Investigations of Redox-Labeled Silica and Gold Nanoparticles in Solution and as Films on Electrodes

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Abstract

Christopher A. Beasley: Investigations of Redox-Labeled Silica and Gold Nanoparticles in Solution and as Films on Electrodes

(Under the direction of Dr. Royce W. Murray)

Chapter One serves as a background for Au nanoparticles (AuNP) and silica nanoparticles (SiNP). A brief history of the synthesis and characterization of AuNPs will be followed by a discussion on the recent application of the particles in sensing and energy-related applications. The second portion of the chapter will be a discussion on the functionalization of SiNPs and their application in a variety of sensing systems.

Chapter Two discusses the irreversible adsorption onto electrode surfaces of highly ionic, mixed-monolayer AuNPs containing an N,N,N-triethylammonium terminated thiol and an 6-(ferrocenylhexane) thiol. The AuNP films are entropically stabilized due to the multidentate nature of the particles and can be transferred to NP-free electrolyte solutions for further investigation. The most interesting aspect of the film is the ability to monitor ion and accompanying solvent transfer between the film and electrolyte solution despite the films being one to two monolayers thick. Comparisons will be drawn to ion transfer between two immiscible electrolyte solutions.

Chapter Three will discuss the controlled growth of films of highly ionic, mixed monolayer AuNPs containing deprotonated mercaptoundecanoic acid and 6-(ferrocenylhexane) thiol.
The controlled deposition of films of AuNPs without the addition of a metal ion to facilitate binding between particles provides a new route to controlling film thicknesses for applications in Surface Enhanced Raman Spectroscopy and energy storage. Electrochemical quartz crystal microbalance studies, impedance spectroscopy and theoretical modeling show that the large peak-to-peak separation for the ferrocene/ferrocnium couple in cyclic voltammograms arises solely from uncompensated resistance effects within the film, i.e., the rates of ion permeation.

Chapter Four examines ferrocenated SiNPs as charge storage devices. Focus is initially on the surface functionalization. Spectroscopic characterizations are used to estimate the number ferrocenes per particle. Next, a variety of electrochemical investigations confirm that approximately 600 ferrocenes reside on the surface of the particles. Several interesting investigations are discussed relating to formation of a slurry of SiNPs upon addition of supporting electrolyte or acetonitrile for electrochemical investigations. Despite the formation of the slurry, reproducible electrochemistry was obtained.
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<td>Two-Dimensional</td>
</tr>
<tr>
<td>3D</td>
<td>Three-Dimensional</td>
</tr>
<tr>
<td>A</td>
<td>Absorbance</td>
</tr>
<tr>
<td>A</td>
<td>Amperes</td>
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<td>A</td>
<td>Electrode area</td>
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<td>abbr.</td>
<td>abbreviation</td>
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<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>Ag/AgQRE</td>
<td>Silver quasi-reference electrode</td>
</tr>
<tr>
<td>Ag/AgCl (aq)</td>
<td>Silver-silver chloride aqueous reference electrode</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>AuCl$_4^-$</td>
<td>Tetrachloroaurate</td>
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<td>Au(I)-SR</td>
<td>Au(I) thiolate</td>
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<tr>
<td>a</td>
<td>Atto-</td>
</tr>
<tr>
<td>aF</td>
<td>AttoFarad</td>
</tr>
<tr>
<td>β-CD</td>
<td>Beta-cyclodextrin</td>
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<tr>
<td>BH$_4^-$</td>
<td>Borohydride</td>
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</table>
Bu$_4$NClO$_4$  Tetrabutylammonium perchlorate

Bu$_4$NPF$_6$  Tetrabutylammonium hexafluorophosphate

C  Carbon

Concentration

Coulombs

°C  Degrees Celsius

CD$_2$Cl$_2$  Deuterated methylene chloride

CH$_2$  Methylene group

CH$_2$Cl$_2$  Methylene chloride (or dichloromethane)

CH$_3$  Methyl group

CH$_3$CN  Acetonitrile

C$_n$  Alkanethiol with n carbon atoms

COOH  Carboxylic acid group

CV  Cyclic voltammetry

ca.  About

cm  Centimeter

D  Diffusion coefficient

D$_{APP}$  Apparent diffusion coefficient

D$_E$  Diffusion coefficient of an electron

D$_{PHYS}$  Physical diffusion coefficient

D$_{NP}$  NP diffusion coefficient
d  Diameter
Length of NP monolayer

E  Potential

ΔE_{peak}  Potential difference between anodic and cathodic peaks

E^o  Formal potential

E_{APP}^o  Apparent Formal Potential

E_{1/2}  Electrochemical half-wave potential

EQCM  Electrochemical Quartz Crystal Microbalance

e  Electronic charge

e^-  Electron

equiv  Equivalent

eV  Electron volts

exp  Exponential

F  Farad

F \text{c}  Faraday constant

μF  MicroFarad

Fc  ferrocene

Fc^+  ferrocenium

FTIR  Fourier Transform Infrared Spectroscopy

g  Gram

H  Hydrogen

\textsuperscript{1}H NMR  Proton Nuclear Magnetic Resonance Spectroscopy

H_{2}O  Water
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<tr>
<th>Symbol</th>
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<tr>
<td>H₂SO₄</td>
<td>Sulfuric acid</td>
</tr>
<tr>
<td>HAuCl₄•xH₂O</td>
<td>Tetrachloroauric acid hydrate</td>
</tr>
<tr>
<td>HO</td>
<td>Alcohol group</td>
</tr>
<tr>
<td>HOOC</td>
<td>Carboxylic acid group</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-Resolution Transmission Electron Microscopy</td>
</tr>
<tr>
<td>HSC6</td>
<td>Hexanethiol</td>
</tr>
<tr>
<td>HSC6Fc</td>
<td>ω-Functionalized ferrocene hexanethiol</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
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<tr>
<td>h</td>
<td>Hour</td>
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<td>I</td>
<td>Intercept</td>
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<tr>
<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>i</td>
<td>Current</td>
</tr>
<tr>
<td>iₐₗm</td>
<td>Limiting current</td>
</tr>
<tr>
<td>i.e.</td>
<td>That is</td>
</tr>
<tr>
<td>J</td>
<td>Joule</td>
</tr>
<tr>
<td>K</td>
<td>Degrees Kelvin</td>
</tr>
<tr>
<td>k</td>
<td>Kilo-</td>
</tr>
<tr>
<td>kₜ</td>
<td>Boltzmann constant</td>
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<tr>
<td>kD</td>
<td>Kilodaltons</td>
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<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
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<tr>
<td>log</td>
<td>Logarithm</td>
</tr>
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<td>M</td>
<td>Metal</td>
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xiv
MeOH  Molar
Methanol

MM  Molar Mass

μM  Micromolar

MHz  MegaHertz

m  Meter

Milli-

mg  Milligram

min  Minute

mL  Milliliter

mM  Millimolar

mol  Mole

mV  Millivolt

N  Newtons

Nitrogen

N₂  Nitrogen gas

Nₐ  Avogadro’s number

NaBH₄  Sodium borohydride

NaCl  Sodium chloride

NMR  Nuclear magnetic resonance

NP  Nanoparticle

n  Number of electrons transferred

order of harmonic
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<td>nA</td>
<td>NanoAmperes</td>
</tr>
<tr>
<td>nm</td>
<td>Nanometer</td>
</tr>
<tr>
<td>nmol</td>
<td>Nanomoles</td>
</tr>
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<td>nM</td>
<td>NanoMolar</td>
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<tr>
<td>O</td>
<td>Oxygen</td>
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<tr>
<td>−OOC</td>
<td>Deprotonated carboxylic acid group</td>
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<td>Oct₄NBr</td>
<td>Tetraoctylammonium bromide</td>
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<tr>
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<td>$-\log [H^+]$</td>
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<td>QDL</td>
<td>Quantized double-layer</td>
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<tr>
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<td>RSH</td>
<td>Alkanethiol</td>
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<tr>
<td>r</td>
<td>Radius</td>
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<tr>
<td>rpm</td>
<td>Rotations per minute</td>
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<tr>
<td>S</td>
<td>Sulfur</td>
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<tr>
<td>S/N</td>
<td>Signal-to-noise ratio</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayer</td>
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<td>SC₆</td>
<td>Hexanethiolate</td>
</tr>
<tr>
<td>SC₆Fc</td>
<td>$\omega$-Functionalized ferrocene hexanethiolate</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated Calomel Electrode</td>
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<td>SP</td>
<td>Surface plasmon</td>
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<td>STM</td>
<td>Scanning tunneling microscopy</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric analysis</td>
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<td>THF</td>
<td>Tetrahydrofuran</td>
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<td>UV-vis</td>
<td>Ultraviolet-visible</td>
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<tr>
<td>V</td>
<td>Volt</td>
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<td>v</td>
<td>Volume</td>
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<td>Versus</td>
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<tr>
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<tr>
<td>μ</td>
<td>Micro-</td>
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<td>Shear modulus</td>
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xvii
\( \nu \)  
Scan rate

\( \pi \)  
Pi

\( \omega \)  
Omega functional group

\( \rho \)  
Density

Packing density

=  
Equals to

Double bond

+  
Positive

–  
Negative

—  
Single bond

<  
Less than

>  
More than

\( \times \)  
Multiplied by
Chapter One

Introduction to Gold and Silica Nanoparticles

1.1 Introduction

A limited global supply of fossil fuel sources coupled with increasing demand for energy prompted the recent establishment of Energy Frontier Research Centers\(^1\) throughout the United States and highlights the need for basic and applied sciences pointing to new ways for generating, transmitting and storing alternative forms of energy. Localized production of energy, through the use of photovoltaics, solar concentrators and wind turbines is driving a need to change the way people think about energy storage since these production environments are subject to the day/night cycles and weather changes. Even basic transportation is likely to change over the several decades as usage of hybrids, plug-in hybrids, and fully-electric vehicles increases. Controlling, understanding and optimizing the science at the molecular (i.e. nanometer) level will be crucial if the vision for cleaner and more sustainable energy utilization is to be realized.

The ability to produce and store energy (charge) locally using such devices as fuel cells, batteries, and supercapacitors is an important step if these technologies are to be implemented on a large scale. Examination of a Ragone plot\(^2\) (Figure 1.1) shows the tradeoff between power densities and energy densities for fuel cells, batteries, supercapacitors and conventional capacitors. This plot also shows the typical discharge rates for each of these devices. As the discharge rate of a device increases, so does its energy density but at the cost
Figure 1.1. Ragone Plot showing characteristics of energy storage and conversion devices.

(Adapted from ref 2.)
Power Density / W kg\(^{-1}\)

Energy Density / Wh kg\(^{-1}\)

- Batteries
- Fuel Cells
- Supercapacitors
- Conventional Capacitors

1 s
60 s
1 hr
10 hrs
of power density. Construction of power supplies based on these devices is likely to take place in a complementary manner. For example, fully-electric vehicles containing a battery stack will likely be supported by supercapacitors during periods of increase energy demand such as merging on to a highway or starting out from a stoplight.

Supercapacitors, which fill the performance gap between the high power densities of conventional capacitors and high energy densities of batteries, are sometimes based on “pseudocapacitance,” a combination of capacitance due to double-layer charging and a capacitance due to fast, highly-reversible, faradaic processes. These supercapacitors are differentiated from batteries by having sloping discharge curves, more rapid charge-discharge cycles and longevity to be cycled hundreds or thousands of times. Already, supercapacitors are seeing use in power backup systems, mass-transit, wireless communication, personal electronics, power quality, and improved energy efficiency via regenerative energy capture devices. Redox-active and redox-functionalized nanoparticles are ideally suited for examination as supercapacitors due to their high charge density and the ease with which they can be synthesized and characterized. These nanoparticles would ideally contain a large number of redox units per nanoparticle, giving rise to high charge density, that are all readily accessible and reversible.

Au Nanoparticles

The advent of the Brust Method was a major step forward in the synthesis of very small, thiol-protected gold nanoparticles (AuNPs) and has helped lead to an ever increasing amount of research regarding their synthesis, characterization and application in a variety of
The two phase Brust synthesis (water-toluene) consists of the creation of an Au(I)-thiolate polymer that is subsequently reduced as shown below

$$\text{AuCl}_4^- \text{ (toluene)} + \text{HSR} \rightarrow (\text{Au(I)-thiolate-})_n$$  \hspace{1cm} (1)

$$(\text{Au(I)-thiolate-})_n + \text{NaBH}_4 \rightarrow \text{Au}_x\text{SR}_y$$  \hspace{1cm} (2)

The feed ratio of HSR to AuCl$_4^-$, the speed at which reducing agent is added, and temperature of the reaction are primary factors controlling the main distribution of AuNP sizes; smaller feed ratios of HSR to AuCl$_4^-$, slower reductant addition and warmer temperatures produce larger particles. Relatively monodisperse size distributions can be obtained through a series of solvent fractionations. More recent advances using modified Brust methods by our lab$^9$, and others$^{10}$ have shown that very monodisperse particle size distributions can be obtained for certain sizes.

Recent X-ray crystallography results$^{11-13}$ have shown that the smaller AuNPs ($< 10^2$ Au atoms) produced consist of an icosahedron core with “staples” or semi-rings covalently attached, consisting of (-thiolate-Au-thiolate-Au-thiolate-) chains. Theoretical$^{14}$ and mass spectrometry results$^{15}$ have shown that somewhat larger particles ($\geq 10^2$ Au atoms) also contain these “staples” extending from the core. Interestingly, the staples or semi-rings on the larger particles are not only (-thiolate-Au-thiolate-Au-thiolate-) but also (-thiolate-Au-thiolate).

Though X-ray crystallographic data provide absolute determination of the overall structure of an AuNP, producing crystals is a time-consuming and difficult process and for thiolated AuNPs has produced only three determinations.$^{11-13}$ Therefore, the analytical chemist must use a combination of techniques for alternative characterization. Transmission
electron microscopy (TEM) has proven useful for approximating the number of gold atoms in the nanoparticle. Thermogravimetric analysis (TGA) has been shown to be useful to measure (relative to the estimated Au atom counts) the number of thiolates on the nanoparticles. Mixed monolayer compositions are typically determined using NMR by examining the responses of the incoming ligand to the ligand used in original synthesis. In addition, various spectroscopic techniques have been used to investigate monolayer packing or band gap determinations.

As-produced AuNPs are generally stable in air, resistant to aggregation, and can be dried and redissolved without loss in functionality. The larger particles, with core diameters between 1.6 and 2.0 nm exhibit\textsuperscript{16,17} quantized double-layer charging in voltammetric experiments, much like coulomb blockade voltammetry exhibited by gold substrates in scanning electrochemical microscopy, due to the extremely low capacitance (< 6 aF) values of the nanoparticles. Smaller particles exhibit HOMO-LUMO gaps and show fine features in the UV-visible region.\textsuperscript{18-20}

The main focus of this introduction will be the background of work on the functionalization of AuNPs with redox-active moieties. Functionalization can take place during the AuNP synthesis or by ligand exchange, post-nanoparticle synthesis. Hostetler et al. were the first to add the redox-active molecule ferrocene (Fc), in the form of Fc(CH\textsubscript{2})\textsubscript{8}SH, to the surface of an AuNP.\textsuperscript{21} These mixed-monolayer AuNPs were noted to adsorb to an electrode surface during cyclic voltammetry experiments. Unlike studies which will be discussed later, the adsorption was weak; rinsing with CH\textsubscript{2}Cl\textsubscript{2} removed 95% of the adsorbed AuNPs. More robust adsorption occurred through the use of a dithiol linker between the electrode and the AuNPs.
Ingram and Murray synthesized HS(CH₂)₃SAQ (SAQ = 1-(1,3-dithiapropyl)anthracene-9,10-dithione) functionalized AuNPs containing 25 redox active units. These anthraquinone units were all reactive in successive one electron transfers for the radical anion but not for the radical dianion. Cyclic voltammetry experiments indicated that some adsorption was present but the electrochemistry was dominated by the freely diffusing particles.

Ingram et al. synthesized redox functionalized AuNPs through ligand exchange using Fc(CH₂)₈SH and HS(CH₂)₃SAQ. Up to 22% of the ligands on the original AuNPs were exchanged with the redox active thiols. Pietron and Murray took advantage of the AuNPs functionalized with the HS(CH₂)₃SAQ, mentioned above, to perform redox-mediated electrocatalysis. These nanoparticles, which contained on average 18 redox-active units, mediated the one electron reduction of 1,1-dinitrocyclohexane at higher catalytic efficiency than the anthraquinone monomer. There were no indications of AuNP adsorption in those studies.

Green et al. synthesized redox-labeled AuNPs by exchanging Fc(CH₂)₈SH onto alkylthiolate stabilized nanoparticles. The obtained nanoparticles contained ca. 15 Fc per nanoparticle and would adsorb to an electrode surface when the potential of the electrode was cycled through the Fc/Fc⁺ couple. Monolayer coverages were obtained, but as discussed, the poly-hetero-functionalized nanoparticles synthesized by Ingram et al. were reversibly adsorbed, meaning that the nanoparticle film could be washed away with CH₂Cl₂. Chen prepared Langmuir-Blodgett films of redox-labeled AuNPs and examined their electronic and ionic conductances. Electronic conductivity decreased as films became thicker, Fc peak potential shifted anodically, and not all Fc was accessed during voltammetric experiments.
The aqueous electrolyte, KNO₃, assured that the hydrophobic nanoparticles did not become dislodged during the experiments.

Another example of redox functionalization of AuNPs was performed by Fujihara and Nakai.²⁷ The researchers functionalized the AuNPs with C₆₀-thiol through a simple ligand exchange reaction with alkylthiolate stabilized AuNPs. Overnight immersion in an AuNP solution resulted in a spontaneous adsorption on an electrode surface. These films exhibited two reversible, one electron transfers when immersed in an electrolyte solution.

Miles and Murray²⁸ prepared phenothiazine functionalized AuNPs and showed that the phenothiazine units all reacted in rapid, successive, one-electron reactions. Adsorption was observed, but the particles were only weakly bound and desorbed from the electrode upon immersion in a nanoparticle-free electrolyte solution. Templeton et al.²⁹ studied viologen-labeled AuNP adsorption by electrochemical quartz crystal microbalance (EQCM) and were able to show that equivalents of monolayer coverages were possible. The strong adsorption was ascribed to the interaction of viologen reduction products. The preceding studies consistently suggested that the AuNPs, especially those involving ferrocene ligands, were adsorption-prone, but reversibly so.

Recently, Wolfe et al.³⁰ synthesized fully-ferrocenated AuNPs using a modified Brust synthesis. This was the first example of the direct synthesis of an AuNP containing a full monolayer of a redox-active species. Cyclic voltammetry investigations showed that these particles strongly adsorbed to any electrode surface, up to monolayer coverages, when the potential of the electrode was cycled through the Fc/Fc⁺ couple (which was typically done 25 times). The adsorbed layer of AuNPs could be transferred to fresh electrolyte solutions and
the ferrocene voltammetry stably observed, so the adsorption was nearly irreversible. The strong adsorption was proposed to involve entropically enhanced (multiple) ion-pairs between oxidized (ferrocenium) sites and adsorbed anions. These results can be analogously compared to the strong adsorption of polyelectrolyte films produced by Decher.31

The above discovery prompted further study to ascertain and obtain an understanding of the strong surface effect. Such investigations have found the adsorption to be anion dependent,32 lending more credence to the hypothesis that the stably adherent films are a result of the multiple ion-pairs formed between ferrocenium sites and adsorbed anions. Sardar et al.33 recently showed that the addition of a sulfonate or carboxylate self-assembled monolayer to the electrode surface resulted in the adsorption of fully-ferrocenated AuNPs at monolayer coverages. Unlike the studies by Wolfe et al.30 and Stiles et al.32 where 25 CV cycles resulted in coverages up to a monolayer, one complete CV cycle of the SAM-modified electrode resulted in monolayer coverages.

Expanding upon the idea that multiple ion-pair formation drives film formation and previous work by others34-37 involving highly ionic nanoparticles, Chapters Two and Three of this thesis examine stably adherent, redox-labeled, highly ionic AuNP films. Utilization of AuNPs as supercapacitors will require controllable film formation and a thorough understanding of the interfacial flux of charge compensating ions through the film/solution interface.

**SiO₂ Nanoparticles**

Labelled silica nanoparticles (SiNP) have been an object of investigation for some time and have for example been used as imaging agents, in coatings applications, for sensing,38-40
catalytic activities\cite{41} and drug delivery\cite{42,43}. SiNPs are also being used to slow corrosion on aluminum current collectors\cite{44} through their incorporation into gel electrolytes. Other gel electrolytes based on lithium modified SiNPs have been prepared.\cite{45} Here, the Li$^+$ is complexed with a sulfonate group that is covalently attached to the SiNP.

The Stöber Method\cite{46} is a convenient way to synthesize SiO$_2$ particles with diameters ranging from ca. 10 nm to > 1000 nm, depending on reaction conditions. These nonporous, relatively monodisperse, polar solvent-soluble particles are stable against aggregation, and are easy to manipulate and functionalize. The gel-like matrix derived from the synthesis makes it amenable to functionalization during synthesis, either simply by adding the species of interest into the reaction (e.g. Fc) or by adding a functionalized silane (e.g., here, (MeO)$_3$Si(CH$_2$)$_3$NHCOFc) which is then permanently incorporated into the matrix. Synthesis of the latter is slightly complicated by the addition of the functionalized silane, making particle size control more difficult along with accessibility of the functionalized silane questionable. Confirmation and quantitation of these functionalized nanoparticles can be accomplished using a variety of techniques. Solid-state NMR (SS-NMR) is an extremely useful tool that allows examination of changes to the surface of the nanoparticle (e.g. consumption of residual silanols). FTIR allows confirmation of functional groups along with changes in the nanoparticle surface. X-ray photoelectron spectroscopy (XPS) allows the confirmation and approximate quantitation of a species of interest. Finally, a variety of electrochemistry techniques allow examination and quantitation of redox active species.

There are several reports regarding functionalization of SiO$_2$ with redox active species. Budny et al.\cite{41} covalently bound Fc, a Ru complex and an aniline derivative to nanoparticles ranging in size from 140 to 750 nm. These particles spontaneously adsorbed to an electrode
surface when the electrode was immersed in a stirred SiNP solution; the adsorption was possibility due to residual silanols residing on the surface of the particle. Cyclic voltammetry, used to quantify the number of electroactive sites, were compared with AAS and ICP-MS results and showed that only a small fraction of the total number of sites are electroactive.

Ling et al.\textsuperscript{47} prepared 60 nm diameter ferrocenyl-functionalized SiNPs for examining guest-host interactions. Though these particles were smaller, the ferrocene coverage was low and the particles exhibited mixed adsorption-diffusion behavior during electrochemical studies. Plumeré and Speiser\textsuperscript{48} synthesized ferrocenyl-functionalized SiNP through hydrosilation. These 200 nm diameter particles spontaneously adsorbed on Pt. Like those studies mentioned above, not all Fc were accessible to electrochemical reaction. In our view, design of systems utilizing redox-active SiNPs requires use of smaller particles such that the rotational diffusion time constant is smaller than the residence time of the nanoparticle near the electrode. This will allow for full reactivity during typical experimental timescales. We therefore focused on very small SiNPs, both for full electrochemical reactivity and for a large volume capacity of electrochemical charge.

Chapter Four of this dissertation will discuss the voltammetry and redox storage capability of ferrocenated SiNPs. These particles are the first example of freely diffusing, fully-ferrocenated SiNPs that show no significant adsorption and full ferrocene reactivity. These results, combined with those results discussed in Chapters Two and Three provide an improved foundation for fabrication of supercapacitors based upon redox-active nanoparticles.
1.2 References


Chapter Two

Entropically Driven Poly-Cationic Au NP Adsorption on an Electrode Surface

2.1 Introduction

Our group has previously reported on the irreversible adsorption of fully-ferrocenated Au nanoparticles (AuFcNPs) on bare or self-assembled monolayer (SAM) modified electrode surfaces. The driving force of strong adsorption was due to multiple ion-pair formation between adsorbed anions on the electrode surface and ferrocenium ions present on the nanoparticle (NP), as well as multiple ion-pair bridging interactions between NPs. In this chapter, we investigate the adsorption in more detail. The adsorption process was followed for a mixed monolayer NP where permanent positive charge \([-\text{N}^+(\text{CH}_2\text{CH}_3)_3]\] was introduced on the nanoparticle surface, \(\text{Au}_{225}(\text{TEA-thiolate})_{225}(\text{SC6Fc})_{9}\). The mixed monolayer NP contained a few ferrocene groups as an internal reference for the determination of nanoparticle coverage on the electrode surface (\(\Gamma_{\text{NP}}\)). The main points of this chapter are (i) incorporation of permanent positive charge influences the surface coverage, (ii) the effects of various electrolytes on the \(\Gamma_{\text{NP}}\), and (iii) support for our original hypothesis that entropically favored ion-pairing drives film formation.

The important aspects of gold nanoparticles have been the breadth of their impact for molecular detection system,\(^4\) in device fabrication,\(^6,7\) and for electronic sensor applications\(^8,9\). Voltammetry of thiolated AuNPs has been studied extensively due to their interesting electrochemical behavior,\(^10\) including bulk-continuum voltammetry, quantized double layer charging voltammetry, and molecule-like voltammetry.\(^11-18\) These near-
molecular species display interesting multi-electron reactivities upon functionalization with various redox groups. The chemistry of interactions of protected Au nanoparticles with electrode surfaces is still an expanding topic. A variety of attachment chemistries has been described, using both covalent and ionic interactions.

Films based on metal nanoparticles as building blocks on planar substrates have attracted substantial interest due to their unique optical, or electrical properties and high thermal, or chemical stability. Moreover, applications using these hybrid films in chemiresistors or biological sensing have been reported by various groups. Films on solid supports, have been prepared using various techniques and one of the most standard procedures is layer-by-layer (LBL) deposition. In this method, multiple electrostatic ionic interactions between functionalized nanoparticles and polyelectrolytes promote the formation of films. The method mostly relies on a simple dipping protocol between functionalized NPs and polyelectrolyte solutions. Multilayer films have also been prepared based on ligand/metal ion/ligand linkers as reported earlier.

Herein, we describe irreversible NP film formation on an electrode surface via an electrochemical method. Three different MPC compositions, Au\(_{225}(\text{TEA-thiolate})_X(\text{SC6Fc})_Y\) (\(X=18, Y=13\); \(X=22, Y=9\); \(X=27, Y=4\)) were used to show that coverages equivalent to 2-4 NP layers are formed. This is the first example where multilayer NP films form on an electrode surface during potential scanning in an electrochemical experiment. The full-width-half-maximum \(E_{\text{fwhm,OX}}\) of the oxidation peak (83, 89 or 130 mV) is considerably higher than the value reported previously and reasons for this will be explored. Finally, as will be explained, the film formation is believed to be entropically driven process.
2.2 Experimental Section

**Chemicals.** 11-Bromo-1-undecene (>95%), triethylamine (NEt₃, >99%), thioacetic acid (>98%), t-Butylammonium borohydride (Bu₄NBH₄, >98%) t-octylammonium bromide (Oct₄NBr, >98%), sodium borohydride (NaBH₄, >98%), t-butylammonium perchlorate (Bu₄NClO₄, >99%), lithium perchlorate (LiClO₄, >98%), t-butylammonium p-toluenesulfonate (Bu₄NC₇H₇SO₃, puress), and t-butylammonium hexafluorophosphate (Bu₄NPF₆, puress), t-ethylammonium perchlorate (Et₄NClO₄, >99%) from Aldrich and toluene (reagent grade), acetonitrile (Optima), methylene chloride (HPLC grade), tetrahydrofuran (HPLC grade), and ethanol (HPLC grade) from Fisher were used as received. HAuCl₄·xH₂O (from 99.999% pure gold) was synthesized using a literature procedure (Brauer, G 1965) and stored in a freezer at -20 °C. Water was purified using a Barnstead NANOpure system (18 MΩ).

**Synthesis of Ferrocene hexanethiol.** Ferrocene hexanethiol (HSC₆Fc) was synthesized as previously described.³¹H NMR (400 MHz, CD₂Cl₂) of the thiol gave the appropriate NMR peaks: δ = 4.0 (Fc, s, 9 H), 2.49 (CH₂SH, q, 2H, J=7.2 Hz), 2.30 (CH₃Fc, t, 2H, J=7.6 Hz), 1.56 (CH₃CH₂SH, m, 2 H), 1.46 (CH₃CH₂Fc, m, 2 H), and 1.32 (m, 4 H) ppm with no dithiol peaks (t, 4H, 2.66 ppm) present and no significant broadening, indicating that the majority of the ferrocenyl groups were in the reduced state.

**Synthesis of N, N, N-triethyl(11-undecynylmercapto)ammonium chloride (TEA-thiolate).** N,N,N-Triethyl-10-undecynylammonium bromide. The thiol was synthesized as previously reported literature.⁴²

**Synthesis of Quaternary-Ammonium Thiolate Functionalized NPs.** The thiol-protected gold nanoparticles were synthesized as previously described.⁴³


**Synthesis of Mixed Monolayer NPs.** Three different mixed monolayer NPs were prepared by ligand exchange between Au$_{225}$((TEA-thiolate)$_{31}$ and HSC6Fc at a 1:0.5, 1:1, or 1:2 mole ratio of $\omega$-ferrocenyl hexanethiol to TEA-thiolate ligand for Au$_{225}$((TEA-thiolate)$_{27}$Fc$_4$, Au$_{225}$((TEA-thiolate)$_{22}$Fc$_9$, and Au$_{225}$((TEA-thiolate)$_{18}$Fc$_{13}$, respectively. A 50-mL ethanol solution of Au$_{225}$((TEA-thiolate)$_{31}$ and HSC6Fc was stirred for 4 hrs at room temperature. Then 0.102 g of LiClO$_4$ was added, resulting in the formation of solid, and the reaction mixture was stirred for 30 additional minutes. The solid then collected by filtering with a fine glass frit, followed by washing with ethanol. Extent of ligand exchange was determined by $^1$H NMR.

**Electrochemistry.** Voltammetry of was typically done in 0.05 mM mM Au$_{225}$((TEA-thiolate)$_{22}$SC6Fc)$_9$ CH$_3$CN solutions containing various concentrations of electrolyte. A 1.6 mm diameter Pt disc and a Pt wire were used as the working and counter electrodes, respectively. The roughness factor (2.8) of the working electrode was determined from the charge under the hydrogen desorption peak in voltammetry of 0.10 M H$_2$SO$_4$, using the standard 210 $\mu$C/cm$^2$. A Ag/AgCl/3M KCl (aq) was used as the reference electrode. Measurements were performed using a CH Instruments (Austin, TX) model 760C electrochemical analyzer. In “scanning” experiments, the adsorption step was carried out by cyclically scanning the electrode in unstirred 0.05 mM Au$_{225}$((TEA-thiolate)$_{22}$SC6Fc)$_9$ solutions in CH$_3$CN containing various concentrations (1.0, 0.1, and 0.01 M) of Bu$_4$NClO$_4$, between the potential limits of -0.1 to 1.0 V vs Ag/AgCl (aq) for one time. The electrode was then rinsed and transferred to fresh electrolyte of a particular concentration. Surface coverages, $\Gamma_{NP}$ (mol NP/cm$^2$), of adsorbed NPs were calculated from the charge, $q$, under the ferrocene oxidation peak using
\[ q = n A_m F \Gamma_{NP} \quad (1) \]

where \( n \) is the average number of ferrocenes per nanoparticle, and \( A_m \) is the Pt working electrode area, corrected for roughness. The experimentally determined values of \( \Gamma_{NP} \) are compared to estimates of a model monolayer, of \( \Gamma_{\text{MONO,NP}} = 5.2 \times 10^{-12} \text{ mol NP/cm}^2 \) (assuming 32.2 nm\(^2\)/ Au\(_{225}\)(TEA-thiolate)\(_{22}\)(SC6Fc)\(_9\), and based on an overall particle radius of ca. 3.2 nm).

In the current vs. time (i-t curve) experiments, a freshly polished Pt electrode was placed into 0.05 mM Au\(_{225}\)(TEA-thiolate)\(_{22}\)(SC6Fc)\(_9\) in 1.0 M Bu\(_4\)NClO\(_4\)/CH\(_3\)CN and applied -0.1 V potential vs. Ag/AgCl (aq) for 5 minutes. The electrode was then rinsed with CH\(_3\)CN and immersed in NP-free 1.0 M Bu\(_4\)NClO\(_4\)/CH\(_3\)CN, and \( \Gamma_{NP} \) was determined by scanning between -0.1 to 1.0 V vs. Ag/AgCl (aq) potential window at 0.5 V/s for one cycle. The electrode was then repolished and returned to the other set of 0.05 mM Au\(_{225}\)(TEA-thiolate)\(_{22}\)(SC6Fc)\(_9\) in 1.0 M Bu\(_4\)NClO\(_4\)/CH\(_3\)CN solution for different applied potential such as -0.2, -0.4, -0.5, -0.75, and -1.0 V vs. Ag/AgCl (aq).

In an isotherm experimental protocol (no-scan survey), a clean Pt disk electrode was exposed at open circuit to an unstirred solution of 0.025 mM Au\(_{225}\)(TEA-thiolate)\(_{22}\)(SC6Fc)\(_9\) in 0.1 M Bu\(_4\)NClO\(_4\)/CH\(_3\)CN for 15 minutes. The electrode was rinsed with CH\(_3\)CN and immersed in NP-free 0.1 M Bu\(_4\)NClO\(_4\)/CH\(_3\)CN, and \( \Gamma_{NP} \) was determined by scanning between -0.1 to 1.0 V vs. Ag/AgCl (aq) potential window at 0.5 V/s for one cycle. This process was then repeated for different MPC concentrations such as 0.04, 0.05, 0.075, 0.085, 0.1, 0.15, and 0.2 mM.

In the electrolyte effects experiments (survey experiment) a freshly polished Pt electrode was placed in unstirred 0.05 mM of Au\(_{225}\)(TEA-thiolate)\(_{22}\)(SC6Fc)\(_9\) in CH\(_3\)CN solutions
contained 1.0 M of Bu₄N⁺X⁻ electrolyte (X⁻ = PF₆⁻, or p-toluene sulfonate⁻) and scanned for one full cycle between the potential limits of -0.1 to 1.0 V vs Ag/AgCl (aq). The electrode was then rinsed with CH₃CN and transferred to NP-free 1.0 M electrolyte/CH₃CN solution for coverage determination. A similar procedure was followed for other electrolytes having different cations, Y⁺ClO₄⁻ (Y⁺ = Li⁺, Et₄N⁺, or Bu₄N⁺).

2.3 Results and Discussion

Study of the Adsorption of Au₂²₅(TEA-thiolate)₂²(SC₆Fc)₀ in CH₃CN. Au₂²₅(TEA-thiolate)₂²(SC₆Fc)₀ was adsorbed to an electrode from a 0.05 mM solution containing 1.0 M Bu₄NClO₄/CH₃CN. After scanning the electrode between the potential limits of -0.1 to 1.0 V vs. Ag/AgCl(aq), the electrode was rinsed with CH₃CN and transferred to NP-free 1.0 M Bu₄NClO₄/CH₃CN solution and scanned over the same potential range to determine the coverage, \( \Gamma_{NP} \) (mol/cm²). Figure 2.1 represents the cyclic voltammogram of the adsorbed film. Coverage was determined to be 9.3 \( \times 10^{-12} \) mol/cm². This coverage is almost 9-fold higher than the previous report, where the electrode was not modified with a SAM² and 3-fold higher than in the case of SAM modified electrode³. A similar experimental protocol was followed to determine the adsorption of Au₂²₅(TEA-thiolate)₂²(SC₆Fc)₀ from 0.1 and 0.01 M Bu₄NClO₄/CH₃CN and transferred to NP-free 0.1, or 0.01 M Bu₄NClO₄/CH₃CN solutions, see Figure 2.1 and Table 2.1. The coverage, \( \Gamma_{NP} \), for 0.1 and 0.01 M Bu₄NClO₄/CH₃CN are 8.7 and 7.5 \( \times 10^{-12} \) mol/cm² respectively. These coverages are also higher in value in comparison to our previous studies.²³ In both those two previous reports, we mentioned that the adsorption was irreversible and promoted by multiple ion-pair formations between oxidized ferrocenes (ferrocenium) and electrolyte anions. We also
showed that ionic interactions between carboxylate ions in a SAM and ferrocenium did play a major role in producing a stably adherent film.\(^3\) Those results suggested that, the oxidized form of ferrocene was almost essential to take part in previously mentioned ionic interactions. In this present study, the mixed monolayer NP contains 22 permanent positive charges in the form of a quaternary ammonium salt-terminated thiol, \([-N^+(CH_2CH_3)_3]\). The positive charges help to form multiple, simultaneous, different ion-pair formations between nanoparticles using electrolyte anions. The \(\Gamma_{NP}\) in these instances varies with electrolyte concentration but it effects is much less prominent than the previous studies. In the present study we have found coverages equivalent to ca. two monolayers are formed on the electrode surface for 0.01, 0.1 or 1.0 M \(Bu_4NCIO_4/CH_3CN\). This multilayer film formation indicates that multiple interactions between adsorbed anions and NP on the electrode surface are present. Additionally, there are numerous lateral interactions, which are mostly directed by the positive charge on particle surface. Now the question arises, while we have observed an electrolyte concentration effect on surface coverage previously,\(^2,3\) we have not observed one in the present study. In this present scenario, \(Au_{225}(TEA-thiolate)_{22}(SC6Fc)_9\) has perchlorate (\(ClO_4^-\)) counter anions and as a result the amount of electrolyte present during the potential scanning did not influence the film formation as much. The \(ClO_4^-\) attached to the NP takes part in multiple bridging-ion pair interactions.

The cyclic voltammetric peak shape has provided us an informative account regarding the ferrocenium/X-/ferrocenium interaction. Previously it was found that the oxidation peak of ferrocene for fully-ferrocenated NPs\(^2,3\) is very sharp and the full width half maximum (\(E_{fwhm}\)) was 35 mV. The results suggested there were multiple ferrocenium/X-/ferrocenium lateral interactions.\(^45,46\) In this present study \(E_{fwhm,OX}\) values for \(Au_{225}(TEA-\)}
Figure 2.1. Cyclic voltammetry of adsorbed Au_{225}(TEA-thiolate)_{22}(SC6Fc)_{9} for different electrolyte concentrations (NP-free) in Bu_{4}NClO_{4}/CH_{3}CN with potential scan rate of 0.5 V/s. The NP film was prepared in 0.05 mM Au_{225}(TEA-thiolate)_{22}(SC6Fc)_{9} in either 1.0 (black curve), 0.1 (red curve), or 0.01 (blue curve) M Bu_{4}NClO_{4}/CH_{3}CN with potential scan rate 0.5 V/s. The film was transferred to NP-free solution containing the same concentration of Bu_{4}NClO_{4}/CH_{3}CN.
Table 2.1. Effect of Concentration of Supporting Electrolyte on Surface Coverage of Au\textsubscript{225}(TEA-thiolate)\textsubscript{22}(SC6Fc)\textsubscript{9} Adsorbed on a Pt Electrode from a 0.05 mM NP solution/CH\textsubscript{3}CN. The Electrode was then Rinsed and Transferred to NP-free Electrolyte Solution at the Same Concentration.\textsuperscript{a,b}
<table>
<thead>
<tr>
<th>Supporting Electrolyte</th>
<th>[Supporting Electrolyte]</th>
<th>$\Gamma_{NP} \times 10^{12}$ mol / cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu₄NClO₄</td>
<td>1.0</td>
<td>9.3</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>7.5</td>
</tr>
</tbody>
</table>

*aThe scan rate is 0.5 V/s. *bScan between -0.1 and 1.0 V vs. Ag/AgCl (aq).*
thiolate)$_{18}$(SC$_6$Fc)$_{13}$, Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$ and Au$_{225}$(TEA-thiolate)$_{27}$(SC$_6$Fc)$_4$ are 83, 89, and 130 mV, respectively. The theoretical $E_{\text{fwhm}}$ for a surface confined, non-interacting electroactive monolayer is 90.6 mV and is based on a linear relationship between surface coverage and activity. Fully-ferrocenated NPs, give rise to a number of opportunities for lateral interactions because the particle surface is covered with ferrocene groups. Scanning was a requirement to produce a stably adherent film in this instance, indicating that the oxidation of ferrocene to produce ferrocenium was crucial, resulting in ferrocenium/X-/ferrocenium attractive interactions. This is why we saw $E_{\text{fwhm}}$ values of 35 mV. Our new particles have ferrocene imbedded within the monolayer due to the longer TEA-thiolate chain, and therefore are harder to access, resulting in a reduced probability of inter-particle ferrocenium/X/-ferrocenium interactions. Additionally, scanning is not a requirement (vida supra) with the present mixed monolayer NPs to produce stably adherent films, meaning interparticle ferrocenium/X-/ferrocenium attractive interactions are not necessary.

The formation of multilayer NP films could be analogous to multilayer polyelectrolyte films on solid supports. In the case of the polyelectrolyte films, the removal of a large solvent and small counter ions gives an entropic gain, imparting stability of the film. The stability Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$ films to repeated cycling was examined by cycling the potential of the electrode between -0.1 and 1.0 V vs. Ag/AgCl (aq). There was an approximate 2.8% loss of coverage between first and 25th scans. After 25 scans ca. two NP layers still remain on the electrode surface. These data suggest a large number of multidirectional lateral interactions are present between the NP and electrolyte anions. The data also imply that adsorption of first layer is very strong which holds the remaining layers on
top of it. This would be only possible if the first layer would interact very strongly with electrode surface. This strong interaction comes between the adsorbed electrolyte anions and quaternary ammonium ions from the NP.

The result we have discussed so far implies that the value of $\Gamma_{NP}$ is mostly directed by vertical and lateral interactions between positively charged [-N(CH$_2$CH$_3$)$_3$] and electrolyte anions. In our previous reports,$^{2,3}$ we discussed that the vertical and lateral interactions were formed between ferroceniums and electrolyte anions. As there are large number of permanent positive charges are present in Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$, the number of ferrocene groups should not influence greatly the surface coverage and stability of the films. To prove that fact, the electrode was scanned over a smaller window, -0.1 to 0.6 to -0.1 V vs. Ag/AgCl (aq), in a solution of 0.05 mM Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$ in 1.0 M Bu$_4$NClO$_4$/CH$_3$CN, then rinsed and transferred to NP-free 1.0 M Bu$_4$NClO$_4$/CH$_3$CN and scanned over the same scale. The purpose of the experiment is to oxidize on a fraction of the ferrocene. In other words, if the ferrocene oxidation process does influence the lateral and vertical interactions, then $\Gamma_{NP}$ would be less than the value we have obtained before for a larger potential scale window, -0.1 to 1.0 V ($\Gamma_{NP} = 9.3 \times 10^{-12}$ mol/cm$^2$). As we expected, the ferrocene oxidation did not influence the $\Gamma_{NP}$ and is found to be $9.6 \times 10^{-12}$ mol/cm$^2$.

Our group has previously reported on the NP adsorption on an electrode surface where either the NP was fully-ferrocenated$^2$ or partially-ferrocenated (10-15% of monolayer)$^{52,53}$. In the case of fully-ferrocenated NPs, even though the coverage was less than the present case, the film was very robust and could only be removed by mechanical polishing. On the other hand, a less robust film was observed for the partially-ferrocenated NPs. In this present investigation, we have observed very high coverage of NP, $6.2-13.9 \times 10^{-12}$ mol/cm$^2$, which
is almost equal to 2-4 monolayers. Such a high coverage could be possible if there is enormous amount of lateral interactions present. This also implies, bridging ion-pair interaction is very strong, which helps irreversible NP adsorption. As the NP contains ClO$_4^-$ as counter anions on its surface, the formation of bridging ion-pair would be entropically favorable process.

**Adsorption Isotherm of Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$.** In a previous report, we showed that adsorption of fully-ferrocenated NPs did take place on the electrode surface without any potential scanning of electrode (*no-scan survey* experiment). Lower surface coverage was achieved in comparison to an experiment where the electrode potential was scanned. We stated that the fully ferrocenated NPs could contain a small number of ferrocenium sites which influence the adsorption process via bridging ion-pair interactions. Besides the NP adsorption phenomenon, ferrocenated dendrimers are also known to adsorb without oxidation. Since the present particles, Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$, contain permanent positive charges, it would be interesting to see how coverage varied in a *no-scan survey* experiment using different NP concentrations. The typical experimental procedure was as follows: a clean Pt disk electrode was exposed at open circuit to unstirred solutions of Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$ in 0.1 M Bu$_4$NClO$_4$/CH$_3$CN for 15 minutes. The electrode was then rinsed with CH$_3$CN and immersed in *NP-free* 0.1 M Bu$_4$NClO$_4$/CH$_3$CN, and $\Gamma_{NP}$ was determined from the charge under the ferrocene oxidation peak by scanning between -0.1 to 1.0 V potential window at 0.5 V/s for one cycle. Depending on the NP concentration, the coverage varies from 6.9-13.8 X 10$^{-12}$ mol/cm$^2$. The highest coverage was achieved when 0.1 mM NP was used. Figure 2.2 shows an isotherm for the NP coverage. Increasing the NP concentration above 0.1 mM did not cause an increase in coverage. From the graph, it is clear
Figure 2.2. MPC concentration dependent coverage of adsorbed film (no-scan survey experiment). Various concentrations, 0.025-0.20 mM, of Au$_{225}$(TEA-thiolate)$_{22}$(SC$_{6}$Fc)$_{9}$ in 0.1 M Bu$_{4}$NClO$_{4}$/CH$_{3}$CN for 15 minutes. The electrode was rinsed with CH$_{3}$CN and immersed in NP-free 0.1 M Bu$_{4}$NClO$_{4}$/CH$_{3}$CN, and $\Gamma_{NP}$ was determined by scanning between -0.1 to 1.0 V vs. Ag/AgCl (aq) potential window at 0.5 V/s for one cycle.
$\Gamma_{NP} \times 10^{-12}$ mol/cm$^2$ vs. [NP] (mM)
that little more than a monolayer coverage (6.9 X 10^{-12} \text{ mol/cm}^2) is achieved at a low NP concentration (0.025 mM) and multilayer coverage does occur at higher NP concentrations.

**Effect on Film-Coverage of Initial Applied Potential.** We have postulated that the adsorption of Au_{225}(TEA-thiolate)_{22}(SC6Fc)_{9} is dependent upon vertical interactions between adsorbed electrolyte anions on electrode surface and -N^{+}(CH_{2}CH_{3})_{3}, on the nanoparticle surface. Another way to examine this interaction is by applying different potentials to the electrode and examining the effect on coverage. Applying a more negative potential should cause a decrease in surface coverage due to decreased electrolyte anions present on the electrode surface. A freshly polished Pt electrode was placed in 0.05 mM Au_{225}(TEA-thiolate)_{22}(SC6Fc)_{9} in 1.0 M Bu_{4}NClO_{4}/CH_{3}CN at an applied potential of -0.1 V vs. Ag/AgCl(aq) for 5 minutes. The electrode then rinsed with CH_{3}CN and placed in NP-free 1.0 M Bu_{4}NClO_{4}/CH_{3}CN solution and scanned over -0.1 to 1.0 V vs. Ag/AgCl(aq) potential window to determine $\Gamma_{NP}$. The experiment was also repeated for applied potentials of -0.2, -0.4, -0.5, -0.75, and -1.0. The corresponding surface coverages are 11.1, 9.4, 9.2, 8.9, 8.6, and 8.0 X 10^{-12} \text{ mol/cm}^2 for -0.1, -0.2, -0.4, -0.5, -0.75, and -1.0 V vs. Ag/AgCl (aq), respectively, see Figure 2.3. These results show an exponential decay of surface coverage against the initial applied potential.

Over the change of potential from -0.1 to -1.0 V, the surface coverage decreased to 8.8 x 10^{-12} \text{ mol/cm}^2, which is almost two monolayers of NP ($\Gamma_{MONO,NP} = 5.2 \times 10^{-12} \text{ mol/cm}^2$). Increasing amounts of electrolyte cation adsorb on the electrode surface as a more negative potential is applied. The electrode surface now appears positively charged resulting in repulsive interactions between the NP and the electrode surface. What is significant is that
the coverage does not decrease to zero, implying that the lateral interactions between particles are important for imparting stability in the film.

**Solvent Effects on Adsorbed Au\(_{225}\)(TEA-thiolate)\(_{22}\)(SC\(_6\)Fc)\(_9\) Film.** The stability and the surface coverage of the NP film were also investigated in various organic solvents. In this study the film was prepared in CH\(_3\)CN and then transferred to NP-*free* electrolyte in various solvents. A fresh film was prepared for each solvent. Adsorption was carried out by cyclically scanning the electrode in unstirred 0.05 mM Au\(_{225}\)(TEA-thiolate)\(_{22}\)(SC\(_6\)Fc)\(_9\) solutions of 0.1 M Bu\(_4\)NClO\(_4\)/CH\(_3\)CN, over the potential limits of -0.1 to 1.0 V vs Ag/AgCl (aq) for one full cycle. The electrode was then rinsed with CH\(_3\)CN and transferred to fresh 0.1 M Bu\(_4\)NClO\(_4\)/CH\(_3\)CN solution. Coverage was 24.2 \(\times\) \(10^{-12}\) mol/cm\(^2\). Under similar reaction conditions and reagent concentrations, films were prepared in CH\(_3\)CN and transferred to various solvents, such as THF, CH\(_3\)OH, and CH\(_2\)Cl\(_2\). Figure 2.4 shows the cyclic voltammogram of adsorbed NP film in different solvents. The coverages in CH\(_3\)CN and CH\(_2\)Cl\(_2\) are 8.7 and 8.4 \(\times\) \(10^{-12}\) mol/cm\(^2\), respectively. In comparison the \(\Gamma_{NP}\) for THF and CH\(_3\)OH are lower, with both these solvents having \(\Gamma_{NP}\) of 6.9 \(\times\) \(10^{-12}\) mol/cm\(^2\), see Table 2.2.

\(\Delta E_{\text{peak}}\) values of NP films in different solvents reveal that the flow of current from the adsorbed layer to the electrode experiences resistance. The \(\Delta E_{\text{peak}}\) values of an adsorbed film in CH\(_3\)CN, CH\(_2\)Cl\(_2\), CH\(_3\)OH, and THF are 28, 108, 66, and 305 mV respectively. In an ideal situation, \(\Delta E_{\text{peak}}\) value should not change with solvent if the adsorbed layer’s resistance involved fast heterogeneous electron transfer. This phenomenon is a defining characteristic of an uncompensated ohmic resistance. The stability of the NP film in all the above-mentioned solvents was also investigated, and it found that the films are stable in organic
Figure 2.3. Comparison of surface coverage of adsorbed film at different initial applied potential, V vs. Ag/AgCl (aq). The current vs. time (i-t) experiment was carried out for five minutes of 0.05 mM Au_{225}(TEA-thiolate)_{22}(SC6Fc)_9 in 1.0 M Bu_4NClO_4/CH_3CN at different initial potential. The electrode then rinsed and transferred to NP-free 1.0 M Bu_4NClO_4/CH_3CN solution and scanned over -0.1 to 1.0 V vs. Ag/AgCl (aq) at a scan rate of 0.5 V/s to determine coverage.
Applied $E / V$ vs. $\text{Ag/AgCl (aq)}$
solvents. For example, in THF, after 25 potential cycles between -0.1 to 1.0 V vs. Ag/AgCl (aq), there is only a 3% loss between the first and 50th scan.

**Study the Coverage of Au$_{225}$(TEA-thiolate)$_{18}$(SC$_6$Fc)$_{13}$ vs. Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$ vs. Au$_{225}$(TEA-thiolate)$_{27}$(SC$_6$Fc)$_4$.** So far, we have discussed about the film formation of Au$_{225}$(TEA-thiolate)$_{22}$(SC6Fc)$_9$ and various interactions present to create stable films on the electrode surface. We have also seen that, the E$_{fwhm,OX}$ is 89 mV, which is higher than the values, 35 mV, that we have reported in our previous publication for fully-ferrocenated NP.$^{2,3}$ We mentioned that the very sharp peaks and E$_{fwhm} < 90$ suggested that there were multiple ferrocenium/X-/ferrocenium lateral interaction.$^{45,46}$ The E$_{fwhm,OX}$ of Au$_{225}$(TEA-thiolate)$_{22}$(SC6Fc)$_9$ film, 89 mV implies negligible ferrocenium/X-/ferrocenium lateral interaction, which makes sense as in the NP, the few ferrocene groups that are present could be well distributed throughout the nanoparticle surface and less likely to interact. Additionally, the ferrocene thiols are shorter in length than the TEA-thiol and therefore embedded inside the monolayer. In order to prove the fact more in detail, we compared Au$_{225}$(TEA-thiolate)$_{18}$(SC6Fc)$_{13}$, Au$_{225}$(TEA-thiolate)$_{22}$(SC6Fc)$_9$, and Au$_{225}$(TEA-thiolate)$_{27}$(SC6Fc)$_4$ films. In Au$_{225}$(TEA-thiolate)$_{27}$(SC6Fc)$_4$, the number of ferrocene groups (4 Fc) reduced by more than half than Au$_{225}$(TEA-thiolate)$_{22}$(SC6Fc)$_9$ (9 Fc). The Au$_{225}$(TEA-thiolate)$_{27}$(SC6Fc)$_4$ and Au$_{225}$(TEA-thiolate)$_{18}$(SC6Fc)$_{13}$ films were prepared as described before (see the experimental section) and transferred to NP-free 1.0 M Bu$_4$NClO$_4$/CH$_3$CN solution. The surface coverage, 10.5 x 10$^{-12}$ mol/cm$^2$, is higher than the film produced by Au$_{225}$(TEA-thiolate)$_{22}$(SC6Fc)$_9$, 9.3 x 10$^{-12}$ mol/cm$^2$. Finally, a Au$_{225}$(TEA-thiolate)$_{18}$(SC$_6$FC)$_{13}$ film was prepared the same way as the other two films and coverage was determined to be 4.6 x 10$^{-12}$ mol/cm$^2$. Comparing the three values, it is not surprising
Figure 2.4. Cyclic voltammetry of adsorbed Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$ for different solvents \textit{(NP-free)} at 0.1 M Bu$_4$NCIO$_4$ with potential scan rate 0.5 V/s. The NP film was prepared in 0.05 mM Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$ in 0.1 M Bu$_4$NCIO$_4$/CH$_3$CN with potential scan rate 0.5 V/s.
Table 2.2 Effect of Solvent on Surface Coverage of \( \text{Au}_{225}(\text{TEA-thiolate})_{22}(\text{SC6Fc})_9 \)
Adsorbed on a Pt Electrode from a 0.05 mM NP containing 0.1 M \( \text{Bu}_4\text{NClO}_4/\text{CH}_3\text{CN} \). The Electrode was then Rinsed and Transferred to \textit{NP-Free} 0.1 M \( \text{Bu}_4\text{NClO}_4 \) Solution in Different Solvents.\textsuperscript{a,b}
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\Gamma_{NP} \times 10^{12} \text{ mol/cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$CN</td>
<td>8.7</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>8.4</td>
</tr>
<tr>
<td>THF</td>
<td>6.9</td>
</tr>
<tr>
<td>EtOH</td>
<td>6.9</td>
</tr>
</tbody>
</table>

*The potential scan rate is 0.5 V/s. *Scan between -0.1 and 1.0 V vs. Ag/AgCl (aq).
that $\text{Au}_{225}(\text{TEA-thiolate})_{27}(\text{SC}_6\text{Fc})_4$ gives the highest coverage, since it more highly ionic, thereby increasing the number of vertical and horizontal interactions in the film.

Comparing the voltammetric wave-shape between $\text{Au}_{225}(\text{TEA-thiolate})_{27}(\text{SC}_6\text{Fc})_4$, $\text{Au}_{225}(\text{TEA-thiolate})_{22}(\text{SC}_6\text{Fc})_9$ and $\text{Au}_{225}(\text{TEA-thiolate})_{18}(\text{SC}_6\text{Fc})_{13}$ reveals that $E_{\text{fwhm,OX}}$ decreased as you increase the number of ferrocene. Figure 2.5 represents the comparison of peak shape for the three different films. There are three possible reasons why $E_{\text{fwhm}}$ can increase above 90 mV, repulsive interactions, spatial distribution of redox sites, and a distribution of formal potentials. The attractive or repulsive forces between two species are driven by the activities. Separating the activity of the highly charged particle from the activity of the ferrocene is likely not possible and the overall repulsive forces between the highly charged particles play some role in increasing $E_{\text{fwhm}}$. Secondly, the ferrocene sites on the particles are likely randomly distributed creating a spatial distribution of redox sites in the films. Thirdly, these sites may have slightly different environments, creating the opportunity for different ferrocene formal potentials. Finally, our group has previously seen no evidence of peak broadening or narrowing for the mixed-monolayer NP, $\text{Au}_{144}(\text{SC}_6)_{45}(\text{SC}_6\text{Fc})_{15}$. Submonolayer films were produced in this instance indicating that the driving force for formation was ion-pair interaction between ferrocenium and electrolyte anions on the surface of the electrode. We can now reasonably conclude that the main reason for an increase in $E_{\text{fwhm,OX}}$ for $\text{Au}_{225}(\text{TEA-thiolate})_{18}(\text{SC}_6\text{Fc})_{13}$, $\text{Au}_{225}(\text{TEA-thiolate})_{22}(\text{SC}_6\text{Fc})_9$ and $\text{Au}_{225}(\text{TEA-thiolate})_{27}(\text{SC}_6\text{Fc})_4$ compared to $[\text{Au}_{225}(\text{SC}_6\text{Fc})_{43}]$ is repulsive interactions due to the highly charged particles, however we cannot definitively say that a spatial distribution of redox sites and a distribution of formal potentials do not contribute to the increase in $E_{\text{fwhm}}$. 
Figure 2.5. Cyclic voltammetry of adsorbed NP in 1.0 M Bu₄NClO₄/CH₃CN with potential scan rate 0.5 V/s. The NP films were prepared in 0.05 mM Au₂₂₅(TEA-thiolate)₁₈(SC₆Fc)₁₃, Au₂₂₅(TEA-thiolate)₂₂(SC₆Fc)₉ or Au₂₂₅(TEA-thiolate)₂₇(SC₆Fc)₄ in 1.0 M Bu₄NClO₄/CH₃CN with potential scan rate 0.5 V/s and then transferred to the same concentration NP-free 1.0 M Bu₄NClO₄/CH₃CN electrolyte solution.
Study of the Adsorption of $\text{Au}_{225}(\text{TEA-thiolate})_{22}(\text{SC}_6\text{Fc})_9$ in Different Supporting Electrolyte. The results we discuss so far provide us substantial information regarding the mixed-NP adsorption on the electrode surface for a particular electrolyte, $\text{Bu}_4\text{NClO}_4$. The remaining part of this report will be focused on the effect of various electrolytes on film formation. For this investigation, we used electrolytes with varying anions, $\text{Bu}_4\text{N}^+X^-$ ($X^-$ = $\text{ClO}_4^-$, $\text{PF}_6^-$, or $p$-toluene sulfonate$^-$)

Previously we have reported that the supporting electrolyte varying anions have strongly influenced the film coverage as well the stability of the film.\textsuperscript{3} Comparing the values of $\Gamma_{\text{NP}}$ for fully-ferrocented NPs, we observed the coverage for 1.0 M $\text{Bu}_4\text{NClO}_4$ is less than that for the same concentration of $\text{Bu}_4\text{NPF}_6$ and no film was detected for 1.0 M of $\text{Bu}_4\text{NC}_7\text{H}_7\text{SO}_3$. In the present study we observe the same trend in coverage for $\text{Au}_{225}(\text{TEA-thiolate})_{22}(\text{SC}_6\text{Fc})_9$ in the presence of 1 M $\text{Bu}_4\text{NClO}_4$ and 1 M $\text{Bu}_4\text{NPF}_6$. We also observed film formation for $\text{Bu}_4\text{NC}_7\text{H}_7\text{SO}_3$. Figure 2.6 represents the cyclic voltammogram of the NP film in three different electrolytes. The $\Gamma_{\text{NP}}$ is strongly dependent on the particular electrolyte anion used, see Table 2.3. The $\Gamma_{\text{NP}}$ results in Table 2.3 taken under survey experiments with potential scanning, are all greater than the model estimate for a full monolayer ca. $5.2 \times 10^{-12}$ mol/cm$^2$. We have seen before that adsorption did not take place for $\text{Bu}_4\text{NC}_7\text{H}_7\text{SO}_3$ even at high concentration in solution, but for $\text{Au}_{225}(\text{TEA-thiolate})_{22}(\text{SC}_6\text{Fc})_9$, the $\Gamma_{\text{NP}}$ is $17.3 \times 10^{-12}$ mol/cm$^2$. 

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Figure 2.6. Cyclic voltammetry of adsorbed NP in different electrolytes with potential scan rate of 0.5 V/s. The NP films were prepared in 0.05 mM Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$ in 1.0 M electrolyte/CH$_3$CN with potential scan rate 0.5 V/s and then transferred to the same concentration NP-free same electrolyte/CH$_3$CN solution. The electrolytes, Bu$_4$NC$_7$H$_7$SO$_3$, Bu$_4$NClO$_4$, and Bu$_4$NPf$_6$ were used in the investigation.
E / V vs. Ag/AgCl (aq)

- Bu$_4$NPF$_6$
- Bu$_4$NClO$_4$
- Bu$_4$NC$_7$H$_7$SO$_3$

Current (μA)

- 0.9
- 0.7
- 0.5
- 0.3
- 0.1
- -0.1

E / V vs. Ag/AgCl (aq)
Table 2.3. Effect of Supporting Electrolyte Anion on Surface Coverage of Au$_{225}$(TEA-thiolate)$_{22}$(SC$_6$Fc)$_9$ Adsorbed on a Pt Electrode from a 0.05 mM NP solution/CH$_3$CN. The Electrode was then Rinsed and Transferred to *NP-free* Electrolyte Solution at the Same Concentration.$^a,b$
<table>
<thead>
<tr>
<th>Supporting Electrolyte</th>
<th>[Supporting Electrolyte]</th>
<th>$\Gamma_{NP} \times 10^{12}\text{ mol/cm}^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bu$_4$NC$_7$H$_7$SO$_3$</td>
<td>1.0</td>
<td>6.2</td>
</tr>
<tr>
<td>Bu$_4$NClO$_4$</td>
<td>1.0</td>
<td>9.3</td>
</tr>
<tr>
<td>Bu$_4$NPF$_6$</td>
<td>1.0</td>
<td>12.5</td>
</tr>
</tbody>
</table>

*a*The potential scan rate is 0.5 V/s. *b*Scan between -0.1 and 1.0 V.
2.4 Conclusions

In conclusion, we have successfully demonstrated that incorporation of permanent positive charge, [-N+(CH2CH3)3] on NP substantially influences the coverage on an electrode. Depending on the reaction conditions, single to multilayers of NP were assembled on the electrode surface in a single potential scanning of the electrode. The high surface coverage and multilayer films imply a large number of lateral interactions have taken place through ion-pair formation. Additionally, the highly-ionic NPs formed ion-pairs with negatively charged anions adsorbed on the electrode surface, which produced a stably adherent film. High surface coverage was obtained even at low supporting electrolyte concentration. This proved our initial hypothesis that in order to have various interactions, some form of positive charge should present on the NP surface. The no-scan survey experiments suggested that, bridging ion-pair interaction is present. The NP adsorption on electrode surface is sensitive to the initial applied potential of the electrode in NP/electrolyte solution. The as-prepared NP film was shown to be stable in variety of solvents. The $E_{\text{fwhm,OX}}$ of the ferrocene oxidation peak depends upon the number of ferrocene on the particle and is larger than those measured for fully-ferrocenated NPs.

2.5 Acknowledgments

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2.6 References


Chapter Three

Deposition and Growth of Highly-Ionic Redox-Labeled Au Nanoparticle Films

3.1 Introduction

Herein is described the controlled electrodeposition of multi-monolayer redox-labeled highly-ionic Au nanoparticle films, of an average composition \( \text{Au}_{225}(\text{S(CH}_2\text{)}_{10}\text{COOH})_{26}(\text{S(CH}_2\text{)}_6\text{Fc})_{17} \) (6 nm dia.). These depositions are akin to those reductively formed\(^1\text{-}^3\) in solutions of vinyl-labeled \([\text{Ru(bpy)}_3]^{2+}\) complexes, and the versatility of the depositions promises to be comparable. Scanning electron microscopy of the films on an Au electrode reveals a porous structure and significant islanding at higher coverages. Electrochemical quartz crystal microbalance (EQCM) measurements demonstrate that in electrolyte/MeCN solutions, the nanoparticle films exhibit permselective behavior in regard to counterion entry/egress, with accompanying transfer of solvent. The principal points of the chapter are that (i) the use of highly ionic nanoparticles allows nanoparticle electrodeposition of multilayer films, without the aid of cross-linking metal/carboxylate coordination.\(^4\text{-}^7\) (ii) an easily controlled growth of the multilayer nanoparticle films, whose stability is ascribed to an entropic advantage of multiple interactions per nanoparticle, and (iii) electron transfers within the film are facile, allowing exhaustive electrochemical reaction of the ferrocene sites attached to as many as 200 monolayers of nanoparticles (NPs). The peak potential separations (\(\Delta E_{\text{PEAK}}\)) observed in
cyclic voltammograms arise solely from uncompensated resistance effects within the film, i.e., the rates of ion permeation.

Our laboratory has previously described the exceptionally strong adsorption onto electrodes, from organic media, of Au$_{225}$ NPs multiply labeled with ferrocene redox sites and/or quaternary ammonium groups. The nearly irreversible adsorption of fully-ferrocenated Au NPs (AuFc) onto bare electrodes and SAM-modified electrodes is believed to reflect multiple ion-pair bridges formed vertically between the NP and the electrode surface and also laterally between the NPs themselves. These stably adherent films contained electrochemically reactive surface coverages of ferrocene sites up to $3.5 \times 10^{-10}$ mol/cm$^2$. The correspondingly strong adsorption of Au$_{225}$ NPs (AuTEAFc) labeled with both cationic quaternary ammonium (TEA) and ferrocene (Fc) further confirmed our hypothesis$^{10,11}$ that the adsorption process was entropically driven due to the multidentate nature of interaction of the highly-ionic NPs with an electrified metal/electrolyte interface.

Considerable research has been aimed at the preparation of Au NP films for various applications, including chemiresistor and biological sensors.$^{13-17}$ The most commonly used methods for preparation of Au NP films involve transfer of Langmuir-Blodgett monolayers,$^{18}$ drop-casting,$^{19}$ and layer-by-layer film growth$^{20}$ from alternating exposure to oppositely charged NPs (LbL, both covalent and electrostatic). Leopold et al.$^4$ prepared films of carboxylic acid-terminated AuNPs using bridging carboxylate/metal ion coordination in a LbL-like fashion. Luo et al.$^{20}$ took advantage of hydrogen bonding between carboxylic acid groups to form films of Au NPs and study the mass flux at the film/solution interface. Variants of the bridging-ligand LbL technique have also been used to assemble nanoparticle
films of many layers.\textsuperscript{5-7} Sih at al.\textsuperscript{21} have prepared Au NP films using electrodeposition by polymerizing a thiophene derivative.

Fundamental understanding of NP film formation and behavior is central to the development of devices containing nanoparticles. The present paper utilizes a measurement tool, the electrochemical quartz crystal microbalance (EQCM), in the described exploration of deposition and properties. EQCM allows unique examination of mass changes associated with interfacial processes at a film/solution interface.\textsuperscript{22,23} There is a ready analogy with redox-active polymer films, where a large body of work exists on studying film behavior, including mobile species transport across the film/solution.\textsuperscript{24-29} Poly(vinylferrocene) (PVF) films have been the subject of many investigations due to the ease of film preparation. We make use of ideas from these earlier works in an investigation of the electrodeposition and behavior of redox-labeled, mixed-monolayer Au NP films. Coverages up to $\Gamma_{\text{Fc}} = 3.8 \times 10^{-8}$ mol Fc/cm$^2$ are reported. Voltammetric response with large $\Delta E_p$ for the Fc/Fc$^+$ couple will be discussed. Finally, a trapping phenomenon, due to Fc$^+$ decomposition will also be discussed.

3.2 Experimental Methods

**Chemicals.** $t$-Octylammonium bromide (Oct$_4$NBr, >98%), sodium borohydride (NaBH$_4$, >98%), $t$-butylammonium perchlorate (Bu$_4$NClO$_4$, electrochemical grade), 11-mercaptoundecanoic acid from Aldrich and toluene (reagent grade), acetonitrile (MeCN, Optima), tetrahydrofuran (THF, HPLC grade), ethanol (HPLC grade) and 1 M tetrabutylammonium hydroxide (diluted to 1 mM in THF) from Fisher were used without further purification. HAuCl$_4$$\cdot$2H$_2$O (from 99.999% pure gold) was synthesized using a
literature procedure and stored in a freezer at -20 °C. Water was purified using a Barnstead (Thermo Scientific, Waltham MA) NANOpure system (18 MΩ). $^1$H NMR spectra were collected on a Varian (Cary, NC) AMX300. XPS spectra were collected on a Kratos (Chestnut Ridge, NY) Axis Ultra$^{\text{DLD}}$ with an Al Kα 1486.6 eV source. Profilometry was performed using a Tencor (Milpitas, CA) Alphastep 200. Scanning electron microscopy and EDAX were performed on a Hitachi (Hitachi High Technologies America, Dallas, TX) S-4700 Cold Cathode Field Emission Scanning Electron Microscope with a 2.0 kV accelerating voltage.

**Synthesis of Ferrocene hexanethiol.** Ferrocene hexanethiol (HSC$_6$Fc) was synthesized as previously described.$^9$ $^1$H NMR (400 MHz, CD$_2$Cl$_2$) of the thiol gave the appropriate NMR peaks: $\delta = 4.0$ (Fc, s, 9 H), 2.49 ($CH_2SH$, q, 2H $J=7.2$ Hz), 2.30 ($CH_2Fc$, t, 2H, $J=7.6$ Hz), 1.56 ($CH_2CH_2SH$, m, 2 H), 1.46 ($CH_2CH_2Fc$, m, 2 H), and 1.32 (m, 4 H) ppm with no dithiol peaks (t, 4H, 2.66 ppm) present and no significant broadening, indicating that nearly all, if not all, ferrocene groups were in the reduced state.

**Synthesis of Fully Ferrocenated Au Nanoparticles.** Au$_{225}$(SC$_6$Fc)$_{43}$ was synthesized according to previously reported literature.$^8$ Briefly, 3.19 g HAuCl$_4$$\cdot$$x$H$_2$O was dissolved in 100 mL deionized water with constant stirring. Separately, 5.20 g Oct$_4$NBr was dissolved in 200 mL toluene and added to the gold salt solution and the stirring was continued for 30 minutes at room temperature until a clear aqueous phase and an orange-brown toluene phase resulted. The aqueous phase was removed, and HSC$_6$Fc (2:1 ligand-to-Au mole ratio) was added to the organic solution. After 20 minutes of stirring the solution became clear indicating formation of the Au(I)-thiolate polymer. This solution was then placed in an ice
bath. 3.8 g of NaBH₄ was dissolved in 20 mL water and the solution was cooled to 0 °C for 30 minutes after which time it was added to the Au(I)-thiolate polymer solution with vigorous stirring. Immediately after the addition of reducing agent, the solution turned black and formation of gas was observed. Rapid stirring was continued for 1 h at 0 °C, after which the dark organic phase was collected and the solvent removed on a rotary evaporator at room temperature. The black solid suspension was stirred in 400 mL of MeCN for 6 h, and the solid product collected and washed with MeCN on a fine glass frit. The average Au core size and the number of ligands, as presented elsewhere, were based on transmission electron microscopy, UV-vis absorbance spectroscopy, cyclic and differential pulse voltammetry, and constant potential coulometry.

**Ligand Exchange Synthesis of Mixed-Monolayer Au Nanoparticles (AuMUAFc).**

Au₂₂₅(SC₆Fc)₄₃ (0.3 g) was dissolved in 25 mL THF. 55 mg of 11-mercaptoundeanoic acid (MUA, ~1:1 with SC₆Fc) were added to the flask and the solution was stirred for two hours. Excess MeCN was added to the flask, resulting in precipitation. Solvent was decanted until approximately 5 mL remained. Additional MeCN was added to the flask and again solvent was decanted off until 5 mL remained. This procedure was repeated two more times at which point all solvent was removed. Product was a fine, free-flowing, black powder. ⁶H NMR revealed no excess thiol and an average composition of Au₂₂₅(S(C₁₀COOH)₂₆(SC₆Fc)₁₇ (AuMUAFc) based on the ratio of Fc peaks to MUA peaks.

**Electrochemistry.** Depositions were carried out in 0.04 mM AuMUAFc solutions in 1 M TBAP/THF containing 0.25 eq of TBAOH (relative to MUA) by cycling the potential of the working electrode between 0 and 0.8 V. Electrodes were rinsed with copious amounts of THF and MeCN after deposition. Voltammetry of films was typically done in 0.1 M
electrolyte/MeCN solutions. Surface coverages are reported as $\Gamma_{\text{Fc}}$ (mol Fc/cm$^2$), based on
the charge, $q$, under the ferrocene oxidation peak using

$$ q = A_m F \Gamma_{\text{Fc}} \quad (1) $$

where $A_m$ is the Pt working electrode area, corrected for roughness by determining the charge
under the hydrogen desorption peak in voltammetry of 0.10 M H$_2$SO$_4$, using the standard 210
$\mu$C cm$^{-2}$. The experimentally determined values of $\Gamma_{\text{Fc}}$ are compared to estimates of a
model monolayer, of $\Gamma_{\text{Mono,Fc}} = 8.8 \times 10^{-11}$ mol Fc cm$^{-2}$ (assuming 32.2 nm$^2$/ AuNP, and
based on an overall particle radius of ca. 3.2 nm). A 2 mm diameter Pt disc and a Pt mesh
were used as the working and counter electrodes, respectively in voltammetric and
impedance studies. Ag/AgCl/ 4M KCl (aq) was used as the reference electrode.
Measurements were performed on a Pine Research Instrumentation WaveNow USB
Potentiostat (Raleigh, NC) or a CH Instruments model 760C Electrochemical Workstation
(Austin, TX).

Electrochemical Quartz Crystal Microbalance (EQCM) studies were performed using a
Stanford Research Systems QCM-200 (Sunnyvale, CA) interfaced to a PC using vendor-
provided software. One inch diameter 5 MHz AT-cut quartz crystals with Cr/Au contacts
were also from Stanford Research Systems. The working electrode area was 1.37 cm$^2$ and the
area of overlap (area of resonance) between the top and bottom Cr/Au contacts was 0.4 cm$^2$.
Simultaneously, voltammetric data were acquired using a CH Instruments model 900
electrochemical analyzer. Data were exported and combined in Microsoft® Excel 2003 or
Origin® 6.1. QCM data were interpreted gravimetrically based on the Sauerbrey$^{32}$ equation
\[
\Delta f = -\frac{2nf_0^2}{(\rho_q \mu_q)^{1/2}} \cdot \Delta m
\]  \hspace{1cm} (2)

where \( n \) is the harmonic at which the crystal is drive (\( n = 1 \) in this case), \( f_0 \) is the resonant frequency of the crystal in Hz, \( \rho_q \) is the density of quartz and \( \mu_q \) is the shear modulus of quartz. For a 5 MHz AT-cut quartz at room temperature, (2) simplifies to

\[
\Delta f = -C_f \Delta m
\]  \hspace{1cm} (3)

where \( C_f \) equals 56.6 Hz cm\(^2\)/ug.

Theoretical modeling of voltammograms was done using BASi DigiSim 3.03 (West Lafayette, IN). See Appendix for details regarding modeling.
3.3 Results and Discussion

Nanoparticle Characterization

$^1$H NMR (not shown) reveals peaks ascribed to both the Fc and MUA ligands and gives an average composition of the nanoparticles as $\text{Au}_{225}(\text{S(CH}_2\text{)}_{10}\text{COOH})_{26}(\text{S(CH}_2\text{)}_{6}\text{Fc})_{17}$ (AuMUAFc). Transmission electron microscopy (TEM) of the AuFc particles prior to ligand exchange with MUA showed that the particles had an average core diameter of 2.0 (±0.3) nm. Previous results show that similar particles do not change size upon ligand exchange. Figure 1 shows voltammetry of a 0.04 mM AuMUAFc solution in 1.0 M Bu$_4$NClO$_4$/THF; there is a single redox couple feature with $E^0$ of 0.451 V as measured from the peak potential average. Several features are noteworthy in the voltammogram. Anodic and cathodic peak currents are different owing to the deposition of nanoparticles bearing Fc$^+$ sites on the electrode. The reduction peak shape is more reminiscent of a surface-localized species than a freely-diffusing one; this is seen by its scant diffusional tailing. Finally, both peaks are more narrow than typical for a diffusion-controlled one electron transfer reaction, owing to lateral interactions between Fc sites on the nanoparticles.

Film preparation and Initial Characterization

Previous reports from our laboratory have described the formation of films of fully-ferrocenated (AuFc)$^{8,9}$ or partially-ferrocenated (AuTEAFc) AuNPs$^{10,11}$. These stably adherent films are the result of entropic gains during adsorption due to the multidentate nature of the NP/surface interaction, analogous to Decher’s$^{34}$ original work on layer-by-layer growth of polyelectrolyte films. Repeated cycling of potential through the Fc/Fc$^-$ couple, of a bare electrode, or of a triethylammonium thiolate (-S(CH$_2$)$_{11}$N(CH$_2$CH$_3$)$_3$ClO$_4$)
Figure 3.1. Cyclic voltammogram of 0.04 mM AuMUAFc in 1 M Bu₄NClO₄/THF, 0.1 V/s, 2 mm diameter Pt WE, Pt Mesh CE. Note that the dashed line represents zero current; arrow indicates direction of scan.
SAM-modified electrode, in the presence of AuFc produces films with coverages up to $2.7 \times 10^{-10}$ and $3.5 \times 10^{-10}$ mol Fc/cm$^2$, respectively. One complete cycle of a bare electrode in the presence of AuTEAFc produced films with coverages up to $1.1 \times 10^{-10}$ mol Fc/cm$^2$. Repeated cycling produced no additional film growth for AuTEAFc. A monolayer is ca $8.8 \times 10^{-11}$ mole Fc/cm$^2$.

Cycling the potential of the working electrode in a solution of the nanoparticles discussed in this report, AuMUAFc, produces stably adherent films, but, unlike AuTEAFc, repeated potential cycling cause increased and continual increases in nanoparticle film, with $\Gamma_{\text{Fc}}$ values over $3.8 \times 10^{-8}$ mol Fc/cm. Thicker films are judged to be possible but have not been investigated; at sufficiently thick films one must expect to encounter incomplete film redox transformation due to finite rates of electron-hopping charge transfer within the film during voltammetry. The discussion here will be limited to films where charge transfer is complete and concentration polarization is not significant.

Scanning electron microscopy of an AuMUAFc film, with $\Gamma_{\text{Fc}} = 1 \times 10^{-8}$ mol Fc/cm$^2$, reveals a porous film with significant islanding (Figure 3.2). Previous research$^8$ suggested that deposition with Au$_{225}$(S(CH$_2$_6)$_6$Fc)$_{43}$ was a stochastic process resulting in up to monolayer coverage after 25 scans. The slow deposition was thought to take place over the entire electrode surface. The deposition process reported here is more rapid, resulting in coverages equivalent to several monolayers in just one scan depending on deposition conditions. Therefore, smaller coverages were not subject to SEM at this time.

Energy Dispersive Analysis of X-Rays (EDAX), shown in Figure 3.3, confirms the presence of Fe in the islands. More uniform films can be prepared (results not shown) by first
Figure 3.2. SEM images of AuMUAFc Film electrodeposited on a quartz crystal with Cr/Au contacts by cycling 100 times at 0.1 V/s in a 0.04 mM AuMUAFc solution in 1 M Bu$_4$NClO$_4$/THF. Scale in lower right is 50 μm. Inset: Zoom of an island. Scale in lower right is 500 nm.
modifying the surface of the electrode with a triethylammonium thiolate SAM prior to nanoparticle film formation, which presumably avoids or levels nucleation effects leading to larger islands. Studies utilizing such films with more uniform coverage of AuMUAFc are underway.

Average film thicknesses (ignoring islanding) based on the area under the ferrocene oxidation wave were estimated and compared with surface profilometry for purposes of modeling voltammetric responses (vide infra). Film thicknesses were estimated according to

\[
d = \frac{\Gamma_{Fc}}{\Gamma_{Mono,Fc}} \cdot d_{Mono} \cdot \rho \tag{4}
\]

where \(\Gamma_{Fc}\) the experimentally determined Fc coverage, \(\Gamma_{Mono,Fc}\) is theoretical monolayer coverage (8.8 x 10^{-11} \text{ mol Fc/cm}^2), \(d_{Mono}\) is the theoretical thickness of a monolayer (6.4 nm) and \(\rho\) is the maximum packing density for a random close pack system (0.64)^{35}. Profilometry of two films showed that the theoretical thicknesses, 1.2 \(\mu\)m and 0.5 \(\mu\)m matched up reasonably well with experimentally determined average thicknesses (n = 5) of 1.5 \(\mu\)m and 0.6 \(\mu\)m, respectively. The islanding thus should not appreciably distort analysis of EQCM results.
Figure 3.3. EDAX of AuMUAFc Film electrodeposited on a QCM crystal with Cr/Au contacts by cycling 100 times at 0.1 V/s in a 0.04 mM AuMUAFc solution in 1 M Bu$_4$NClO$_4$/THF.
Voltammetry and Ac Impedance of AuMUAFc Films

As noted above, the potential cycling of the working electrode in the presence of AuMUAFc causes film growth. Currents of voltammograms of four different potential cycles, Figure 3.4A, during film formation increase in magnitude due to film growth. No attempt is made to interpret the overall peak shape or position during deposition. The frequency response during deposition, Figure 3.4B, shows a significant decrease indicating the addition of AuMUAFc mass to the electrode surface. The inset in Figure 3.4B is the frequency response for a single cycle (the 36th of 100 cycles) during deposition. The arrows contained in the inset mark the beginning and end of the individual cycle. Note the frequency decrease overall, indicating the addition of AuMUAFc mass. The sharp frequency decrease and subsequent increase during the cycle are the entry and egress of anion and solvent during the oxidation and reduction and will be discussed later in light of film redox cycling. No attempt is made to interpret the voltammetry observed during deposition other than to note the increase in current during cycling, indicative of film growth.

Converting the frequency decrease observed during deposition to a mass correlates to a $\Gamma_{\text{Fc}}$ of $8.5 \times 10^{-9}$ mol Fc/cm$^2$. Voltammetry of the film at several potential scan rates after removing the QCM holder, rinsing with copious amounts of THF and MeCN, followed by immersion in 0.1 M Bu$_4$NClO$_4$/MeCN, shown in Figure 3.5, gave a calculated $\Gamma_{\text{Fc}}$ of $8.3 \times 10^{-9}$ mol Fc/cm$^2$, which agrees with the above mass change. The last cycle during deposition has a decrease in frequency of 150 Hz which compares well to the 125 Hz decrease obtained during cycling of the film in electrolyte. These results indicate that the mass increase is indeed correlated with the electrodeposition of ferocenated nanoparticles, and that no significant quantity is lost upon rinsing with solvent and transfer to fresh electrolyte.
Figure 3.4. EQCM of NP deposition from 0.04 mM AuMUAFc in 1 M Bu4NCIO4/THF, 0.1 V/s, 100 Cycles. A: Black – 1st cycle, Red – 25th cycle, Orange – 50th cycle, Blue – 100th cycle. B: Frequency response during deposition. Black arrows indicate beginning and end of deposition. Inset: Frequency response for a single cycle.
Figure 3.5. Cyclic voltammetry at different scan rates of an AuMUAFc Film in 0.1 M Bu₄NClO₄/MeCN, 1.37 cm² Au WE, Pt mesh CE. Red – 0.005 V/s, blue – 0.01 V/s, purple – 0.02 V/s, brown – 0.05 V/s, black – 0.1 V/s. Arrow indicates direction of scan.
Note the large $\Delta E_p$ values in Figure 3.5. At first glance, this can be attributed to the large currents and uncompensated resistance, $R_u$. This is not surprising considering that voltammetry (not shown) of a 50 mM ferrocene solution (0.1 Bu$_4$NClO$_4$/MeCN), prepared to give similar currents to those observed in redox cycling of the film, has a $\Delta E_p$ of 300 mV. Even optimal electrode placement (< 1 cm separation between all three electrodes) still results in significant peak splitting. Drawing an approximate line from the anodic peaks through the cathodic peaks gives a slope of 70 $\Omega$. Also, the absence of significant diffusional tailing, suggests complete charge depletion of Fc sites (i.e., no concentration polarization of Fc sites within the film on the timescales sampled here). Therefore, theoretical modeling was undertaken to confirm the peak separation was an artifact due to $R_u$.

The large peak separation for a film can be modeled two different ways. Method one involves inputting a large diffusion coefficient (0.999 cm$^2$/s in this instance) and small film thickness so that no concentration polarization occurs. This method is appropriate if only $R_u$ is to be examined. The second method utilizes calculated diffusion coefficients and film thicknesses. We chose the latter method in order to also examine the small amount diffusional tailing observed.

Electrochemical impedance spectroscopy (EIS) was used to calculate the diffusion coefficient of ClO$_4^-$ in the film. The diameter of the semi-circle in a Nyquist plot is a measure of the resistance to charge transfer, $R_{CT}$ (i.e. the impedance to moving a ClO$_4^-$ in and out of the film). The $R_{CT}$ can then be used to calculate an ionic conductivity, $\sigma$, according to the equation,
\[
\sigma = \frac{d}{A R_{CT}} \tag{6}
\]

where \(d\) is the film thickness and \(A\) is the electrode area. The ionic conductivity can then be used to calculate the diffusion coefficient of an anion in the film based on the Nernst-Einstein relation,

\[
\sigma = \frac{F^2}{RT} \left( z_{Fc}^2 D_{\text{phys}} C_{Fc} + z_{\text{ClO}_4}^2 D_{\text{ClO}_4} C_{\text{ClO}_4} \right) \tag{7}
\]

where \(D_{\text{phys}}\) is the diffusion coefficient of Fc in the film, \(C_{Fc}\) is the concentration of Fc in the film, \(D_{\text{ClO}_4}\) is the diffusion coefficient of the \(\text{ClO}_4^-\) in the film, and \(C_{\text{ClO}_4}\) is the concentration of \(\text{ClO}_4^-\) in the film. The first term in the parenthesis is assigned a value of zero since the charge on Fc is zero and there is no physical diffusion of Fc in the film. Since \(\text{ClO}_4^-\) would be the counter ion to \(\text{Fc}^+\) in the film, \(C_{\text{ClO}_4}\) was assigned a value based on the probability that a Fc site was oxidized to \(\text{Fc}^+\) at 0.1 V or 0.2 V, the potentials at which EIS was performed. The probability of an Fc site being oxidized was then multiplied by the total concentration of Fc in the film (0.147 M) to give \(C_{\text{ClO}_4}\). \(D_{\text{ClO}_4}\) was estimated to be \(4 \times 10^{-7}\) cm\(^2\)/s based on two different films (see Figures 3.6 and 3.7).

Our interpretation of the impedance data has been kept relatively simple solely for the purpose of calculating a correct order-of-magnitude diffusion coefficient. The impedance data could be modeled in a number of ways including a distribution of resistance/capacitance values due to surface inhomogeneity, inductive effects depressing the semi-circle below the x-axis and/or a distribution of resistance values due to a distribution of \(E^0\) values associated with different Fc sites. Therefore at this time, we model our film as a simple Randles...
Figure 3.6. EIS plot of a 170 nm thick AuMUAFc film in 0.1 M Bu4NClO4/MeCN at 0.1 V vs Ag/AgCl. 5 mV amplitude. 100 kHz to 1 Hz.
Figure 3.7. EIS plot of an 800 nm thick AuMUAFc film in 0.1 M Bu₄NClO₄/MeCN at 0.2 V vs Ag/AgCl. 5 mV amplitude. 100 kHz to 1 Hz.
\[ Z'/10^5 \Omega \quad \text{vs} \quad -Z''/10^5 \Omega \]

\[ 49^\circ \]
equivalent circuit containing a Constant Phase Element, for the purpose of grouping nonidealities, in series with R_{CT}.

Feldberg recently described the effect of R_u on voltammograms of an electrochemically reversible surface attached redox couple. Using Feldberg’s equation R_u was calculated to be approximately 90 \Omega.

Theoretical models were generated using DigiSim (see Appendix for model details) based on data extracted from experimentally obtained results. Four different comparisons, 0.01, 0.02, 0.05, and 0.1 V/s are shown in Figure 3.8. At 0.1 and 0.2 V/s, the models match up well (\Delta E_p) with experimentally obtained voltammograms. At 0.5 and 0.1 V/s, \Delta E_p begins to differ and more significant diffusional tailing emerges which can be modeled by increasing film thickness. Since the film varies in thickness, it is a reasonable assumption that the thicker areas of the film contribute to diffusional tailing. We will also examine an alternate possibility behind the diffusional tailing.

The hopping diffusion of the electron in films and melts is thought to be rapid since in the ion atmosphere relaxation model, self-exchange constants (k_{EX}) are typically quite high. The self-exchange constant for Fc^{0/+} is indeed 8.1 x 10^6 M^{-1} s^{-1}.40 The apparent diffusion coefficient (D_{APP}) is given by the Dahms-Ruff equation

\[
D_{APP} = D_{PHYS} + D_E = D_{PHYS} + \frac{k_{EX} \delta^2 C}{6}
\]

(8)

where D_{PHYS} is the diffusion coefficient of Fc in the film (assumed to be zero in this case), \delta is the center-to-center distance between donor and acceptor (assuming a cubic lattice
Figure 3.8. Comparison of Theoretical (black curves) and Experimental (red curves) Cyclic Voltammetry of an AuMUAFc Film in 0.1 M Bu$_4$NClO$_4$/MeCN. A – 0.01 V/s, B – 0.02 V/s, C – 0.05 V/s, D – 0.1 V/s.
model), and C is the overall concentration of Fc in the film. Electron hopping between the Fc sites on the surface of a particle or with a neighboring particle or even with the particle core (see Figure 3.9) give the use of the cubic lattice model validity. It would also be valid to assume that electron hopping only takes place on the surface of the particle at the ends of the ligands, however, the center-to-center distance between donor and acceptor is only slightly increased from 2.24 nm to 2.58 nm. The second term in (8) is now divided by four to account for a square-planar model rather than the cubic-lattice model. $D_E$ values for the cubic-lattice and square-planar models are $1 \times 10^{-8}$ cm$^2$/s and $2 \times 10^{-8}$ cm$^2$/s, respectively. This difference is not significant and therefore, the smaller cubic-lattice model value was chosen when comparing experimental voltammograms to theoretical voltammograms. Theoretical voltammograms at 0.05 V/s generated for the film discussed directly above, at varying thicknesses, using $D = 1 \times 10^{-8}$ cm$^2$/s, are shown in Figure 3.10. Also shown in is a theoretical voltammogram with $D = 4 \times 10^{-7}$ cm$^2$/s. The results show that the slower diffusion coefficient is better able to model the diffusional tailing observed experimentally. Several thicknesses are shown for comparison and show that at 50 mV/s, even doubling the film thickness surpasses the limit of complete charge accessibility on the experimental timescale. The most important conclusion from the comparisons, though, is that the peak splitting observed in the voltammograms is due solely to $R_u$ effects.
Figure 3.9. Cartoon Representation for Mobile Species Movement during Oxidation of AuMUAFc Film in 0.1 M Bu$_4$NClO$_4$/MeCN. C$^+$ = Bu$_4$N$^+$, A$^-$ = ClO$_4^-$, S = MeCN.
Figure 3.10. Comparison of Theoretical and Experimental Curves for Cyclic Voltammetry of AuMUAFc Films at Varying Thicknesses and Diffusion Coefficients in 0.1 M Bu$_4$NClO$_4$/MeCN at 0.05 V s$^{-1}$. Red – Experimental, Black – 1 μm, D = 4 x 10$^{-7}$ cm$^2$/s; Orange – 1 μm, D = 1 x 10$^{-8}$ cm$^2$/s; Blue – 2 μm, D = 1 x 10$^{-8}$ cm$^2$/s; Green – 3 μm, D = 1 x 10$^{-8}$ cm$^2$/s.
E / V vs. Ag/AgCl (aq)

1 mA
EQCM Behavior of AuMUAFc Films

Ion and solvent entry/egress during redox cycling of electroactive polymer films has seen extensive research.\textsuperscript{22,25,27,29} AuMUAFc films were subjected to redox cycling while concurrently monitoring film mass changes. Mass-charge ($\Delta m$-$q$) plots, obtained from the combination of gravimetric and voltammetric data, provide a measure of ion, solvent and electrolyte population changes throughout a partial or complete redox cycle. Varying the experimental timescale, in the form of different scan rates, reveals differences in kinetic and thermodynamic.

The ability to access all oxidizable sites in a film is of crucial important should redox-labeled AuNPs be used to fabricate charge storage devices. The amount of charge accessed should not vary as a function of scan rate if all oxidizable sites are being accessed. Although at some higher scan rate, the amount of charge accessed will decrease due to the reduced experimental timescales preventing charge propagation through the film. Figure 3.11 is a plot charge versus the square root of the scan rate for an AuMUAFc film in 0.1 M Bu$_4$NCIO$_4$/MeCN. Interestingly, the amount of charge accessed 0.005 and 0.01 V/s is less than the amount of charge accessed at 0.02, 0.05, and 0.1 V/s. Subjecting the film to repeated cycling reduces the amount of charge accessed during each cycle and also shows that the failure to return to the original film mass as shown in Figure 3.12.

The mass change during an experiment is a sum of all mobile species into and out of the film. Fc oxidation requires the injection or ejection of anion or cation, respectively in order to maintain electroneutrality throughout redox cycling. Movement of solvent into or out of
the film is necessary to maintain activity. Partitioning of supporting electrolyte (SE) is also possible. Therefore, the total mass change ($\Delta m_T$) is given by the equation

$$\Delta m_T = \Delta m_A + \Delta m_C + \Delta m_{SE} + \Delta m_S$$ (9)

where $\Delta m_A$ is the mass change due to anion, $\Delta m_C$ is the mass change due to cation, $\Delta m_{SE}$ is the mass change due to SE and $\Delta m_S$ is the mass change due to solvent. During redox cycling the film gains mass continuously throughout oxidation and loses mass continuously during reduction. This result means that it is unlikely that cation is being ejected during oxidation and injected during reduction because doing so would require nonmonotonic ion flux. It is possible that cation ejection or anion injection can dominate during different parts of the cycle, as been evidenced by previous authors,25,44 however, to the best of our knowledge no group has observed simultaneous cation ejection and anion injection. Previous work from our lab of highly ionic Au NP films support the hypothesis that the change in mass is due to anion and solvent injection during oxidation.10,11

The overall end-to-end (fully-reduced to fully-oxidized) slope during each cycle shown in Figure 3.12 is 200 g/mol indicating the transfer of one ClO$_4^-$ (99.5 g/mol) and 2.45 MeCN (41 g/mol). A comparison between 0.05 M and 0.1 M Bu$_4$NClO$_4$ in MeCN (data not shown) confirmed that the trapped species was MeCN and not likely electrolyte. Based on previous EQCM,45 and neutron reflectivity results46 for poly(vinylferrocene) films, SE will not typically partition into films when concentrations in solution are $\leq$ 0.1 M. The slope of the $\Delta m$-q plot for 0.05 M Bu$_4$NClO$_4$ was
Figure 3.11. Plot of q vs $v^{1/2}$ for an AuMUAFc film in 0.1 M Bu$_4$NClO$_4$/MeCN.
Figure 3.12. Change in mass as a function of AuMUAFc Film oxidation level for five cycles at 0.005 V/s. Grey – cycle 1, Red – cycle 2, Blue – cycle 3, Maroon – cycle 4, Brown – cycle 5.
206 g/mol while the slope for 0.1 M Bu₄NCIO₄ was 197 g/mol confirming that it is unlikely that SE is partitioning into the film and is not the source of the Fc site disconnection.

Considering the total change in mass is due to anion and solvent, the change in solvent population can be calculated throughout the complete redox cycle. The change in solvent population, not the absolute solvent population, is given by the equation

\[
\Delta \Gamma_s = M M_s^{-1} \left( \Delta m_T - M M_a \frac{q}{F} \right)
\]

where \( M M_s \) is the molar mass of the solvent, \( M M_a \) is the molar mass of anion, \( q \) is the charge and \( F \) is Faraday’s Constant.\(^{44}\) The films change in solvent and ion content (directly related to charge), along with potential can be represented as a vector in 3D compositional space \((E, q, \Delta \Gamma_s)\) to provide more information on kinetic and thermodynamic effects during redox cycling of the AuMUAFc film. The use of 3D compositional space to examine thermodynamic and kinetic effects of model mobile species in redox films has been studied extensively by Hillman and coworkers.\(^{44,45}\) Two different scan rates were chosen to examine kinetic effects.

Figures 3.13 and 3.14 are 3D representations for an AuMUAFc film during redox cycling at 0.1 and 0.005 V/s, respectively. Hysteresis in the \( \Delta \Gamma_s \)-q plane at 0.1 V/s indicates differences in ion and solvent flux while curvature upwards is indicative of an attractive force between the film and solvent at low levels of film oxidation. Upon reversal, solvent exit is more linear indicating that there is neither an attractive force nor a repulsive force. This is a possible manifestation of the two-phase behavior observed by Daum and Murray\(^{48}\) for PVF films in perchloric acid.
Note that at 0.005 V/s, little hysteresis is observed, meaning kinetic effects have been lessened or removed and thermodynamic effects can dominate the response. The lack of hysteresis suggests that both anion and solvent flux rates are similar. Again, as in Figure 3.12, the trapping of a species is seen as a failure of $\Delta m$ to return to zero at the end of the cycle.

Plotting the real-time molar differential changes due to anion and solvent enables examination of rate limiting processing throughout the cycle. Figures 3.15 and 3.16 show the molar differentials as a function of potential for 0.1 and 0.005 V/s, respectively. The rate of transfer of MeCN during the first portion of both oxidation and reduction is initially faster than $\text{ClO}_4^-$ at 0.1 V/s. At the end of oxidation and end of reduction, MeCN flux slows compared to $\text{ClO}_4^-$. The rates of transfer of MeCN and $\text{ClO}_4^-$ during oxidation and reduction are similar throughout the complete redox cycle at 0.005 V/s and indicate that solvent egress is not thermodynamically unfavorable.

An alternative hypothesis to the decrease in charge per cycle is that Fc, once oxidized to Fc$^+$, is decomposing at these slow scan rates. Abbott and Whitesides$^{49}$ have reported similar phenomenon of Fc-terminated SAMs in NaClO$_4$ decomposing at oxidizing potentials. The half-life of Fc$^+$ in an organic solvent is typically on the order of hours. Dividing the amount of charge that becomes inaccessible per cycle by the time it takes to traverse from initial oxidation to final reduction can give a rough estimate of a half-life.

In this instance, the half-life of Fc$^+$ in the film ranged from 1-3 hours depending on the film. The trapping phenomenon observed at 0.005 V/s is thus likely a combination of Fc$^+$ decomposing and trapping solvent and electrolyte.
Figure 3.13. 3D Representation of EQCM Data for a Complete Voltammetric Cycle for an AuMUAFc Film in 0.1 M Bu₄NOClO₄/MeCN at 0.1 V/s. Arrows Indicate Direction of Scan.
Figure 3.14. 3D Representation of EQCM Data for a Complete Voltammetric Cycle for an AuMUAFc Film in 0.1 M Bu₄NClO₄/MeCN at 0.005 V/s. Arrows Indicate Direction of Scan.
Figure 3.15. Mass Differential for the Redox Cycling of AuMUAFc in 0.1 M Bu₄NClO₄/MeCN at 0.1 V/s.
$d(\Delta \Gamma)/dE$ / nmol V$^{-1}$

$E - E^0$ / V vs. Ag/AgCl (aq)

- ClO$_4^-$
- MeCN
Figure 3.16. Mass Differential for the Redox Cycling of AuMUAFc in 0.1 M Bu₄NClO₄/MeCN at 0.005 V/s. Arrows Indicate Direction of Scan.
The graph shows the relationship between \( \frac{d(\Delta \Gamma)}{dE} \) in nmol V\(^{-1} \) and the potential \( E - E^0 \) in V versus Ag/AgCl (aq). The graph includes two curves, one for ClO\(_4^-\) and the other for MeCN, demonstrating the difference in their responses.
3.4 Conclusion

The controlled formation of highly-ionic AuMUAFc films simply by controlling the number of cycles during cyclic voltammetry is reported. The large $\Delta E_p$ for the Fe/Fe$^+$ couple is attributed solely to uncompensated resistance, i.e. ion movement within the film. EQCM experiments show that anion and solvent enter during film oxidation and exit during reduction. Charge lost during each cycle at 0.005 V/s is attributed to a combination of mobile species trapping and Fe$^+$ decomposition during redox cycling.

3.5 Acknowledgement

This research was supported in part by grants from the Office of Naval Research and the National Science Foundation.

3.6 References


37. Probability of Fc being oxidized at a given potential: Probability of Fc$^+$ = $1/(1+\exp(F/RT*(E-E_0))$.


3.7 Appendix

DigiSim Parameters – These are the parameters for a 1 μm film at 50 mV/s with $D = 4 \times 10^{-7}$ cm$^2$/s.

source program: DigiSim for Windows 95
program version: 3.05
file type: CV

charge transfer reactions:
reaction[1]: $A(0) + e = A(1)$
reaction[2]: $A(1) + e = A(2)$
reaction[3]: $A(2) + e = A(3)$

experimental parameters:
Estart (V): 0
Eswitch (V): 0.8
Eend (V): 0
v (V/s): 0.05
temperature (K): 298.2
Ru (Ohms): 90
Cdl (F): 2E-005
cycles: 1
electrode geometry: planar
area (cm2): 1.37
diffusion: finite
thickness (cm): 0.0001
pre-equilibrium: enabled for all reactions

charge transfer parameters:
E0[1] (V): 0.35
alpha[1]: 0.5
ks[1] (cm/s): 1000
E0[2] (V): 0.355
alpha[2]: 0.5
ks[2] (cm/s): 1000
E0[3] (V): 0.36
alpha[3]: 0.5
ks[3] (cm/s): 1000

species parameters:
Canal[A(0)] (M/l): 0.04 (blocked right boundary)
Cinit[A(0)] (M/l): 1.2041E-019
D[A(0)] (cm2/s): 4.4E-007
Canal[A(1)] (M/l): 0.04 (blocked right boundary)
Cinit[A(1)] (M/l): 9.8947E-014
D[A(1)] (cm²/s): 4.4E-007
Canal[A(2)] (M/l): 0.04  (blocked right boundary)
Cinit[A(2)] (M/l): 9.8865E-008
D[A(2)] (cm²/s): 4.4E-007
Canal[A(3)] (M/l): 0  (blocked right boundary)
Cinit[A(3)] (M/l): 0.12
D[A(3)] (cm²/s): 4.4E-007

model parameters:
expanding space factor: 0.1
potential step (V): 0.0001
iterations: 1
noise_level (A): 0
D/k: 50
thickness/dx: 200
r0 minimum: 20

simulation statistics:
CPU-time: 2.468
maximum number of boxes: 48
model diffusion coefficient: 3197.1
total number of corrections: 0
number of potential steps with corrections: 0
Imin: -0.0016341
Imax: 0.001634
Cmax: 0.12
Chapter Four

Voltammetry and Redox Charge Storage Capacity of Ferrocene-Functionalized Silica Nanoparticles

4.1 Introduction

As methods of nanoparticle synthesis and characterization improve, their envisioned applications continue to gain interest. Nanoparticles can be designed for unique and optical, electronic, and magnetic properties, allowing a wide range of functionality. Our laboratory and others have contributed work on redox-active nanoparticles. These previous reports utilizing ferrocene functionalized gold monolayer protected clusters have focused on a variety of issues including synthesis and characterization,\textsuperscript{1-7} kinetics of ligand exchange,\textsuperscript{8} redox sensing,\textsuperscript{9-11} and formation of nanoarchitectures\textsuperscript{11-14}. Our recent report\textsuperscript{15} on gold monolayer-protected clusters having 1.1 to 2.2 nm diameter cores and coated with full monolayers of thiolated ferrocenes show that these new materials offer substantial redox charge storage capacity, as much as $7 \times 10^9$ C m$^{-3}$, which arises from the combination of a dense surface coverage by ferrocene sites, and the very small nanoparticle dimensions. This discussion expands on that idea, using inexpensive and easily fabricated nanoparticle materials, with a study of silica nanoparticles bearing a full monolayer of attached ferrocenes and having overall 15 nm diameters (including the ferrocene layer).
Several combinations of silica nanoparticles with redox moieties have been previously described, but none thus far have demonstrated exhaustive, kinetically rapid reactions of the redox sites. Ferrocene-doped silica nanoparticles have been proposed as electron transfer mediators for glucose determination, in one case entrapping the ferrocene within 15 nm diameter silica nanoparticles\textsuperscript{16} and in the other amide-linking it to the surfaces of 80 nm nanoparticles\textsuperscript{17}. Ling et al.\textsuperscript{18} prepared 60 nm diameter ferrocenyl-functionalized silica nanoparticles, aiming at improving guest-host interactions with $\beta$-CD coated nanoparticles. These nanoparticles had a low ferrocene (10-15\%) coverage, and their solution dispersions exhibited sluggish electron transfer (large $\Delta E_{\text{PEAK}}$) in cyclic voltammetry, and mixed diffusion-adsorption behavior. Budny et al.\textsuperscript{19} functionalized large (140 to 735 nm diameter) nanoparticles with various redox-active species and, although surface coverages were higher (ca. 50\% in the case of ferrocene), the ferrocenes were incompletely redox-active. A similar result was reported by Plumeré and Speiser,\textsuperscript{20} who used hydrosilanization to covalently attach ferrocene to 200 nm diameter particles. These previous incomplete reactivity outcomes are possibly a result of the large nanoparticle dimensions, as we discuss later. Xu and Aoki\textsuperscript{21} described vinylferrocene-immobilized polystyrene latex particles of various sizes, where only those Fc groups within ~70 nm of the electrode were thought to be electroactive.

Finally, two other recent reports have described freely diffusing redox-active silica nanoparticles, but lacking fully reversible electrochemistry. Jiang et al.\textsuperscript{22} report that silver nanoparticles on 200 nm silica nanoparticle surfaces could migrate to the working electrode surface. Sun et al.\textsuperscript{23} used 12 nm lithium modified silica nanoparticles as a lithium cation source to prepare lithium conductive gel electrolytes; these nanoparticles
were freely diffusing but so were the lithium ions, which moved freely between electrode
and nanoparticles during voltammetry.

The aim of the present study was to prepare full redox monolayers on very small silica
nanoparticles by straightforward synthetic means, to achieve a complete analytical
characterization of surface coverage, and to demonstrate a fully reactive redox layer—with
an eye on potential usefulness in redox-based supercapacitors (charge storage devices).24-26
In the latter light, it was important to attain a reasonable level of nanoparticle solubility and
well-behaved, reversible ferrocene voltammetry. Complete reactivity of siloxane-attached
ferrocene sites on 15 nm diameter silica nanoparticles (abbrev. FcSiO2) was attained, at what
was estimated to be a complete ferrocene monolayer coverage of $ca. 600 \pm 24$ Fc per
nanoparticle. The coverage was determined by three different measurement procedures.
Well-behaved voltammetry was accessible in both dilute methanol solutions and in
concentrated slurries in acetonitrile. This is the first report of diffusion-controlled
voltammetry of fully reactive ferrocene-labeled silica nanoparticles devoid of any substantial
adsorption effects. This is also a proof-of-concept of redox functionalization of silica
nanoparticles as potential charge storage media.

4.2 Experimental

Chemicals. (3-Aminopropyl)trimethoxysilane (APTMS), ferrocenecarboxylic acid, N-(3-
dimethylaminopropyl)-N’-ethylcarbodiimide hydrochloride (EDAC), tetrabuylammonium
 perchlorate (Bu4NClO4), Cu(II)(ClO4)·6H2O, were obtained from Aldrich and used as
received. Organosilicasol MT-ST silica particles in MeOH were purchased from Nissan
Chemical Corp. (Houston, TX). Toluene (ACS grade), acetonitrile (ACS grade),
dimethylformamide (DMF, Optima) was obtained from Fisher and used as received.

**Instrumentation.** $^1$H NMR spectra were collected on a Varian AMX300. $^{29}$Si NMR spectra were collected on a Varian AMX360 using CP/MAS at a spin rate of 10 kHz. XPS spectra were collected on a Kratos Axis Ultra$^{\text{DLD}}$ with an Al Kα 1486.6 eV source. Electrochemistry was performed using a standard three-electrode cell interfaced to a CH Instruments CH660A potentiostat, using solutions of methanol, acetonitrile, and Bu$_4$NClO$_4$ electrolyte (electrochemical grade). TEM images were acquired on a Philips (FEI) CM12, operating at 100 kV. Digital images were collected with a Gatan camera system. Centrifugation was performed using an Eppendorf 5810 centrifuge with a fixed-angle rotor at 6000 rpm for 15 minutes.

**Synthesis of N-(3-(trimethoxysilyl)propyl)ferrocene.**$^{19}$ To a solution of ferrocenecarboxylic acid in CH$_2$Cl$_2$ (1.0 g, 4.3 mmol) was added 0.98 g (5.1 mmol) of EDAC. The solution was sonicated for 10 minutes followed by the addition of (3-aminopropyl)trimethoxysilane (0.67 g, 3.7 mmol). The solution was then stirred for four hours. The product was purified by filtration through Celite to remove by-products, followed by column chromatography over silica gel using 12/88 vol:vol CH$_2$Cl$_2$/acetone as eluent.

1H NMR (300 MHz, CD$_2$Cl$_2$) $\delta$ (ppm): 5.95 (broad s, 1H, NH), 4.64 (t, 2H, Fc), 4.35 (t, 2H, Fc), 4.21 (s, 5H, Fc), 3.57 (s, 9H, OCH$_3$), 3.34 (q, 2H, NHCH$_2$), 1.69 (m, 2H, CH$_2$), 0.71 (t, 2H, SiCH$_2$).

**Preparation of Ferrocene-Functionalized Silica Nanoparticles, FcSiO$_2$.**$^{27}$ 3 g of MT-ST silica particles were precipitated from MeOH (the purchased solution in which they were
delivered) by adding toluene. Particles were washed four times by centrifugation followed by redispersion in toluene. 300 mg of N-(3-(trimethoxysilyl)propyl)ferrocene in 10 mL toluene was added to the MT-ST silica particles in toluene followed by heating at 80 °C for 18 hours. The nanoparticles were then washed four times by centrifugation and redispersion in toluene, and then four times with methanol and left dispersed in methanol for experimental use. We have seen no visual evidence of hydrolytic cleavage loss of ferrocenes from the nanoparticles; the solvent layer is colorless after centrifuging the nanoparticles out of solution, including following electrochemical studies.

**TEM of FeSiO₂.** Particles were dropcast from dilute solutions onto a 200 mesh copper grid with a Formvar Carbon support film (Electron Microscopy Sciences, Hatfield, PA).

### 4.3 Results and Discussion

**Nanoparticle phase behavior.** The solubilities of the silica nanoparticles as received in methanol solution vs. after ferrocene functionalization are different and display novel characteristics in the latter case. The slightly opaque dispersion of the as-received nanoparticles in methanol is quite stable, although the nanoparticles can be centrifuged into a compact layer. Addition of toluene to the methanol dispersion causes precipitation as a gel, which is incompletely dispersed by shaking; large agglomerates remain and the toluene phase is more opaque than the original methanol solution. TEM (see Figure 4.1) revealed that the ~13 nm diameter silica nanoparticles in such agglomerates remain intact as discrete entities.
Following ferrocene-functionalization, the orange-colored nanoparticles (abbrev. FcSiO₂), now ~15 nm (~13 nm core plus ~2 nm ligand shell), are readily dispersed as a cloudy phase in polar organic solvents like methanol, ethanol, and DMF. The cloudiness may reflect scattering caused by some larger nanoparticle agglomerates; over days these slowly settle out, especially at functionalized nanoparticle concentrations higher than ~15 μM in methanol (MM = 1.75x10⁶ g/mol is used to estimate molar concentrations.²⁸)

When a supporting electrolyte (for voltammetry), typically 0.1 M LiClO₄, is added to a FcSiO₂ dispersion in methanol, the nanoparticles settle out (over a period of hours) into a separate, cloudy layer, leaving a clear solvent/supporting electrolyte layer above. The nanoparticle concentrations in the separated layer could be as high as ca. 60 μM, and the clear solvent layer above can be removed without evident consequence to the nanoparticle-containing phase. The latter is stable and is not a gel or aggregate. From its sensitivity to the presence of electrolyte (which would screen electrostatic repulsions), we infer that the nanoparticle solvent layer’s stability is electrostatically based, probably due to residual silanols that give the silica nanoparticles an inherent negative charge.²⁹ We will arbitrarily refer to the nanoparticle phase (or layer) as a “slurry”. We estimate that the average edge-edge spacing of the nanoparticles in a stable 60 μM FcSiO₂ slurry is ca. 55 nm. Formation of a FcSiO₂ slurry phase can also be provoked by addition of cosolvents. For example, adding acetonitrile to a >15 μM FcSiO₂ solution in methanol can cause prompt formation of an opaque nanoparticle slurry layer, leaving a clear solution phase above. Addition of acetonitrile to a more dilute, 5 μM FcSiO₂ solution in methanol did not cause formation of a slurry layer, at acetonitrile/methanol ratios as high as 3/1. Adding Bu₄NClO₄ electrolyte in acetonitrile at concentrations >10 mM to a 5 μM FcSiO₂ dispersion in an
Figure 4.1. TEM image of intact nanoparticles in agglomerate after the addition of toluene to the methanol solution of as-received nanoparticles.
equal volume of methanol caused formation of a nanoparticle slurry layer. The volume of
the slurry layer formed was approximately the same as the volume of the methanol solution
prior to the addition of acetonitrile and supporting electrolyte.

While the cause(s) of the nanoparticle slurry layer formation were not explicitly studied, the
phenomenon was useful in making available different forms of ferrocenated silica
nanoparticle dispersions for voltammetric investigation.

$^{29}$Si NMR. $^{29}$Si NMR spectra of nanoparticles before and after functionalization (Figure
4.2) are consistent with covalent attachment of the ferrocene ligand, according to the general
reaction

\[
\begin{align*}
\text{Si} &\quad \text{MeO} \quad \text{MeO} \\
\text{MeO} &\quad \text{MeO} \quad \text{Fc} \\
\text{SiO} &\quad \text{SiO} \quad \text{O} \\
\text{O} &\quad \text{Si} \quad \text{MeO} \quad \text{MeO} \\
\text{MeO} &\quad \text{MeO} \quad \text{Fc}
\end{align*}
\]

Prior to functionalization (Figure 4.2, curve a), resonances reflecting non-surface (bulk)
silicon (Q$^4$ band) and silicon bonded to OH groups (Q$^3$ and Q$^2$ bands) are present. After
functionalization (Figure 4.2, curve b), the Q$^4$/Q$^3$ and Q$^4$/Q$^2$ peak intensity ratios increased,
as expected for consumption of nanoparticle surface silanol groups by binding of the
ferrocene ligand. New peaks appear at chemical shifts expected for the ferrocene reagent,
containing silicon bonded to both carbon and oxygen (T$^3$, T$^2$ and T$^1$ bands). The residual
Si(OCH$_3$) groups (T$^2$ and T$^1$ bands) are presumed to become hydrolyzed with subsequent
handling of the nanoparticles. The peak assignments are based on literature chemical shift
data.$^{30}$

**Nanoparticle surface coverage of the ferrocene reagent.** X-ray photoelectron
spectroscopy was used to assess the overall atomic composition of films of FcSiO$_2$
Figure 4.2. $^{29}$Si NMR of Silica nanoparticles before (a) and after functionalization (b) (see text). Assignments based on literature chemical shift values (Ref. 30).
Table 4.1. XPS data for elemental composition of FeSiO$_2$ nanoparticles
<table>
<thead>
<tr>
<th>Element</th>
<th>% Atomic Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>25.9</td>
</tr>
<tr>
<td>N</td>
<td>1.8</td>
</tr>
<tr>
<td>Fe</td>
<td>2.0</td>
</tr>
<tr>
<td>Si</td>
<td>22.5</td>
</tr>
<tr>
<td>O</td>
<td>47.9</td>
</tr>
</tbody>
</table>

Each concentration was calculated using the following equation:\(^{32}\)

\[
C_x = \frac{I_x / S_x}{\sum_{i} I_i / S_i}
\]

where \(S\) is the atomic sensitivity factor, and \(I\) is the peak area.
nanoparticles cast on ITO glass slides. ITO coated glass slides were used to avoid interfering Si 2p peaks of glass, and to minimize charging effects. Nanoparticle atomic percentages are given in Table 4.1. The results for %Fe yield an estimate of ca. 630 ferrocene sites per nanoparticle. In a grafting study on silica particles, Harrak et al.31 report that approximate monolayer coverage corresponds to reaction of one silane modifier per nm². The FcSiO₂ XPS result, and the surface area (520 nm²) of a 13 nm diameter sphere (core), amounts to binding of slightly more (20%) than one ferrocene silane per nm². The experimental objective of a complete monolayer coverage in Reaction (1) appears to have been satisfactorily achieved. The possibly above-monolayer coverage indicated could reflect a minor amount of siloxane oligomerization of the ferrocene reagent on the nanoparticle surface.

A potentiometric titration gave a second and more direct measure of the average number of ferrocenes per FcSiO₂ nanoparticle (Figure 4.3). Cu(II)(ClO₄)₂ has been previously used for the titrimetric determination of ferrocene derivatives.33 From the equivalence point, the total number of ferrocenes per silica nanoparticle was determined to be 590, in good agreement with the XPS result above. Though the presence of a single end point suggests that the ferrocene groups exhibit a single redox potential, previous work on redox polymers has shown that the sites on poly-redox substances should exhibit a statistical distribution of formal potentials provided that they react independently and serially.34 This point will be discussed in the following section.

**Voltammetry of FcSiO₂ nanoparticles.** As noted above, a 60 μM solution of FcSiO₂ in methanol containing electrolyte (0.1 M LiClO₄) forms an opaque “slurry” nanoparticle phase. Cyclic voltammetry (Figure 4.4, curves B,C) in this phase reveals typical ferrocene behavior
Figure 4.3. Potentiometric titration of 10 μM FeSiO₂ with Cu(ClO₄)₂ in 0.1 M Bu₄NClO₄/methanol.
Figure 4.4. Cyclic voltammetry of 60 μM FcSiO$_2$ in methanol (0.1 M LiClO$_4$). A: 20 mV/s, B: 400 mV/s, C: 3200 mV/s. The dashed vertical line represents the $E^\circ$ for FcSiO$_2$. Positive-going potential scans initiated at the right.
Figure 4.5. Plot of oxidation peak current ($i_p$) vs square root of potential scan rate for FcSiO$_2$ in methanol (triangles, $R^2 = 0.998$; $y = 1.66 \times 10^{-5} + 1.82 \times 10^{-5} x$ ; squares, $R^2 = 0.995$; $y = 2.24 \times 10^{-5} x$) and methanol /acetonitrile slurry (circles, $R^2 = 0.999$; $y = 1.36 \times 10^{-5} x$).
Current (A)

$60 \mu M, \text{MeOH}$

$10 \mu M, \text{MeOH}$

$10 \mu M, \text{MeOH/MeCN}$
—a one-electron, chemically reversible wave with formal potential at 0.60 V vs. Ag/AgCl (aq). The wave shows no sign of splitting, indicating a relatively uniform environment for the ferrocene sites. Results at higher potential scan rates (curves B,C) show that the oxidation peak current is proportional to the square root of the potential scan rate, indicating control of currents by linear diffusion of nanoparticles (Figure 4.5, upper curve). However, the convective transport at slower scan rates (vide infra) in the 60 μM slurry and the large charging current background under the peak currents at higher scan rates result in a non-zero y-intercept. Therefore, the solution was diluted to 10 μM FcSiO₂ using methanol (0.1 M LiClO₄). The peak currents in the now well-behaved cyclic voltammograms (not shown) for the 10 μM FcSiO₂ are proportional to the square root of the potential scan rate (Figure 4.5, middle curve) and are expressed (ideally) by the equation

\[ i_p = 2.69 \times 10^5 n^{3/2} AD^{1/2}C^{1/2} \]  

(2)

where \( n \) is the number of electrons delivered (per ferrocene) by a diffusing species having diffusion coefficient \( D \) and net ferrocene concentration \( C \) (mol cm\(^{-3}\); the product of nanoparticle concentration and the number of ferrocenes per FcSiO₂), and \( v \) is potential scan rate. The values of \( D \) and \( C \) are treated as nominal unknowns. The value of the nanoparticle \( D \) was estimated from the Stokes-Einstein equation as 5x10\(^{-7}\) cm\(^2\) sec\(^{-1}\), based on a hydrodynamic radius of 7.5 nm and methanol viscosity of 0.59 cP:

\[ D = \frac{kT}{6\pi\eta r} \]  

(3)

Using this value of \( D \), we calculate that \( C = 5.85 \times 10^{-6} \) mol cm\(^{-3}\) in the slurry and consequently that there is an average of 585 ferrocenes per silica nanoparticle. Not-
withstanding the approximation inherent in the use of a pure solvent viscosity in Eqn. (3), the agreement with the XPS and potentiometric results provides strong confirmation that the ferrocene sites on the FcSiO₂ nanoparticles are fully reactive on the nanoparticle diffusion-controlled voltammetric timescale.

The single voltammetric wave in Figure 4.4 does not mean that all of the ferrocenes on the nanoparticle actually have the same formal potential. Based on previous analyses of poly-redox species (redox polymers, including polyvinylferrocene), it is rather expected that there is a statistical distribution of ferrocene site formal potentials, around the nominal formal potential inferred from the Figure 4.4 voltammetry.³⁴ A single, one electron waveshape is nonetheless expected provided that the multiple redox sites are non-interacting and react independently, which seems to be the case for the FcSiO₂ sites. This result has previously been observed in other analogous systems where molecules contain a number of non-interacting redox centers that react independently and serially.¹³,³⁵-³⁷

At slow potential scan rates (<0.1 V s⁻¹) in the methanol slurry of Figure 4.4 (Curve A), the voltammetry develops a pseudo-steady-state waveshape. The 1.6 mm diameter working electrode is much too large to anticipate any radial diffusion effects on waveshape. We interpret the aberrant voltammetric behavior at slow potential scan rates as convective transport caused by density gradients in the near-electrode solution, due to production of large, localized (on the nanoparticles) concentrations of ferrocenium species and their necessary counterions. Such density gradient-convective effects are well-known in analogous circumstances.³⁸,³⁹
Figure 4.6. Cyclic voltammetry of 10 μM FcSiO$_2$ in methanol / acetonitrile (1:1 vol:vol, 0.1 M Bu$_4$NClO$_4$), 0.1 V s$^{-1}$. 
E/V vs. Ag/AgCl (aq)
As noted above, dilute methanol dispersions of FeSiO₂ nanoparticles are stable with little evidence of settling. However, if an equal volume of acetonitrile containing 0.1 M Bu₄NClO₄ electrolyte is added to a 10 μM solution of FcSiO₂ in methanol, the nanoparticles fairly promptly settle into a translucent slurry layer, with a clear layer of solvent above. The volume of the nanoparticle slurry layer formed is approximately the same as the volume of the original methanol solution, and the concentration of FcSiO₂ nanoparticles in the slurry layer remains as 10 μM. (Cyclic voltammetry with the electrodes in the clear solvent layer reveals only background current.) Placing the working electrode into the slurry layer gives a well-defined wave attributed to ferrocene sites on FcSiO₂ nanoparticles (Figure 4.6). Varying the scan rate (Figure 4.5, lower curve) shows that the peak current is again proportional to the square root of the scan rate, an indication of diffusion-limited currents. The peak potential separation in Figure 2.6 is ΔE_{PEAK} = 69 mV, larger than the reversible 59 mV value. This is a minor uncompensated resistance effect; a plot of ΔE_{PEAK} versus ν^{1/2} is linear with a ν = 0 intercept of 62 mV, close to the reversible expectation for ferrocene. As mentioned above, others have reported that not all of the redox groups immobilized on redox-active silica nanoparticles were electroactive²⁰ or exhibited sluggish electron transfers and mixed diffusion-adsorption voltammetry¹⁸. The present nanoparticles clearly differ in these respects.

An interesting issue in electrochemical reactions of redox-coated nanoparticles with non-conductive cores (as in FcSiO₂) is how all of the redox sites become electrochemically consumed. A requirement would seem to be nanoparticle rotational diffusion time constants that exceed the nanoparticle diffusion residence time at the electrode.³ The rotational time constant can be estimated as τ_{rot} ~ 0.25 μs, from the Debye theory of rotational diffusion
\[
\tau_{\text{rot}} = \frac{V_{\text{NP}} \eta}{kT}
\]  

(4)

where \( V_{\text{NP}} \) is the nanoparticle volume. This value is much smaller than the 18 \( \mu \text{sec} \) diffusional residence time near the electrode, estimated from

\[
l = \sqrt{2Dt}
\]

(5)

assuming a diffusion path-length of twice the particle diameter (e.g., once in and out) and \( D = 5 \times 10^{-7} \ \text{cm}^2 \ \text{sec}^{-1} \).

One other possible scenario for how the redox sites all react is the process of electron hopping (i.e., electron “diffusion”) along the surface of the particle, i.e., The time required for an electron to half-circumnavigate a particle is given by,

\[
\tau_E = \frac{2D_E}{L^2}
\]

(6)

where \( L \) is the half-circumference and \( D_E \) is the electron diffusion coefficient. Taking 2.3 \( \times 10^{-6} \ \text{cm} \) for \( L \), and \( D_E \) as \( 7 \times 10^{-8} \ \text{cm}^2 \ \text{sec}^{-1} \), predicts an electron hopping time constant of 40 \( \mu \text{sec} \), which is significantly longer than the rotational time constant of 0.25 \( \mu \text{sec} \). We conclude—as we did earlier\(^3\) in discussing ferrocenated Au nanoparticles—that all of the ferrocene sites on the FcSiO\(_2\) nanoparticles studied here should, during their reactions, be most rapidly accessible to the electrode by the process of rotational diffusion.

The above discussion emphasizes the probable importance of nanoparticle size in designing redox-coated nanoparticles to exhibit full reactivity of their surface redox
constituents. Note that nanoparticle volume $V_{NP}$ varies as the cube of nanoparticle radius. Thus, a 75 nm nanoparticle radius would correspond to $\tau_{rot} \sim 250 \, \mu \text{sec}$ which for $D = 1 \times 10^{-7} \, \text{cm}^2 \, \text{sec}^{-1}$ would almost surely yield limitations in adequate electrode/ferrocene contacts for exhaustive reaction. This effect may have been operative in the incomplete reactivities observed in past studies using larger SiO$_2$ nanoparticles.

While the voltammetry in Figure 4.6 is well behaved, the currents for the FcSiO$_2$ nanoparticles in the methanol/acetonitrile slurry layer are smaller (factor of 1.6, Figure 4.5, lower curve) than those for the same concentration of FcSiO$_2$ nanoparticles dispersed in methanol alone (Figure 4.5, middle curve). It would be expected, given the lower viscosity of the added acetonitrile, that currents (and D) would increase, not decrease, in the methanol/acetonitrile mixture (assuming that all of the Fc sites remain accessible).

We subsequently determined that the above discrepancy occurs by a slight settling of the FcSiO$_2$ nanoparticles just below the (down-facing) electrode (gravitationally or for some other reason), reducing the effective nanoparticle concentration and ferrocene flux to the electrode during voltammetry. Indeed, if the working electrode is allowed to remain immersed (undisturbed) in the slurry layer overnight, an ensuing voltammogram showed no ferrocene voltammetry and a resistive solvent (Figure 4.7). The apparent solution resistance (calculated from the slope of the current-potential curve) was $ca. 10 \, \text{M}\Omega$. Thus, neither electrolyte or ferrocene-bearing nanoparticles are present in a thin layer of solvent directly under the electrode. This layer could not be visually seen owing to the opacity of the slurry layer. In contrast, if the working electrode was upward-facing (a simple folded-over Pt flag) during an overnight immersion in the nanoparticle slurry layer, a subsequent voltammogram (Figure 4.8) clearly displays the ferrocene oxidation wave. The wave is distorted, at least in
Figure 4.7. Cyclic voltammogram of FcSiO$_2$ in MeOH/MeCN (0.1 M Bu$_4$NClO$_4$) after electrode is left immersed in slurry overnight. 0.1 V/s.
Figure 4.8. Cyclic voltammogram of inverted flag electrode placed in 10 μM FeSiO₂ in methanol / acetonitrile (0.1 M Bu₄NClO₄), 0.1 V s⁻¹.
E/V vs Ag/AgCl (aq)
part owing to the large currents attendant to the large area of the Pt flag electrode, and possibly some compaction of settled FcSiO₂ nanoparticles. No attempt was made to analyze the Figure 4.8 distortions in further detail.

The large resistance of the thin film of solution accumulated over time under a downward-facing electrode suggests that the inferred settling of the FcSiO₂ nanoparticles causes a sequestering of the electrolyte from this thin solution layer. Interactions between electrolyte ions and nanoparticle surfaces, when the nanoparticles seem marginally soluble as in this case, are an unfamiliar subject. The actual quantity of electrolyte sequestered from the thin solvent film must be quite small, since analysis of the solvent and electrolyte concentrations in the clear solvent layer above the nanoparticle slurry layer (formed when 0.2 M Bu₄NClO₄/acetonitrile is added to an equal volume of 10 μM FcSiO₂ in methanol), was still ~0.1 M. This was determined by evaporating a known volume of the clear layer and weighing the supporting electrolyte that it contained. The clear solvent layer contained, as determined by NMR, a 0.8:1 molar ratio, ~45:55 vol:vol, of acetonitrile/methanol, so the slurry phase is slightly enriched in acetonitrile.

**Hydrodynamic voltammetry of FcSiO₂.** Because of the large nanoparticle surface area/volume ratio, the ferrocene-coated silica nanoparticles contain up to 5 x 10⁷ C m⁻³ of redox charge as a dry phase, and 6 x 10⁵ C m⁻³ in a concentrated (60 μM) slurry. Extraction of the large electrochemical charge from a nanoparticle slurry phase, were the slurry to be deployed as a supercapacitor element, is a challenging issue. Diffusion of the nanoparticles is relatively slow. Rotated-disk voltammetry (up to 7500 rpm) was tested in the concentrated FcSiO₂ nanoparticle slurry phase; while ferrocene currents were seen, the wave was very drawn out and a current plateau was not reached.
A more extreme form of hydrodynamic mass transport was tested by subjecting a 9 μM dispersion of FeSiO₂ in 0.1 M LiClO₄/methanol to sonication. The use of sonication to achieve fast hydrodynamic transport to electrodes is well documented.41-43 With the cell placed in a sonication bath, with electrodes in the nanoparticle slurry phase, a scan of electrode potential produced the noisy voltammogram in Figure 4.9. The limiting current of ca. 40 μA corresponds to an effective diffusion transport layer thickness of 1.2 μm, calculated from

\[ i_{\text{lim}} = \frac{nFADC}{\delta} \]  

(7)

where A is electrode area, D the diffusion coefficient of the nanoparticles in methanol (5 x 10⁻⁷ cm² sec⁻¹), and C is the concentration of Fe sites. This transport layer thickness is equivalent to a rotated disk electrode rotation rate, ω, of 1.4x10⁵ rpm, using the equation,

\[ \delta = 1.6D^{\frac{1}{2}}\omega^{-\frac{1}{2}}\nu^{\frac{1}{6}} \]  

(8)

where ν is kinematic viscosity. This high apparent rate of mass transport may have some usefulness in supercapacitor discharge.

4.4 Conclusions

Silica nanoparticles containing a full monolayer of ferrocene, covalently bound through siloxane coupling have been prepared. The total number of ferrocenes per particle are 630, 585, and 590, as determined by XPS, cyclic voltammetry, and potentiometric titration, respectively. These particles also exhibit interesting behavior of settling into a slurry phase,
Figure 4.9. Cyclic voltammetry of a sonicated solution of 9 µM FcSiO₂ in methanol (0.1 M LiClO₄). The dashed line estimates the limiting current.
$E / V$ vs. $\text{Ag/AgCl (aq)}$
yet still yielding typical solution electrochemistry results. All ferrocenes are electrochemically accessible and non-interacting. The redox-coated nanoparticles containing a substantial electrochemical charge, amounting as a dry phase to $5 \times 10^7$ C m$^{-3}$ and to $6 \times 10^5$ C m$^{-3}$ in a concentrated slurry.\textsuperscript{40}

4.5 Acknowledgements

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4.6 References


28. a) MW calculation – density of 2.3 g/cm³ is used to estimate the molar mass for the silica particles. b) Iler, R. K. *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties, and Biochemistry.* Wiley: NY, 1979; p 22.


32. Wagner, C.D.; Riggs, W.M.; Davis, L.E.; Moulder, J.F. In *Handbook of X-Ray Photoelectron Spectroscopy*; Muienberg, G.E., Ed.; Perkin-Elmer Corporation: Eden Prairie, MN, 1979; p 22. Assuming the MW of the nanoparticle (core + monolayer ligand) to be 1.75x10^6 g/mol, an individual particle would weigh 2.9x10^{-18} g. Multiplying by 0.02 (Fe atomic composition) and dividing by the MW of Fe gives 1.04x10^{-21} g Fe per particle, equaling 630 Fc per particle.


40. Charge Density calculation assumes the volume of the particle to be 1.8 x 10^{-24} m^3; the charge density was calculated from

\[
\frac{C}{m^3} = \frac{n}{V_{NP}} \cdot \frac{F}{N_A}
\]

where n is the number of Fc per particle, F is the Faraday constant, \(N_A\) is Avogadro’s number and \(V_{NP}\) is the volume of the particle.

