, Figure 1.3 shows the images of HOPG derivatized via anodic oxidation of arylacetates, the Köhle reaction (Andrieux et al., 1997). The regular array of white spots...
has been assigned to surface groups. It should be noted that these surface groups have either 2 (Figure 1.3A) or 3 (Figure 1.3B) benzene rings.

Figure 1.2 STM images of a HOPG electrode after grafting of 4-nitro- (a) and 4-bromo (b) -phenyl groups by reduction of 2 mM nitrobenzene and bromobenzene diazonium salts respectively in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$ at -250 mV vs. SCE. STM current: 2 nA, bias voltage: 20 mV. [Reprinted with permission from J. Am. Chem. Soc. 1997, 119, 201-207. Copyright 1997 American Chemical Society]
Figure 1.3 Bi- and tridimensional 10 × 10 nm STM images of HOPG surfaces. From top to bottom: clean surface, surface derivatized by oxidation of 1-naphthylmethyl carboxylate (at a potential of 1.10 V vs. SCE during 15 min in a 2 mM solution), surface derivatized by oxidation of 9-(10-methylanthyl) methyl carboxylate (at a potential of 0.65 V vs. SCE during 30 min in a 1 mM solution). Bias voltage: 17, 43, and 37 mV, respectively. [Reprinted with permission from J. Am. Chem. Soc. 1997, 119, 4292-4300. Copyright 1997 American Chemical Society]
1.3 Adsorption of Acetonitrile on Hydrophobic Surfaces

Water/acetonitrile mixtures are commonly used as mobile phase for reverse-phase liquid chromatography (RPLC). As a result, the effect of the mobile phase composition on the selectivity and retention mechanism in RPLC has been the subject of many studies (Melander and Horvath, 1980; Dorsey, 1989). It has been found that aqueous/acetonitrile solutions are governed by the formation of aggregates of acetonitrile molecules called clusters (Stalcup et al., 1988; Rowlen and Harris, 1991). However, systems involving water-rich mobile phases are very difficult to describe, particularly those containing > 90% water (Guillaume and Guichard, 1996; 1997). Acetonitrile (CH$_3$CN), which is less polar than water, may adsorb more strongly on hydrophobic surface of the alkyl-bonded reverse-phase stationary phase. A detailed model of the interfacial region of water-organic solvent mixtures on such surfaces is almost impossible in view of the complex surface chemistry of alkyl-bonded surfaces and the various types of polar and non-polar interactions. Therefore, a simple surface-layer model has been proposed to provide a qualitative estimation of the interfaces of such systems (Koch et al., 1987). This model assumes that the adsorbed phase consists of $t$ layers of molecules, and the following relationship between the specific surface excess amount, $n_2^{\sigma(n)}/m_s$, and the molar fraction, $x_2^a$ of the adsorbed phase is obtained:

$$x_2^a = \frac{[t a_s x_2^1 + a_i^0 n_2^{\sigma(n)}/m_s]}{[ t a_s - (a_2^0 - a_1^0) n_2^{\sigma(n)}/m_s]}$$

where $n_i^{\sigma(n)}$ represents the amount of component $i$ in the system ($n_i$) minus the amount of $i$ in a reference system, $m_s$ is the mass of the system, $a_s$ is the specific surface area of the...
adsorbent and $a_i^0$ represents the molar cross-sectional area of component $i$. For a binary system, $i = 1, 2$. For H$_2$O/CH$_3$CN system, the minimum number of layers, $t_{\text{min}}$, was estimated to be 3 in order to satisfy the thermodynamic stable condition for two-phase conexistence. In general, unfavorable interactions between unlike molecules exist in H$_2$O/CH$_3$CN system, and CH$_3$CN molecules tend to segregate at the interface, causing an enhancement of its adsorption, which is favored by the hydrophobic surface.

Since carbon electrodes are one of the most commonly used electrochemical detectors in HPLC (LaCourse, 1997), the influence of interactions between H$_2$O/CH$_3$CN mixtures and carbon electrodes on ET is of practical importance.

### 1.4 Objectives of this Study

The objective of this study is to explore the effect of surface modification of carbon electrode by electrochemically reducing aromatic diazonium salts on the electrochemical response of HOPG and glassy carbon electrodes. The modified surfaces are studied by electrochemical methods and STM. The effect of organic solvent (primarily CH$_3$CN) on the blocking of ET at HOPG electrode is also studied. An additional objective of this work is to explore the possibility of designing sensor arrays with various functionalities on carbon electrode interfaces to differentiate structurally similar compounds such as substituted hydroquinones.
2.1 Materials

Acetonitrile (99.99%), methanol, ethyl ether, toluene, concentrated HCl, HClO₄ and H₂SO₄ were obtained from EM Sciences. Potassium chloride (KCl) and L-ascorbic acid (AA) were purchased from Fisher Scientific and Potassium nitrate (KNO₃) (99.999%) from GFS Chemicals. Hexaammineruthenium (III) chloride (Ru(NH₃)₆Cl₃) (99%) was obtained from Strem Chemicals. 3-Methylcatechol (MCAT) was purchased from Pfaltz & Bauer. L-adrenaline (ADR) was obtained from J.T. Baker. tert-Butyl nitrite (t-BuNO) was purchased from Fluka. Chemicals purchased from Aldrich include fluoroboric acid (HBF₄) (48 wt%), sodium nitrite (NaNO₂), boron trifluoride diethyl etherate ((C₂H₅)₂O·BF₃), tetrahydrofuran (THF), acetone, 4-nitroaniline, 4-chloroaniline, 4-aminobenzoic acid, 4-bromoaniline, 4-hexadecylaniline, p-toluidine, tetrabutylammonium tetrafluoroborate (Bu₄NBF₄), potassium ferricyanide (K₃Fe(CN)₆), catechol (CAT), DL-DOPA, anthraquinone-2,6-disulfonic acid disodium salt (AQDS), ferrocene, pentane, hexane, and 1-phenyloctane. THF was distilled before use. Ferrocene was sublimed and stored in dark before use. Other chemicals were used as received. HOPG (ZYH grade) was obtained from Advanced Ceramics Corporation. Glassy carbon rods were obtained from Atomergic Chemetals Corporation. Polishing cloth, 3 µm diamond paste and 0.5 µm colloidal silica were purchased from LECO. The 18.0 MΩ deionized water was purified with the Barnstead EASYPure system.
2.2 Instrumentation

Electrochemical measurements were carried out with a Bioanalytical Systems electrochemical analyzer, BAS-100. A platinum wire or foil was used as the counter electrode, and the reference electrode was either an Ag/AgCl or an Ag quasireference electrode (AgQRE). Working electrodes were GC or HOPG. Measurements with GC were performed in a conventional three-electrode cell. Measurements with HOPG were carried out in an electrochemical cell which consists of a plastic (Kel-F) top plate, a viton O-Ring seal, and an Invar steel bottom plate.

STM measurements were carried out on a Digital Instruments Nanoscope III Scanning Probe Microscope. The Pt-Ir tips were prepared by mechanically cutting a Pt-Ir wire. The tungsten STM tips were prepared by etching tungsten wires in 1.0 M KOH solution electrochemically. A platinum foil was used as counter electrode, and an AC potential of 30 V was applied. The tip and substrate were isolated from air by a drop of 4 µL 1-phenyloctane (Claypool et al., 1997).

2.3 Experimental Procedures

2.3.1 Synthesis of Substituted Benzenediazonium Tetrafluoroborate Salts

Preparation of substituted benzenediazonium tetrafluoroborate salts was based on published procedures (Dunker et al., 1936; Doyle et al., 1979). Caution: although the substituted benzenediazonium tetrafluoroborate salts are stable, other salts can be
explosive. Schemes of two typical methods for the preparation of aromatic diazonium tetrafluoroborate salts are shown in Figure 2.1. Method 1 is suitable for diazotization of aromatic amines that are soluble in aqueous mineral acid. In this method, 2.0 mmol aromatic amine was added to 4.0 mL 48% HBF₄ (31 mmol). A minimum amount of water was added to dissolve the suspension, and the solution was then cooled down to 0 °C in an ice bath. Then 2.1 mmol of NaNO₂, dissolved in 2 mL of cold water, was added dropwise while stirring. The mixture solution was kept cool in an ice bath for 10 minutes and a precipitate was formed. The precipitation was suction filtered and washed once with cold 5% HBF₄, twice with cold water and ethanol, and finally with copious amounts of cold ether. The product was air-dried and stored at 0 °C.

**Method 1**

$$\text{X-NH}_2 + \text{NaNO}_2 + 2\text{HBF}_4 \rightarrow \text{X-N}_2\text{BF}_4^- + \text{NaBF}_4 + 2\text{H}_2\text{O}$$

**Method 2**

$$\text{X-NH}_2 \xrightarrow{\text{BF}_3, \text{t-BuNO}} \text{X-N}_2\text{BF}_4^-$$

$\text{X=} \text{NO}_2, \text{CH}_3, \text{OCH}_3, \text{COOH}, \text{F, Cl, Br, I, CH}_2\text{COOH, C}_16\text{H}_{33}$

**Figure 2.1** Schemes of two typical methods for the preparation of aromatic diazonium tetrafluoroborate salts. Method 1 is suitable for diazotization of aromatic amines that are soluble in aqueous mineral acid. Method 2 can be used to diazotize aromatic amines that are soluble in organic solvents.
Method 2 was used to diazotize aromatic amines that were soluble in organic solvents, usually THF or methylene chloride. To 2 mL THF contained in a 25 mL reaction tube was added 0.75 mmol \((\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3\) and cooled at \(-10^\circ\text{C}\) in an ice-methanol bath. The aromatic amine (0.5 mmol) dissolved in a minimal volume of THF, usually 1 mL, was added and a homogeneous solution of amine-BF₃ formed. \(t\)-BuNO (0.6 mmol) in 1 mL of the same solvent was added dropwise to the solution while stirring. A crystalline precipitate usually formed during the addition of \(t\)-BuNO and the reaction solution was maintained at \(-10^\circ\text{C}\) overnight to let the reaction complete. The product was suction filtered, washed with cold ether, air-dried and stored at 0 °C before use. In this study, hexadecylbenzenediazonium tetrafluoroborate was prepared using this method because hexadecylaniline is not soluble in mineral acid.

2.3.2 Electrode Preparation

GC electrodes consisted of a 2 mm length of 3 mm diameter glassy carbon rod was sealed in epoxy. The electrodes were polished with 3 μm diamond paste then 0.5 μm colloidal silica on a polishing wheel, followed by ultrasonically for 5 minutes. HOPG surfaces were prepared by cleaving the basal plane using adhesive tape. Typically, the peeled surfaces had visible defects.
2.3.3 Electrochemical Techniques

2.3.3.1 Cyclic voltammetry

Cyclic voltammetry (CV) involves ramping of potential at a working electrode in the presence of redox active species in solution (Nicholson and Shain, 1964). In CV experiments the potential is scanned from an initial value where no reaction occurs to a value where the reaction rate is limited by diffusion and then ramped back to the initial potential. The time scale of the experiment is expressed as scan rate, \( v (V \cdot s^{-1}) \), and is the rate at which the potential is ramped.

CV can be used to identify adsorption and determine kinetic information (Bard and Faulkner, 1980). For diffusion controlled systems, anodic peak current is proportional to bulk concentration \( C_0^* \) and \( v^{1/2} \). For strongly adsorbed or immobilized electroactive species, there exists a linear dependence of peak current with scan rate \( v \).

Nicholson has reported a method of determining kinetic information from CV data (Nicholson, 1965). The standard heterogeneous rate, \( k^o \), can be calculated from:

\[
k^o = \psi (\pi \alpha D_{Red})^{1/2} (D_{Red}/D_{Ox})^{a/2}
\]

where \( \alpha = nFv/RT \). Values of \( \psi \) used in calculations were determined from separation of anodic and cathodic peak potentials, \( \Delta E_p \), and have been published (Nicholson, 1965). In calculations using equation 2.1 it was assumed that \( D_{Ox} = D_{Red} \).

In this work, \( \Delta E_p \) was used as a qualitative measure of heterogeneous rate.
2.3.3.2 Chronocoulometry

Chronocoulometric (CC) experiments involve stepping the potential of a working electrode from a value where the rate of the redox reaction of interest is negligible to a potential value where the rate is diffusion limited (Bard and Faulkner, 1980). The transient response, \( Q(t) \), is then monitored as a function of time and described by the integrated Cottrell equation:

\[
Q(t) = 2nFAD^{1/2} \pi^{-1/2} C^* t^{1/2}
\]  

(2.2)

CC can be used for a number of purposes including: (i) to determine electrode area; (ii) to determine diffusion coefficients; and (iii) to quantitate adsorption. Electrode areas were determined from the slopes of CC plots of \( Q \) versus \( t^{1/2} \) (eq 2.2). The charge due to adsorbed material can be determined from the intercept of \( Q \) versus \( t^{1/2} \) plot where the intercept, \( Q \), contains two components due to double layer charging, \( Q_{dl} \), and adsorption, \( Q_{ads} \):

\[
Q = Q_{dl} + Q_{ads} \tag{2.3}
\]

where \( Q_{ads} \) is related to the amount of adsorbed material (surface excess, \( \Gamma^* \), mol-cm\(^{-2} \)) by:

\[
Q_{ads} = nF\Gamma^* \tag{2.3}
\]

2.3.4 Surface Derivatization with Dizaonium salts

The covalent attachment of aromatic groups onto carbon surfaces was achieved by an electrochemical reduction method (Delamar, 1992). Cleaned GC and freshly peeled HOPG surfaces were used as cathodes in the electrolysis of 5 mM aromatic diazonium salt at a pre-chosen potential in CH\(_3\)CN containing 0.1 M Bu\(_4\)NB\(_4\). After
derivatization, the GC surfaces were rinsed thoroughly with water, methanol, and acetone, and sonicated in CH$_3$CN for 3 min. The modified HOPG surfaces were rinsed with water, methanol, and acetone, but not sonicated in order to avoid mechanical damage. All modified carbon surfaces were dried with a stream of nitrogen gas.

2.3.5 Preparation of Solutions Containing Redox Species

Solutions containing redox species (K$_3$Fe(CN)$_6$, Ru(NH$_3$)$_6$Cl$_3$ and ferrocene) were prepared and used within 3 days. AQDS solutions were prepared and used within 2 days. The redox solutions containing CH$_3$CN were prepared as follows. To 1.0 mL solution of 2.0 mM K$_3$Fe(CN)$_6$ in 2 M KCl was added corresponding amounts of CH$_3$CN, then added water until the total volume was 2.0 mL. The resulting solutions with various amounts of CH$_3$CN all contained final concentrations of 1.0 mM K$_3$Fe(CN)$_6$ and 1 M KCl. For experiments in which air was excluded, CH$_3$CN was degassed in N$_2$ and aqueous solution was degassed with water saturated N$_2$, and the aqueous/CH$_3$CN mixture was prepared and used immediately.
3.1 Grafting in Aprotic Medium

A variety of diazonium salts have been used to graft GC and HOPG basal plane electrodes. Typically, in a CH$_3$CN + 0.1 M Bu$_4$NBF$_4$ solution, a broad and irreversible cathodic peak appears in the CV of 4-nitrobenzenediazonium salt (Figure 3.1). Repetitive cycling results in the disappearance of the peak indicating that modification blocks electron transfer. As shown in Figure 3.1, the rate of disappearance (and in turn modification) is a function of scan rate and potential window. Similar behavior was observed for other substituted benzenediazonium salts (-CH$_3$, -COOH, -C$_{16}$H$_{33}$, -Br, -Cl) resulting in cathodic peak potential ranging from -250 to 135 mV vs. AgQRE.

In addition to voltammetry, carbon electrodes can be grafted by electrolysis of corresponding diazonium salt in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$ at a potential negative to the peak potential for 10 to 20 min. It has been shown by several groups that close to monolayer coverage of aromatic groups are formed on the electrode surface by using this method (Allongue et al., 1997; Liu and McCreery, 1995).

The covalent attachment of the substituted phenyl radicals onto the carbon surface is postulated to undergo the following mechanism (Allongue et al., 1997):
\[ \text{Ar-N=N}^+ + e^- \rightarrow \text{Ar}^* + \text{N}_2 \]  
(3.1)

\[ \text{Ar}^* \rightarrow \text{product in solution} \]  
(3.3)

Apparently, the aryl radicals formed upon cleavage of the C-N bond (eq 3.1) are not reduced at the potential at which they are produced and may thus react with the carbon surface or in the solution.

Figure 3.1 Cyclic voltammograms of HOPG basal plane in a 5 mM solution of 4-nitrobenzenediazonium tetrafluoroborate in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$. Scan rate: 200 mV·s$^{-1}$ (A), 20 mV·s$^{-1}$ (B).
3.2 Redox Behavior of 4-Nitrophenyl Modified Surfaces in Aqueous Medium

Once modified, the electrodes with redox active surface functional groups can be further studied. For example, Figure 3.2 shows the redox behavior of 4-nitrophenyl modified HOPG in acidic aqueous medium. When the potential is scanned in the negative direction, the reduction of surface bonded nitrophenyl groups results in a large irreversible cathodic peak at -445 mV. Upon reversing the scan direction, a single oxidation peak at 410 mV is observed with a corresponding reduction peak at 330 mV. This observation is similar to that reported by Ortiz et al. (1998) for modified GC.

![Cyclic voltammograms of a 4-nitrophenyl modified HOPG electrode in 0.5 M H2SO4 at 25 °C. The modified electrode surface was obtained by electrolysis of 5 mM 4-nitrobenzenediazonium tetrafluoroborate in CH3CN + 0.1 M Bu4NBF4 at -600 mV vs. AgQRE for 10 min. First scan: (----); second scan: (--). Scan rate: 20 mV-s⁻¹.](image)
Based on previous studies of nitrobenzene in homogeneous solution (Rubinstein, 1985; Baizer and Lund, 1983) and 4-nitrothiophenol modified electrodes in acidic media (Tsutsumi et al., 1995), the redox reaction of the grafted nitrophenyl group in acidic solution is considered to proceed according to the following mechanism:

\[
\begin{align*}
\text{NO}_2^- + 4e^- + 4H^+ & \rightleftharpoons \text{NHOH} + H_2O \\
\text{NHOH} + 2e^- + 2H^+ & \rightleftharpoons \text{NH}_2^- + H_2O \\
\text{NHOH} & \rightleftharpoons \text{NO} + 2e^- + 2H^+
\end{align*}
\]

The irreversible cathodic peak at -445 mV corresponds to the reduction of \(-\text{NO}_2\) groups to \(-\text{NH}_2\) groups with six-electron and six-proton transfer (eq 3.4, 3.5). However, the conversion of \(-\text{NO}_2\) into \(-\text{NH}_2\) is not complete. As indicated by the mechanism, the interconversion between 4-hydroxyaminophenyl and 4-nitrosophenyl (eq 3.6) occurs when the 4-nitrophenyl group is partially reduced to 4-hydroxyaminophenyl group (eq 3.4). This redox process is characterized by the anodic and cathodic redox peaks at 410 mV and 330 mV respectively. Since oxidation of amine does not occur in this potential range, the presence of this redox response suggests that the nitro groups are not completely reduced to amine.

The presence of hydroxyaminophenyl/nitrosophenyl redox couple can also be used to demonstrate the immobilization of nitrophenyl groups on carbon surface upon
electrochemically reduction of 4-nitrobenzenediazonium salt (Ortiz et al., 1998). Figure 3.3 shows the scan rate dependence of the anodic peak current (410 mV peak). An approximately linear dependence is observed up to 200 mV·s⁻¹ indicating that the electroactive species is surface bonded (Bard and Faulkner, 1980).

![Graph showing the relationship between scan rate and peak current.]

**Figure 3.3** Relationship between the scan rate and peak current at 410 mV of a 4-nitrophenyl modified HOPG electrode in a 0.5 M H₂SO₄ solution at 25 °C (R=0.987).

### 3.3 Electrochemical Control of Surface Coverage

Electrochemical reduction of diazonium salts provides a facile way of controlling surface coverage on carbon electrode surfaces. By varying concentration of diazonium salt, electrolysis potential and time, one can obtain a surface coverage from submonolayer to a full monolayer. Figure 3.4 shows the surface coverage of GC electrode by electrolysis of 5 mM 4-nitrobenzenediazonium salts in CH₃CN + 0.1 M
Bu₄NBF₄ at 250 mV vs. AgQRE for various periods of time. The grafted electrode was reduced in a degassed 0.5 M H₂SO₄ solution at a rate of 20 mV-s⁻¹. Surface coverage was calculated by integrating cathodic wave from 0 to 650 mV. The electrode area was determined to be 0.094 cm² by CC of 1.0 mM K₃Fe(CN)₆ solution. In Figure 3.4, the maximum surface coverage was approximately 18 × 10⁻¹⁰ mol-cm⁻². Considering the incompleteness of reduction of nitro group to amine group, this value represents an underestimation of the real surface coverage of nitrophenyl groups. It should be noted that the area under the 330 mV peak is about 16% that of the -445 mV peak. Saveant and coworkers have reported a surface coverage of 41 × 10⁻¹⁰ mol-cm⁻² for the 4-nitrophenyl groups on GC (Allongue et al., 1997). However, the surface coverage was determined by integration of the reduction peak (nitro group to the radical anion at ca. -1.2 V vs. SCE) in CH₃CN + 0.1 M Bu₄NBF₄. A more negative electrolysis potential (-0.6 V vs. SCE) was employed in their study and geometrical area of GC was used in obtaining their surface coverage. The theoretical coverage of nitrophenyl groups has been reported to be 12 × 10⁻¹⁰ mol-cm⁻² for ideal close packing on a flat surface (Liu and McCreery, 1995). This value corresponds to 13.9 Å² per nitrophenyl group bonded at the edge of the phenyl ring based on Van der Waals radii. Although surface concentrations shown in Figure 3.4 do not represent all the surface groups, the ability to control the surface coverage is clear.
Figure 3.4 Electrochemical control of surface coverage of nitrophenyl groups on GC surface. Electrolysis of 5 mM 4-nitrobenzenediazonium tetrafluoroborate in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$ at 250 mV vs. AgQRE for various periods of time (o). Electrolysis at 0 mV vs. AgQRE for 8 min (■).

3.4 STM/STS of Modified HOPG Surface

STM images of organic molecules on HOPG surface have been obtained in many studies (Magonov and Whangbo, 1996; Smith and Frommer, 1993). In all of these cases the image contrast depends on the tunneling gap resistance, $R_{\text{gap}}$, which is a qualitative measure of the tip-sample distance. To avoid injuring the sample, high $R_{\text{gap}}$ is adopted for STM of organic molecules on conducting substrates. In air, a typical high $R_{\text{gap}}$ would be $10^5$ MΩ to $10^4$ MΩ. This corresponds to a gap voltage of 1 V when passing a tunneling current of 10 to 100 pA (Smith and Frommer, 1993). Claypool et al. (1997)
have reported the bias dependence of the STM images of alkanes and alkanols on HOPG. At low bias \((R_{gap} = 76 \text{ M}\Omega)\), the STM height image is dominated by the graphite substrate. At high bias \((R_{gap} = 2020 \text{ M}\Omega)\), the height image is dominated mostly by the adsorbate. In our experiments, the imaging of HOPG surfaces has been carried out under a variety of bias conditions (-1.1 to 1.1 V) and setpoint currents (0.65 to 2 nA). Figure 3.5 shows some typical images obtained under these conditions. The left column contains images obtained at low bias (0.1 V), whereas the right column contains images obtained at high bias (1 V). The modified surfaces were obtained by electrolysis of corresponding diazonium salts for 2 min, thus the surface coverage was less than a monolayer. As can be seen, the modified surfaces were dominated by the HOPG pattern. This is tentatively explained in terms of the covalent bond between phenyl molecules and substrate making it difficult to separate substrate and adsorbate properties. The average distances between adjacent bright spots on each image are listed in Table 3.1. A value of 2.55 Å is reported for clean HOPG, and was used to calibrate the STM.

| Table 3.1 Average Distance (Å) between Bright Spots on HOPG Surfaces, |
|-----------------|-----------------|-----------------|
| Clean Br-Ar C\textsubscript{16}H\textsubscript{33}-Ar |
| Low bias 2.5 ± 0.2   2.6 ± 0.3    2.4 ± 0.3 | |
| High bias 2.6 ± 0.3  2.6 ± 0.4    2.6 ± 0.4 | |

In order to investigate the electronic properties of the modified surfaces, a series of scanning tunneling spectroscopy (STS) experiments were performed, in which tunneling current, \(I\), was recorded as a function of bias, \(V\). Figure 3.6 shows typical I-V curves of bare and modified HOPG basal plane. Before I-V curves were obtained, the surface was imaged to make sure that the tip was located over a defect-free region at the
basal plane. Each I-V curve shown in the figure represents the average of seven I-V curves over the same position. Error bars represent one standard deviation. The curves are nearly antisymmetrical with respect to bias polarity, and the tunneling current observed for the bare HOPG surface increases more rapidly with bias than for the modified surfaces. This behavior is opposite to that observed by Claypool et al. (1997), who have shown that the tunneling current observed for the tetradecanol-covered surface increases more rapidly with bias than for the bare HOPG surface. This behavior likely accounts for the inability to observe grafted functional groups.
Figure 3.5 5 nm × 5 nm Images of HOPG surfaces under low (left) and high (right) bias conditions. From top to bottom: unmodified surface, surface derivatized by reduction of bromobenzene diazonium salts (at a potential of −0.2 V vs. AgQRE for 2 min in a 5 mM solution), surface derivatized by reduction of hexadecylbenzene diazonium salts (at a potential of −0.4 V vs. AgQRE for 2 min in a 5 mM solution). Bias potential: 100 mV for low, and 1000 mV for high. Setpoint (from top to bottom): 1 nA, 0.65 nA, and 2 nA respectively.
Figure 3.5 5 nm x 5 nm Images of HOPG surfaces under low (left) and high (right) bias conditions. From top to bottom: unmodified surface, surface derivatized by reduction of bromobenzene diazonium salts (at a potential of -0.2 V vs. AgQRE for 2 min in a 5 mM solution), surface derivatized by reduction of hexadecylbenzene diazonium salts (at a potential of -0.4 V vs. AgQRE for 2 min in a 5 mM solution). Bias potential: 100 mV for low, and 1000 mV for high. Setpoint (from top to bottom): 1 nA, 0.65 nA, and 2 nA respectively.
Figure 3.6 STS curves of bare HOPG basal plane and modified HOPG basal plane. The tip-sample separation is defined by a sample bias of 50 mV and setpoint current of 650 pA.
CHAPTER 4

BLOCKING OF ELECTRON TRANSFER AT MODIFIED HOPG

4.1 Blocking Effect of Surface Functional Groups

The Fe(CN)$_6^{3/4-}$ redox couple is commonly used to investigate the kinetics of electron transfer across the electrode/solution interface. The anodic/cathodic peak separation, $\Delta E_p$, increases as the ET becomes slow. HOPG basal plane with a $\Delta E_p$ value larger than 700 mV for a 200 mV-s$^{-1}$ scan rate is considered having minimal defect density (Kneten and McCreery, 1992). The CV of Fe(CN)$_6^{3/4-}$ on edge plane graphite gives a $\Delta E_p$ at or near the Nernstian value of 59 mV indicating the standard heterogeneous rate is much higher than the basal plane (McCreery, 1991). As a result, $\Delta E_p$ has been used to estimate the density of exposed edge plane. The CVs for the reduction of Fe(CN)$_6^{3-}$ on bare (containing defects) and modified HOPG surfaces are shown in Figure 4.1. The modified surfaces were obtained by electrolysis of corresponding diazonium salts for 2 min. The $\Delta E_p$ value of our HOPG basal plane is approximately 80 mV indicating a significant amount of edge defects existed on the bare HOPG surface. The CV of nitrophenyl modified surface indicates that the ET rate is totally suppressed. Similar blocking effects were also observed with ferrocene in CH$_3$CN + 0.1-M Bu$_4$NB$	ext{F}_4$. As shown in Figure 4.2, ET at nitrophenyl and methylphenyl modified surfaces were significantly blocked.
Figure 4.1 Cyclic voltammograms of 1 mM K$_3$Fe(CN)$_6$ in 1 M KCl on bare HOPG basal plane (−), CH$_3$CN treated HOPG basal plane (−−−), and nitrophenyl modified HOPG basal plane (−−−). Scan rate = 200 mV-s$^{-1}$.

Figure 4.2 Cyclic voltammograms of 1 mM ferrocene in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$ on bare HOPG basal plane (−), nitrophenyl modified HOPG basal plane (−−−), and methylphenyl modified HOPG basal plane (−−−). Scan rate = 200 mV-s$^{-1}$.
Although the phenyl radical generated by electrochemically reducing aromatic diazonium salts has been shown to be aggressive enough to add to both the basal and edge plane of HOPG, preferential adsorption of diazonium salts on edge plane and subsequent chemical or electrochemical reaction may provide a means for selective modification of HOPG surfaces. Evidence of the strong adsorption of polar molecules on edge plane has been reported (Xu et al., 1998; McDermott et al., 1992). In addition, a recent study has shown that the reduction reaction of nitroazobenzenediazonium salt occurs more rapidly at defects (Ray and McCreery, 1997). It is therefore reasonable to think that aromatic diazonium salts might adsorb more strongly on the edge plane. Experiments in our lab have shown that there are small amounts of diazonium salts left on HOPG or GC electrode after exposing these electrodes in 5 mM diazonium salts solution for a period of time followed by rinsing process or even sonication. Electrodes thus treated with nitrobenzenediazonium salt solution gave $\Delta E_p$ values of $632 \pm 23$ mV ($n=4$) for the $\text{Fe(CN)}_6^{3+/4-}$ redox couple, which suggests that edge planes are partially blocked. However, this conclusion is only true if the organic solvent (CH$_3$CN in this case) has a negligible effect on $\Delta E_p$ measurements. In the control experiments, we have found a considerable blocking effect of CH$_3$CN on HOPG, as shown in Figure 4.1. The $\Delta E_p$ value of $\text{Fe(CN)}_6^{3+/4-}$ increases dramatically simply by exposing HOPG electrode in CH$_3$CN for a few minutes. Therefore, it is not clear whether CH$_3$CN or the surface groups are accounted for the increases in $\Delta E_p$. The large effect of organic solvents (CH$_3$CN in particular) prompted us to investigate the blocking effects of organic solvents on the heterogeneous ET in aqueous solution.
4.2 The Role of Acetonitrile in Blocking Electron Transfer

4.2.1 Effect of Acetonitrile Exposure

Our intention of using Fe(CN)$_6^{3-/4-}$ to test partially modified HOPG surfaces was complicated by the strong influence of CH$_3$CN on the measurement of $\Delta E_p$ values. The $\Delta E_p$ of Fe(CN)$_6^{3-/4-}$ increased from 71 ± 3 mV (n=3) for clean HOPG to 794 ± 59 mV (n=3) after CH$_3$CN exposure (soak electrode in CH$_3$CN for 5 min followed by blowing dry with N$_2$). When HOPG were exposed to lab environment for 36 hours after CH$_3$CN exposure, the $\Delta E_p$ of Fe(CN)$_6^{3-/4-}$ increased to 1047 ± 164 mV (n=3). If the CH$_3$CN treated HOPG were exposed to water for 24 hours, a value of 1065 ± 135 mV (n=3) was obtained. These results indicate that the blocking effect was irreversible. HOPG electrodes exposed to CH$_3$CN inside and outside the cell yielded similar results suggesting that the swelling of O-ring or extracted contaminants had little effect on the $\Delta E_p$ measurements. If the freshly peeled HOPG was exposed to lab environment for 24 hours before CH$_3$CN exposure, $\Delta E_p$ of Fe(CN)$_6^{3-/4-}$ was 700 ± 18 mV.

The blocking effect was also found with other organic solvents. The results are shown in Figure 4.3. After exposure to these organic solvents, the $\Delta E_p$ of Fe(CN)$_6^{3-/4-}$ on HOPG increases to over 700 mV. However, the blocking effect was not observed for ferrocene. The $\Delta E_p$ of ferrocene varies from 100 to 220 mV, which is much smaller than that observed on modified HOPG surfaces (Figure 4.2). It should be noted that CH$_3$CN exposure had a minimal effect on $\Delta E_p$ of Fe(CN)$_6^{3-/4-}$ on Pt, GC and Au electrodes. These results suggest that the blocking effect be related to surface structure of HOPG.
Figure 4.3 The $\Delta E_p$ of 1 mM $K_3Fe(CN)_6$ in 1 M KCl and 1 mM ferrocene in CH$_3$CN + 0.1 M Bu$_4$NBF$_4$ after exposing HOPG in various organic solvents followed by blowing dry with nitrogen. Error bars indicate one standard deviation ($n=3$).

The blocked surface can be re-activated by electrochemical treatment, as shown in Figure 4.4. The blocked HOPG electrode was oxidized at 1.9 V vs. Ag/AgCl in 0.1 M KNO$_3$ for 2 min and then reduced at −0.1 V for 30 seconds (Bowling et al., 1989). The $\Delta E_p$ of $Fe(CN)_6^{3-/4+}$ returned to 72 mV, which is very close to the value obtained prior to CH$_3$CN exposure (68 mV). It should be noted that the electrochemical treatment resulted in a large charging current, consistent with reports of increasing surface oxides (McCreery, 1991).
Figure 4.4 Cyclic voltammograms of 1 mM K₃Fe(CN)₆ in 1 M KCl on HOPG basal plane. Freshly cleaved HOPG (—); after acetonitrile exposure (---); after electrochemical treatment (---). Scan rate = 200 mV·s⁻¹.

Ruthenium hexaamine (III) (Ru(NH₃)₆³⁺), which carries a positive charge, has also been used to investigate the blocking effect (Saby et al., 1997). The ΔEₚ of Ru(NH₃)₆²⁺/³⁺ as a function of time in the aqueous redox solution after CH₃CN exposure is plotted in Figure 4.5. On untreated HOPG it gave a ΔEₚ value of 68 mV, whereas after CH₃CN exposure a value of 260 mV was obtained. The ΔEₚ of Ru(NH₃)₆³⁺/²⁺ for the untreated HOPG was quite stable, whereas for the surface after CH₃CN exposure the ΔEₚ decreased to 130 mV after exposing to aqueous solution for 18 min with CV taken every 2 min. Upon addition of a drop of 1 M HCl, the ΔEₚ increased back to 220 mV. This behavior suggests the existence of negative species at the surface. The electrostatic
attraction between the positively charged redox species and the negatively charged species on the surface may favor the ET at the interface, and thus $\Delta E_p$ decreases. When HCl was added, the number of negatively charged species decreased, and thus the ET rate decreased resulting in increases of $\Delta E_p$. The $\Delta E_p$ values of Fe(CN)$_6^{3+/4-}$ for CH$_3$CN exposed HOPG surfaces as a function of time are also listed in Figure 4.5. The $\Delta E_p$ decreased from 857 to 795 mV after exposing to aqueous solution for 18 min with CV- taken every 2 min. Clearly, the decrease rate of Fe(CN)$_6^{3+/4-}$ is less than that of the Ru(NH$_3$)$_6^{3+/2+}$ redox couple.

Figure 4.5 $\Delta E_p$ values of 1 mM Ru(NH$_3$)$_6$Cl$_3$ and K$_3$Fe(CN)$_6$ in 1 M KCl at HOPG basal plane as a function of time. Ru(NH$_3$)$_6^{2+/3+}$ on freshly cleaved HOPG ($\bigcirc$); Ru(NH$_3$)$_6^{2+/3+}$ on HOPG after acetonitrile exposure (•). Fe(CN)$_6^{3+/4-}$ on HOPG after acetonitrile exposure ($\nabla$). Scan rate = 200 mV$\cdot$S$^{-1}$. 
4.2.2 Effect of Acetonitrile in Aqueous Solution

Experiments in section 4.2.1 suggest that acetonitrile and other organic solvents are able to block active sites of HOPG. To further investigate this phenomenon, CH$_3$CN was added to aqueous solutions containing redox species and CVs of the mixtures were recorded. To minimize the influence of oxygen, the K$_3$Fe(CN)$_6$ solutions and CH$_3$CN were degassed prior to use, and electrochemical cell was placed in a glass chamber through which a slow stream of water saturated nitrogen was passed. Under these conditions the $\Delta E_p$ value of pure K$_3$Fe(CN)$_6$ solutions in the absence of organic solvents was found to remain constant up to 30 cycles over a 30 min time period.

The influence of oxygen on the measurements of $\Delta E_p$ of Fe(CN)$_6^{3/-4}$ can be seen from the following experiment. The freshly cleaved HOPG surfaces were exposed to lab environment overnight. The $\Delta E_p$ of Fe(CN)$_6^{3/-4}$ on these surfaces increased to 90 ± 7 mV (n=3). The increase of $\Delta E_p$ (and in turn decrease of ET rates) can be explained in terms of decrease of surface active sites due to the oxidation reaction with oxygen present in solution and atmosphere.

Figure 4.6 shows the values of $\Delta E_p$ as a function of mole fraction of acetonitrile in solution. Each data point was repeated three times and each series was run on the same HOPG surface. The concentrations of K$_3$Fe(CN)$_6$ and KCl were kept constant as described in Section 2.3.5. It is clear that the observed ET rate decreases as mole fraction of CH$_3$CN increases. Several possibilities concerning the increase of $\Delta E_p$ are considered. First, increase of surface oxides due to exposure to lab environment can be excluded because experiments were carried out under inert condition. Second, the level of
impurities in acetonitrile has negligible effect. The CH$_3$CN we used has 0.44 ppt ECD (electron capture detection) responsive substances and 2 ppm evaporation residues. To test this hypothesis, CH$_3$CN solution was intentionally evaporated under nitrogen to about one tenth of its original volume and used in the control experiments. No significant differences were found in parallel experiments using the original and pre-concentrated CH$_3$CN. Moreover, a 50 mL CH$_3$CN was evaporated in a glass beaker under nitrogen till dry, and then 5 mL 1 mM K$_3$Fe(CN)$_6$ in 1 M KCl solution was added and mixed by stirring. Presumably the concentration of non-evaporated impurities in this solution is 20 times higher than that normally used. The reduction for this Fe(CN)$_6^{3-}$ solution gave a $\Delta E_p$ value of 95 ± 7 mV (n=3), which is larger than that of the clean solution. However, considering the volume percentages of CH$_3$CN used in Figure 4.6 are significantly less than that described in the above experiment, we believe that impurities in CH$_3$CN have minimal contribution to the increases of $\Delta E_p$. Third, the change of bulk property of the solution upon addition of CH$_3$CN has little effect on the heterogeneous ET rate. This can be seen from Figure 4.7. In the presence of 20% v/v acetonitrile (x= ~0.1), the formal potentials shift to more negative values for both Pt and GC electrodes, and the peak currents decrease. These may be due to the change of activity coefficient and diffusion coefficient of the analytes, and/or junction potential. Nevertheless, the $\Delta E_p$ values did not change with the presence of CH$_3$CN.

The above experiments indicate that the presence of CH$_3$CN in aqueous solution blocks the ET rate of Fe(CN)$_6^{3-/4+}$ redox couple, and the blocking is not due to changes in bulk properties of the solution but to some surface phenomena on HOPG.
Figure 4.6 $\Delta E_p$ value of 1 mM K$_3$Fe(CN)$_6$ in 1 M KCl at HOPG basal plane as a function of mole fraction of acetonitrile. Scan rate = 200 mV-s$^{-1}$.

Figure 4.7 Cyclic voltammograms of 1 mM K$_3$Fe(CN)$_6$ in 1 M KCl on Pt (A) and GC (C) electrodes. 1 mM K$_3$Fe(CN)$_6$ in 1 M KCl + 20% v/v CH$_3$CN on Pt (B) and GC (D) electrodes. Scan rate = 200 mV-s$^{-1}$. 


4.2.3 Effect of Electrochemical Pretreatment

ECP of GC and HOPG has been shown to greatly improve ET rates for a variety of redox systems (McCreery, 1991). ECP of HOPG generally involves application of a fixed potential of 1.9 V vs. SCE in 0.1 M KNO₃ for 2 min, followed by a reduction step at -0.1 V for 30 s. It is believed that the formation of edge plane during oxidation is responsible for the fast ET kinetics (Bowling, et al., 1989). ECP also leads to a large increase in background current due to the increase of surface oxides (McCreery, 1991).

![Figure 4.8](image)

**Figure 4.8** Cyclic voltammograms of 1 mM K₃Fe(CN)₆ in 1 M KCl on ECP treated HOPG (A, B) and GC (C, D) electrodes before (A, C) and after (B, D) CH₃CN exposure. Scan rate = 200 mV-s⁻¹.

Figure 4.8 shows the CVs of HOPG and GC electrodes with EPC before and after CH₃CN exposure. ECP of HOPG was carried out by setting the potential for 2 min at 1.9
V vs. Ag/AgCl in 0.1 M KNO₃, and then at -0.1 V for 30 seconds. A polished GC electrode was oxidized for 5 min at 1.7 V, followed by reduction at -1.0 V for 1 min (Engstrom and Strasser, 1984). For HOPG electrode, $\Delta E_p$ increases from 70 to 190 mV. This increase is significantly smaller than that observed on HOPG without ECP. For GC electrode, no increase in $\Delta E_p$ has been observed. Clearly, the smaller $\Delta E_p$ on HOPG with ECP coincides with the morphological changes (e.g., increase of oxidized edge plane density) resulting in improvements of ET kinetics (Bowling et al., 1989).

4.2.4 Effect on Adsorption of AQDS

To further investigate the effect of CH₃CN on HOPG, AQDS was used. AQDS is reported to adsorb strongly on surface defects (Xu et al., 1998; McDermott et al., 1992). If the surface has minimal defects (e.g., a doped diamond electrode), or the surface oxides are eliminated (e.g., a hydrogenated GC electrode), the adsorption of AQDS is weak. Figure 4.9 shows the CV of 10 $\mu$M AQDS in 0.1 M HClO₄ before and after CH₃CN exposure. A strong adsorption was found on clean HOPG electrode resulting in a $\Delta E_p$ value of 6 mV. After the surface was exposed to CH₃CN for 5 min, adsorption of AQDS was found to be very weak. This indicates that the surface sites that used to be active for AQDS molecules are blocked by CH₃CN. The blockage was found to be strong enough to withstand higher AQDS concentrations (100 $\mu$M) and longer exposure times (overnight). In addition, adsorbed AQDS on untreated HOPG can be easily removed by rinsing with H₂O/CH₃CN mixture (1:1). Experiments were performed by rinsing the electrode after AQDS adsorption and replacing the solution with 0.1 M HClO₄.
(no AQDS). The results are shown in Figure 4.10. If the electrode was rinsed with pure water, adsorption of AQDS can still be seen, only the peak currents decrease significantly. However, if the electrode was rinsed with H₂O/CH₃CN mixture, no adsorption waves were found. This suggests that the existence of CH₃CN can help remove AQDS either by replacement or solvation.

Figure 4.9 Cyclic voltammograms of 10 μM AQDS in 0.1 M HClO₄ at basal plane HOPG before (—), and after (---) acetonitrile exposure. Scan rate = 200 mV-s⁻¹.
Figure 4.10 Cyclic voltammograms of 10 μM AQDS in 0.1 M HClO₄ on HOPG. Bare HOPG (———); rinsed with water (---); rinsed with H₂O/CH₃CN (1:1) mixture (····). 

The effect of ECP on adsorption of AQDS was also investigated and the results are shown in Figure 4.11. After ECP, adsorption of AQDS on HOPG is strong. If HOPG with ECP was exposed in CH₃CN for 5 min, adsorption of AQDS can still be seen but the current decreases. This suggests that CH₃CN block part of the active sites on electrochemically treated HOPG. Apparently, the blockage is not as significant as that on the untreated HOPG. As discussed in Section 4.2.3, CH₃CN is not likely to block electrochemically treated HOPG surfaces.
Figure 4.11 Cyclic voltammograms of 10 μM AQDS in 0.1 M HClO₄ at electrochemically treated HOPG before (---), and after (—) acetonitrile exposure. Scan rate = 200 mV·s⁻¹.

4.2.5 Conclusions

Acetonitrile has a large and irreversible blocking effect on ET rates of Fe(CN)₆³⁻/⁴⁻ and adsorption of polar molecules at HOPG surfaces. The blocking effect of CH₃CN is related to the surface chemistry of HOPG basal plane. Electrodes that have faster kinetics, such as GC and electrochemically treated HOPG, are not likely to be blocked by CH₃CN exposure.
CHAPTER 5
APPLICATION OF MODIFIED CARBON ELECTRODES IN SENSOR DESIGN

5.1 Background

The covalent modification of carbon electrodes with aromatic diazonium salts provides a facile method for generating a wide range of chemically diverse electrode interfaces. Researchers in this lab have used an array of individually addressable gold electrodes modified with different self-assembled monolayers (SAMs) to produce a chemically diverse electrode array to differentiate several substituted hydroquinone compounds (Hsueh et al., 1999). In this work we use a sensor array based on GC electrodes modified with various substituted benzene groups to distinguish the same hydroquinones in pH 7 aqueous solutions. Modification of GC electrode was achieved by electrochemical reducing corresponding aromatic diazonium salts in CH\textsubscript{3}CN + 0.1 M Bu\textsubscript{4}NBF\textsubscript{4} for 8 min resulting in a closely packed monolayer on the GC surfaces.

Structures of the interfacial groups are shown in Figure 5.1A. Analytes, whose structures are shown in Figure 5.1B, are several substituted hydroquinones and ascorbic acid. A 5 mM solution of each analyte was prepared daily in 0.1 M phosphate buffer solution (0.05 M KH\textsubscript{2}PO\textsubscript{4} + 0.05 M K\textsubscript{2}HPO\textsubscript{4}, pH = 7). Since surface modifiers are covalently attached onto the GC electrode, the interface functionalities are inherently more stable than SAMs.
Figure 5.1 Surface functional groups covalently modified on GC electrodes (A) and analytes detected with the array in aqueous solutions (B). Charges on molecules reflect state at pH 7.
5.2 Influence of Surface Chemistry on Electrode Responses

The performance of electrode arrays depends on the molecular recognition capabilities of the electrode material used, as well as the ability to generate useful analytical signals as a result of such interactions. CV was used to demonstrate that the chemical variability between the electrodes could in fact induce measurable and distinct changes in electrode response (Hsueh et al., 1999). Each set of voltammograms in Figure 5.2 shows variations in response for a particular analyte at all of the modified electrodes. On a particular electrode some analytes have large variations while others have subtle variations. Electrode I, the bare electrode, serves as a reference point from which the relative blocking abilities of the surface functional groups as well as the influence of varying chemical interactions on response can be gauged. For example, electrode IV is considered to possess a net negative charge at the interface under pH 7 conditions (Saby, et al., 1997; Cheng and Brajter-Toth, 1992). A significantly blocking effect is observed for negatively charged species such as AA (Fig. 5.2A). In contrast, positively charged analytes such as ADR experience an enhancement effect due to the interaction with the negatively charged interface. The responses for CAT, MCAT and DOPA all show enhancement but with less degree relative to that observed on ADR (Fig. 5.2C, D and E respectively). This can be attributed to the neutral state of these analytes under pH 7 conditions. In fact, catechol has a pK$_1$ value of 9.23, which means it is slightly protonated at pH 7, and thus the response of electrode IV is slightly enhanced.
Figure 5.2 Cyclic voltammograms of 5 mM analyte in 0.1 M, pH 7 phosphate buffer, on various modified electrodes. Scan rate = 100 mV-s\(^{-1}\). Analytes and monolayers are indicated in Figure.
Electrode VI blocks the response for all of the analytes to a large extent, presumably due to the hydrophobic nature of the immobilized long alkyl chain on the surface. However, slight variation can still be observed. The blocking of neutral species, CAT and MCAT, were less severe than that of charged species, AA and ADR, and zwitterionic DOPA at pH 7. The blocking effects of electrode II and III are different for different analytes. For example, electrode II blocks ADR and DOPA more than electrode III, whereas electrode III blocks AA and MCAT more than electrode II. A large blocking effect is also found for electrode V, but the degrees of blocking vary from analyte to analyte. For example, the blocking of neutral species (CAT and MCAT) was less significant than positively charged ADR and zwitterionic DOPA, whereas response from negatively charged AA was significantly suppressed.

The above discussion illustrates just a few examples of the influence of variations in surface chemistry (in these case primarily electrostatic and hydrophobic interactions) on response. Other factors such as interactions between the surface and reaction intermediates and products, as well as the density and structure of the monolayer are also expected to influence the response. Based on these results, it is evident that chemical diversity among electrodes in an array provides additional information over and above that obtained using voltammetry at a single electrode.

Although variations in responses for different analytes on a particular electrode could be observed through the changes in responses among the various analytes as a function of electrode, several issues should be noted concerning the selection of surface functional groups of this array system. First, variations of electrode V and VI in response for these hydroquinones are very subtle and in turn contribute little to differentiation of
these analytes. No specific interaction between electrode V and analytes is expected, and the long alkyl chain of electrode VI may not be as good as shorter alkyl chain to provide hydrophobic interactions. Our works of SAMs on gold electrodes showed that t-butyl terminal groups blocked CAT and MCAT to a lesser degree than the other analytes (Hsueh et al., 1999). Second, attempts to introduce a positively charged interface did not provide expected information. Electrode III, which is presumably positively charged under pH 7 condition, was made by electrochemically reduction of electrode II. However, this reaction is not complete as discussed in Chapter 3. Besides $-\text{C}_6\text{H}_4\text{NH}_2$, $-\text{C}_6\text{H}_4\text{NO}$, $-\text{C}_6\text{H}_4\text{NHOH}$ as well as unreacted $-\text{C}_6\text{H}_4\text{NO}_2$ groups exit on the surface and the surface composition may change as function of time and electrode potential. These complications were evident by the observed changes in CVs obtained with electrode III from cycle to cycle. As a result, the surface of electrode III is not sufficiently well defined.

In summary, electrochemical reduction of aromatic diazonium salts provides a facile means to introduce chemical diversity on the carbon electrode surface. Preliminary tests show that variations exit in response of a particular interface toward different analytes. Differentiation of structurally similar compounds is possible through an array design by choosing proper surface modifiers. Furthermore, the ability to control the surface coverage of GC electrodes may allow optimization between surface chemistry and blocking of electron transfer. For example, electrode VI might be useful in probing hydrophobic interaction if density of the functional groups on the surfaces is optimized.

Future works include construction of sensor arrays based on modified carbon fiber electrodes and double-potential-step experiments for fast array interrogation.
REFERENCES


McDermott, M.T.; McCreery, R.L. Scanning Tunneling Microscopy of Ordered Graphite and Glassy Carbon Surfaces: Electronic Control of Quinone Adsorption, 


BIOGRAPHICAL SKETCH

Yi Liu was born on January 1, 1966 in Beijing, China. He is the eldest son of Mr. Gutian Liu and Mrs. Tong Zhao. He began his college education at Peking University in 1984. In the last semester of his undergraduate years, he began research in the area of solid state chemistry under the supervision of Manling Gong. In July 1988, he received his B.S. degree in chemistry with an honor of Excellent Graduate Award.

After graduated from Peking University, Mr. Liu became a research engineer in General Research Institute for Non-ferrous Metals where he participated in research on rare earth luminescence materials under the supervision of Junxiang Han. He provided technical consulting for Shenzhen Chirong Minmetal Co. from 1991 to 1992. In 1994 he received CNNC Science & Technology Progress Award.

In 1996 Mr. Liu started his graduate study at Lehigh University. He is working in the area of electrochemistry under the supervision of Michael S. Freund. Mr. Liu received Heim Fellowship in 1997 and Buch Fellowship in 1998. After he completed his MS degree in 1999, Mr. Liu decided to continue pursing his Ph.D. degree in Analytical Chemistry at Lehigh University under the supervision of Marie C. Messmer.
END OF TITLE