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Fabrication of Chemically Modified Nanometer-sized Gold Electrodes and Their Application in Electrocatalysis at Pt Nanoparticles.

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Fabrication of Chemically Modified Nanometer-sized Gold Electrodes and Their Application in

Electrocatalysis at Pt Nanoparticles

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A thesis

presented to

the faculty of the Department of Chemistry

East Tennessee State University

In partial fulfillment

of the requirements for the degree

Master of Science in Chemistry

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by

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Platinum Nanoparticles

ABSTRACT

Fabrication of Chemically Modified Nanometer-sized Gold Electrodes and Their Application in

Electrocatalysis at Pt Nanoparticles

by

Jude Chimi Lakbub

Hydrogen evolution via proton reduction occurs at a high rate at the surface of Pt than at Au

electrodes. Using cyclic voltammetry, chemically modified nanometer-sized Au electrodes,

prepared by the Laser-Assisted Puller Method, were employed to examine current amplification by

electrocalysis at Pt nanoparticles adsorbed on the modified Au electrode surfaces. The electrodes

were modified with Self-Assembled Monolayers (SAMs) of cysteamine and soaked in Pt colloid

solutions overnight. Monitoring the decrements of the characteristic steady-state catalytic current

for proton reduction indicated that aggregates of Pt nanoparticles are adsorbed on the cysteamine

monolayers and desorb from them particle by particle. The results also indicate that some particles

are strongly attached to the modified electrode surface and do not deplete even after thorough

rinsing.

DEDICATION

This work is dedicated to my loving and ever caring grand mom, Monica. N. Menyong (RIP).

ACKNOWLEDGEMENTS

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CHAPTER 1

INTRODUCTION

<u>Electrode Modification and Electrocatalysis by Nanoparticles</u>

The use of molecules to modify electrode surfaces has been of increasing interest to electrochemists in recent years. The resulting electrode is known as a chemically modified electrode (CME) which as a result of the modification has very thin monolayer or multilayer film of a particular chemical species at the electrode surface [1]. Molecules that spontaneously assemble on electrode surfaces to form self-assembled monolayers (SAMs) have attracted great attention as electrochemists continuously study the structures, chemical and electrochemical properties, and characteristics and explore the applications of electrodes modified by such molecules [2-5]. One major application of electrodes modified by SAMs is in the study of electrocatalysis by nanoparticles adsorbed on the thin monolayer films of the modified electrodes [6-8]. In such application, the modified electrode is held at a potential where the reaction to be catalyzed is slow, or does not occur at all at the bare electrode (Figure 1). For example, Xiaol et al. [6] used hydrazine oxidation to study electrocatalysis by Pt particles that are adsorbed on a modified Au electrode. The electrode potential was held at 0.1 V, a potential at which oxidation of hydrazine does not occur at the Au electrode but occurs at Pt particles at high rates when they are adsorbed on the electrode. This research focuses on the same phenomenon, but rather uses the electrocatalysis of protons at the Pt nanoparticles (PtNPs) adsorbed on a cysteamine modified electrode to study the depletion of the particles from the electrode surface. At the applied potential, proton reduction does not occur at the bare Au electrode or at the Au/Cysteamine electrode when scanned in acid, but occurs significantly when PtNPs are adsorbed on the cysteamine monolayer and scanned in sulfuric acid.
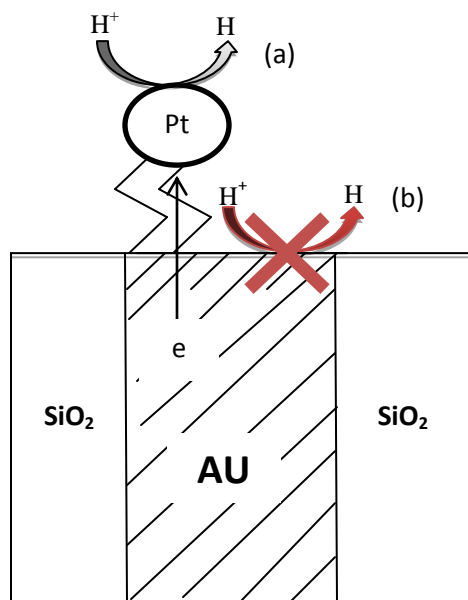
Figure 1: Schematic of proton reduction at PtNPs and bare electrode. (a) Reduction of proton at a Pt NP adsorbed at a monolayer producing leading to high current flow, (b) Reduction of proton at the bare electrode does not occur or occurs at a low rate, producing a very low current that is close to the background current

The properties of metal nanoparticles adsorbed on a monolayer on a CME surface differ from those in bulk solution as well as a bare electrode of the same metal, and they are affected by interplay of different factors such as interaction with the monolayer, quality of the monolayer, inter-particle spacing, and size distribution of the particles [8]. For instance, the catalytic current generated will depend on the size of the particles. Larger particles, or aggregates of particles, will produce higher current [9]. Although the concentration of the species to be reduced, hydrazine and protons for example, also influence the magnitude of the current produced [9], the concentration of such species is always held constant such that any change in current is as a result of a change at the Pt particle surfaces where the reduction occurs.

Despite the availability of several substrates and molecules that can be used to prepare, study, and apply CMEs, gold-alkanethiol couples are those that are widely used. This is because alkanethiols spontaneously form very stable, well-ordered monolayers on gold. The stability and organization of the monolayer on Au depend on factors such as concentration of the alkanethiol, the temperature, chain length, nature of the solvent used, and the cleanliness and structure of the Au prior to modification [10]. L. M. Fischer et al. [11] have reported several methods such as using a weak form of Aqua Regia for a maximum of 2 mins (they observed gold was etched after about 8 mins), reducing agent solutions, Piranha solution, sulfuric acid potential cycling etc for cleaning gold electrodes in preparation for applications in electroanalysis. Widig et al. [12] described the bond between alkanethiols and gold to be very strong and of covalent character, hence the stability of alkanethiols on gold.

Alkanethiols of varying chain lengths, C3, C4, and C5 up to C14, C15, C16, etc. have been studied. Xiao et al. [6] showed that the catalytic current at Pt nanoparticles on SAMs-Au couple decreases dramatically with increase in the chain length. A plot of the catalytic current versus the carbon chain length of the SAMs showed an exponential decay in the current. They reported that the decay was similar to that of electron transport through SAMs. This is consistent with work that has been done by our research group, Sun's Group [13]: Hexadecanethiol $(C_{16}H_{33}SH)$, a long chain alkanethiol, was used to modify a nanometer-sized Au electrode with an effective radius of about 51nm. The limiting current after modification decreased dramatically as well as the effective radius of the electrode which decreased to about 2.1 nm, an outrageous decrease of over 90%. The current was attributed to defects in the monolayer. Thus, to get a good and relatively high current flow for studies of electrocatalysis by metal nanoparticles immobilized on Au CMEs surfaces, short chain alkanethiols such as cysteamine

can be used to modify the electrodes. Also, with such short chain molecules, the metal nanoparticles adsorbed on them will be at close proximity to the Au surface, hence a short distance for electrons tunneling from the Au surface to the particles to induce electrocatalysis, which is indicated by the flow of a current (catalytic current).

The current, I, generated at the surface of a metal nanoparticle is given by

$$I = 4\pi(\ln 2)nFDCr \tag{1}$$

Where: $4\pi(\ln 2)$ is a geometric factor that depend on the particle shape and how it is situated on the electrode surface, D and C are the diffusion coefficient and concentration of the reactants respectively, F is Faraday constant, r is the radius of a nanoparticle, n the number electrons transferred. Clearly from (1), the current is directly proportional to the radius of the particle provided the diffusion coefficient and the concentration of the electroactive species are kept constant. However, some current flow may not result from a single particle but from single particles that have collided to form a mass of particles. Hence, to distinguish between current flow resulting from a single particle and that from an aggregate of particles, it is important to know the approximate sizes of the particles used in the experiment. As such the current flow observed can be used to calculate the approximate radius of the particle size, and if the calculated radius is far larger (more than double or almost double) the known radius of the particles used, then it is evident that the current resulted from a mass of particles. Even though equation (1) can be used to judge whether current flow is from a single particle or a mass of a particles, it cannot be used to tell the exact size of a mass of particles. This is because particle aggregates would definitely not be spherical; hence the equation can only be used to approximate the sizes of aggregates of particles.

Although most of the works on electrocatalysis have been done using ultramicro electrodes, the use of nanometer-sized electrodes in electroanalysis is expediting. Nanometer-sized electrodes were used in this research because of the outrageous advantages found for using such small electrodes. For example, they have been used for studies of microenvironments of biological systems such as cells [14], they have been used in scanning probe microscopies as local probes [11, 15], used to detect and study single molecules (sensors) [16], and also applied in the study of fast electron-transfer reactions [17]. Another important advantage of nanometer-sized electrodes is the small charging current associated with them that enable better flow of Faradaic current. Faradaic and charging currents both flow when an electrode is scanned in solution, but the current of interest is the Faradaic current. For large electrodes, the charging current is large and 'disturbs' the precise detection of Faradaic current. But charging current is proportional to electrode size, and is therefore smaller for nanometer-sized electrodes than larger electrodes. Although Faradaic current also decreases with electrode size, the decrease is much smaller than that for the charging current.

Chemically Modified Electrodes

As mentioned above, CMEs are electrodes that are prepared by the adsorption of chemical species (especially SAMs) on bare electrode surfaces. Generally, the chemical and electrochemical properties of a chemically modified electrode are tailored to a great extent by the specific chemical species used for its modification. Hence, while CMEs undergo reduction and oxidation reactions like bare electrodes, their unique feature is a thin layer/film of a selected chemical that is coated or spontaneously absorbed at the surface of a bare electrode endowing the electrode with some desirable properties such as electrical, chemical, transport, optical, or electrochemical properties as well as selectivity and permeability [1]. Because of their ease of

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preparation and the possibility to use different techniques and chemicals to manipulate their structures and properties, CMEs, particularly those modified with SAMs, find numerous applications in electrocatalysis at single nanoparticles [6, 9, 18], electrochemical, chemical, and biosensors [19] corrosion studies [20], kinetics of electron transfer [21], ion transport [22], and so forth.

The first step involved in preparing a CME is the preparation of the bare electrode.

Fabrication of Nanometer-Sized Electrodes

CMEs have been prepared using ultramicro electrodes. However, in recent years, electrochemists are switching to nanometer-sized electrodes. Nanometer- sized electrodes are electrodes whose effective radii are in the nanometer range. This switch is due to the numerous advantages associated with their use. Some of these advantages have been mentioned above. The size of a CME depends largely on the size of the bare electrode on which the modifying species is adsorbed. Although the modification of an electrode can be relatively easy and straightforward, the fabrication of electrodes with effective radii of several nanometers is challenging. Three main techniques have been used to fabricate such small electrodes. These include the Laser Assisted Puller Method, the etching method, and deposition method. The Puller method is discussed in the experimental section and therefore only the etching and deposition methods are discussed here.

Etching Method

Electrochemical etching has been used to prepare very sharp tips of several nanometers in radius from mircrowires that are then treated and used as electrodes. For example, O. Sklyar et al. [15] and S. K. Lee et al. [23] prepared nanometer-sized electrodes with effective radii from

4nm to about 300nm using this method. They used a three-step procedure: electrochemical etching, coating with a non-conducting chemical, and treatment with heat. The process begins with the electrochemical etching of a microwire, gold microwire for example, to form a sharp tip, followed by electrophoretic coating with a suitable non-conducting chemical to cover the whole electrode surface. Lastly the coated electrode is heated to expose a very small conductive electrode area at the tip.

Instead of using a direct method of heating the insulating material to expose the nanometer-sized tip, S. K. Lee et al. reported an enchanting method where the size of the tip can be controlled while stripping the insulating coat. *In situ* cyclic voltammetry measurements were used to monitor the exposed tip by measuring the current flow while thermally stripping the insulating coat in hot aqueous solution. There was no current flow at room temperature, but as the temperature of the solution was increased, and stripping of the insulating coat began, current started flowing. Stripping could be stopped when the current corresponding to the desired size of the electrode was obtained. Although their method is challenging, it is very interesting because electrodes of about a particular radius can be fabricated.

The tips of electrodes prepared by this method are approximated to be hemispherical [23]. The effective radius of such a hemispherical electrode is calculated from the steady-state limiting current using the equation below.

$$i_{\lim} = 2\pi \text{nFDC} r \tag{2}$$

In equation (1), $i_{\lim}$ is the steady-state limiting current, 2π is the electrode geometric factor, n the number of electrons transferred per molecule, F is Faraday constant, D the diffusion coefficient

of the electroactive species, C the bulk concentration of the electroactive species, and r the effective radius of the electrode.

Relatively larger electrodes have been prepared by electrochemically etching microwires and using them as electrodes without coating with insulating material. M. C. Baykul [24] prepared gold electrodes (200 to 500 nm) to use for STM by direct etching without coating the tips. However, the set-up for the etching process was unique. A set up was done where gold wire, 0.25 mm, was used as anode with a copper ring as the cathode and 0.8 M KCN solution as the electrolyte. The gold wire was clamped in a vertical position in the solution and dc potential of 8 V or more applied. The wire was etched at the position of the meniscus of the electrolyte. The part of the gold wire in solution dropped off when its weight exceeded the etched neck, and the tip of the other part on the clamp was used as the nano electrode.

Deposition Method

This is an electrochemical deposition method that is mainly used to fabricate Au nanoelectrodes as small as 4 nm in radius. It relies on the Puller method. The method takes advantage of the fact that it is relatively easy to produce disk-shaped Pt nanoelectrodes of about 4 nm in radius using the Laser-Assisted Puller method, but difficult for Au. Bo Zhang et al. [25] used this technique to produce Au electrodes of about 4 nm in radius. The method consists of four steps as shown in Figure 2. First a disk-shaped Pt nanoelectrode is prepared by using the Puller method. Second, Pt is electrochemically etched from the Pt nanoelectrodes, producing a Pt nanopore electrode. In the third step, Au nanowire is electrochemically deposited in the nanopore and lastly the tip is polished, exposing disk-shaped Au nanoelectrode, whose radius is same as the radius of the initial Pt nanoelectrode.
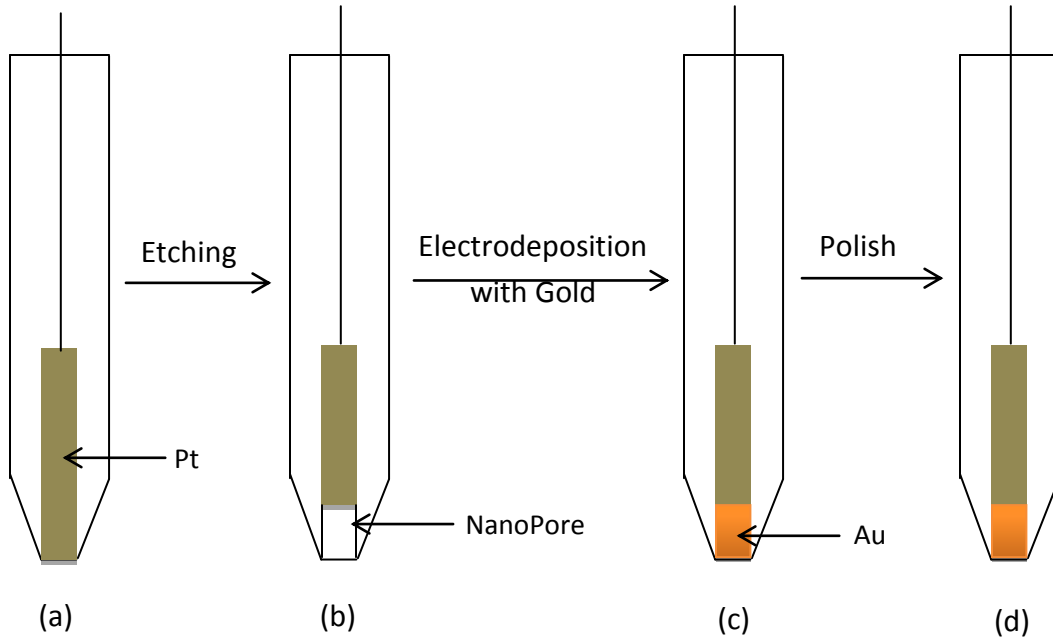
Figure 2: Electrodeposition method for the fabrication of nanometer-sized Au electrode using a Pt nanoelectrode. (a) Polished Pt nanoelectrode, (b) Etched Pt nanoelectrode, (c) Electrodeposited Au in Pt nanoelectrode template, and (d) Polished Au nanoelectrode

Polishing the electrode gives it a disk shape, thus the effective radius can calculated from the steady-state limiting current equation as shown below:

$$i_{\text{lim}} = 4nFDCr \qquad (2)$$

$$r = \frac{i_{\text{lim}}}{4nFDC} \qquad (3)$$

Where: i_{lim} is the steady-state limiting current, n the number of electrons transferred per molecule, F is Faraday constant, D the diffusion coefficient of an electroactive species, and C the bulk concentration of the electroactive species.

Self-Assembled Monolayers (SAMs)

Monolayers formed on electrode surfaces by the spontaneous adsorption of molecules on bare electrode surfaces are known as self- assembled monolayers (SAMs). They have attracted considerable attention in recent years. This is mainly because they are well ordered, stable, easy to produce, and can contain a variety of functional groups, hence a variety of properties. Like any other CME, they also give the modified electrodes different properties from the bare or traditional electrodes.

Research in the area of SAMs goes far back to 1946 when Ziesman et al. published their work on the formation of a monomolecular layer on a metal surface by adsorption (self-assembly) of a surfactant onto a metal surface [26]. The technique would become more popular through the work of Allara and Nuzzo [27] published in 1983. They prepared the first gold-alkylthiolate monolayer by the adsorption (self-assembly) of di-n-alkyl disulfides from solution on the gold substrates. Maoz and Sagiv [28] introduced trichlorosilanes on silicon oxide. In recent years however, many different substrates and modifying species (both electroactive and nonelectroactive) have been used to prepare SAM-substrate couples. However, gold-alkylthiolate monolayers remain the most widely studied substrate-SAMs systems.

Preparation Methods of Chemically Modified Electrodes

The preparation, characterization, electrochemical behavior, structure, and application of modified electrodes are the main areas of concern for researches who use CMEs. In order to prepare a modified electrode for a particular function, choosing a substrate and the modifying species are important. The substrate is the bare, or unmodified, electrode on which the

modifying species bond or are coated. There are four main methods by which CMEs are made. J. M. Zen et al. [29] and R. A. Durst et al. [1] discussed these four routes in detail.

Preparation by Sorption

Sorption based CMEs are prepared by using the physical and chemical interaction properties of both the bare electrode and the modifying chemical [1]. Hence, physisorption (coating for example) and chemisorption are two ways by which a CME can be prepared by sorption. Although those prepared by the physisorbed method find applications in electroanalysis, Zen et al. [29] reported that they are very unstable. Monolayer formation by chemisorption involves the adsorption of the molecules on the electrode surface by means of chemical bonds. Formation of the monolayers on substrates can be done in several ways.

Preparation from solution

This is a widely used simple and straightforward method to prepare chemically modified electrodes. It involves the immersion of the unmodified electrode in a suitable solution of the modifying species for a length of time during which the adsorbate spontaneously adsorb on the electrode surface forming the monolayer. Ethanol is mostly used as solvent, but depending on the modifying compounds, other solvents such as water, chloroform, toluene, acetone, acetonitrile, and dichloromethane can also be used. V. Lakshminarayanan and Ujjal Kumar [30] have reported on solvent effects on monolayers and stated that the permeability of alkanethiol SAMs depend on the solvent used for their preparation.

Several groups have used different lengths of time for this process, from 2hrs [31], 15hrs [32], up to overnight [33]. Kind and Woll reported that only one layer is formed on the electrode surface because the anchor groups of the modifying species are highly specific and would attach

only to the electrode surface and not to the surface of the first monolayer [34]. Bard and

Faulkner [35, pp 581-585] describe this adsorption as specific adsorption, referring to a strong

interaction between the substrate and the modifying compound. They describe three ways by

which monolayers are formed in solution; irreversible adsorption, covalent attachment, and

organized assemblies, and further attribute the spontaneity of the adsorption to the fact that the

substrate environment is energetically more stable than that of the solution.

<u>Structure of Chemically Modified Electrodes</u>

Atomic force microscopy (AFM) and scanning tunneling microscopy (STM) are the most

widely used techniques to determine and study the structures of CMEs, particularly SAMs.

Despite the wide use of these and other techniques, some researchers have reported that the

structures of SAMs have not been fully understood as there are still debates about them [36].

The generally accepted structure of SAMs on substrates is shown in Figure 3. The thin films on

modified electrodes are mostly used to immobilize electroactive species on the electrode surface,

making it possible to study the electrochemical reactions that occur between the electrode and

the immobilized electroactive species as well as the monolayers themselves.
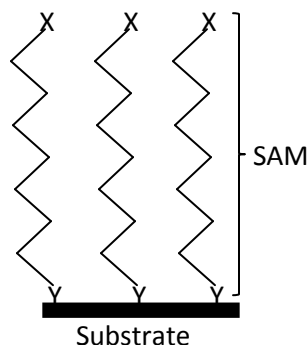
Figure 3: General representation of a substrate-SAMs couple. Y is the head

group that is chemisorbed on the substrate and X is the tail functional

group. Between Y and X are carbon chains, can also be cyclic compounds

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Characterization of Chemically Modified Electrodes

There are a good number of spectroscopic and electrochemical techniques that are widely used for the characterization of CMEs. These include spectroscopic methods like X-ray Photoelectron Spectroscopy (XPS), infrared (IR), Raman and UV/visible spectroscopies, X-ray Diffraction (XRD), Scanning Tunneling, Scanning Electron, and Atomic force microscopies (STM, SEM, and AFM respectively) as well as electrochemical methods such as cyclic voltammetry. A brief discussion of some of the techniques is also given below, followed by Table 1 that summarizes uses and principles of other characterization techniques that have not been discussed. The references provided in the table are for researches where the techniques have been used for characterization or where they are discussed in detail. The majority of the techniques are surface techniques, that is, they are used to study the nature or structure of the electrode surface.

Cyclic Voltammetry

Cyclic voltammetry is the most widely used method for electrochemical studies. It is based on oxidation/ reduction reactions by electrochemical species.

$$O + e \rightleftharpoons R \tag{4}$$

Either a two (working and reference electrodes) or three (working, reference, and counter electrodes) compartment setup can be used. A potential is applied between the working and reference electrode that leads to the flow of current. The current produced, as a result of oxidation/reduction processes, can be measured and plotted against time or voltage. The plot is called a cyclic voltammogram. This method has been used to study the reactions at chemically modified electrodes.

Scanning Tunneling Microscopy (STM)

STM has been widely used for the structural characterization of CMEs [37]. The method depends on the tunneling of currents between a very small conducting tip of a scanning tunneling microscope and the surface of the electrode. The current measured as the tip scans across the electrode surface is recorded on a computer in the form of a contour plot (image) [38], hence the image of the surface is obtained and can be studied. Because the method depends on the flow of current, it therefore requires the sample to be conductive, thus a good method for investigating redox and conducting CMEs [39]. Using this method, Christof Woll and Martin Kind [34] were able to find structural anomalies on a decanethiolate SAM on gold substrate.

Infrared (IR) Spectroscopy

Generally, IR spectroscopy relies on the vibrational modes of chemical species. It is applied in the chemistry of CMEs to obtain a great deal of information about the orientation, chemical identity, and lateral arrangements of the ultrathin layers of SAMs at an electrode surface [5, 34]. Using IR spectroscopy, it is possible to obtain the vibrational spectra of only absorbed species, especially those like OH and CO that have high IR absorption coefficients. Thus, the technique has been used to study the species (Reactants, intermediates, and products) absorbed in the thin layer of a CMEs [35, pp703]. For instance, Korzeniewski et al. [40] applied *in situ* FTIR reflectance spectroscopy to investigate the structural properties of polymer polyaniline coated on Pt electrode and the interactions between a dopant anion and the polymer. They were able to study the nature of the polymer-dopant bonding and observed that for anions within the polyaniline film, their vibrational bands were blue shifted relative to the same anions in the bulk solution and concluded that it was engendered by weak ionic interactions between the polyaniline film and the dopant anions.

This is a technique that is used to study film growth and changes in the thickness of a film on an electrode surface. For example, it can be used to observe changes in the thickness of a monolayer before and after reaction with molecules to detect if there is any adsorption of the molecules onto the layer. The method is based on measuring the change in amplitude and phase of a polarized light beam after reflection at the surface of a CME. The refractive index and thickness of a film on the CME can be determined. It measures precisely the polarization state of light reflected at a surface [41].

Table 1: Summary of uses and principles of some characterization methods

Technique	Uses and Principle	Reference
AFM	-Useful for studying changes in electrode surfaces as a result of adsorption, etching, etc. Provides high resolution image of surface. -Done by measuring changing deflections when the sharp tip of a cantilever is brought close to the electrode surface.	34, 35
SECM	-Useful for studying the rates and pathways of electrochemical reactions. Also used in imaging electrode surfaces. - Based on measurement of current resulting from an electrochemical reaction at the electrode tip.	14
XRD	-Provides structural information about atoms at the electrode surface. -Done by determining the diffraction pattern of a monochromatic x-ray beam that is scattered at the electrode surface.	36
SPRS	-Study absorption of molecules on electrode surfaces (e.g biological molecules and SAMs). Determine changes in thickness of layers. -Based on collective vibrations of electrons (plasmons) at electrode surface after interaction with light.	35

Table 1 (continued)

XPS	-Provides atomic information about the surface of an electrode. -Based on the detection and measurement of energies of electrons ejected from the surface when irradiated with monochromatic x-rays.	42
AES	-Used to determine elemental composition of electrode surfaces and can also identify chemical states of atoms at the surface. -Based on the analysis of energy distribution of Auger electrons emitted from the surface when irradiated with an electron beam.	34, 35
LEED	-Characterize electrode surfaces by providing information about their geometric pattern of atoms. - Observation of diffraction pattern of low energy electrons (10-500 eV) from the electrode surface.	34, 35
NEXAFS	-Used for studying electrode surfaces. -Provides information about the surfaces by determining the absorption of x-ray photons by atoms at the core of the surfaces as a function of the energy of the incident photon.	34, 35
HAS	-Provides information about electrode surfaces via diffraction patterns of low-energy helium atoms emitted from the surfaces.	34

The abbreviations of the techniques are : Atomic Force Microscopy (AFM), Scanning Electrochemical Microscopy (SECM), X-Ray Diffraction (XRD), Surface Plasmon Resonance Spectroscopy (SPRS), X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectrometry (AES), Low Energy Electron Diffraction (LEED), Near-Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS), Helium Atom Scattering (HAS).

Applications of Chemically Modified Electrodes

"Although electrode surfaces can be modified by adsorption, it would be of interest to more drastically and permanently modify the surface by covalently binding molecules to it. If a method for securely anchoring such molecules could be found, advantage could be taken of the molecular structure to build surfaces with unique and widely varying properties." [43] The choice of this quote (from reference 43 published in 1975) to introduce applications of CMEs is because in recent years, more than three decades after it was mentioned, advantage has actually been taken of the numerous properties of molecules like alkanethiols that covalently bind on electrode surfaces for a good number of applications of the modified electrodes. The thin layer/film on CMEs formed by the molecules, endows the CMEs with some desirable properties such as electrical, chemical, optical, and electrochemical properties that have been exploited in various applications of such electrodes. As such CMEs have established their applications in areas such as electrocatalysis, sensors (single nano particles and single molecules detection), corrosion prevention, and study of the kinetics of electron transfer. Because of the progressive use of CMEs in the manufacture of sensors and in electrocatalysis, only these two applications are discussed.

Chemical Sensors

A chemical sensor is a device that can detect a particular chemical species (analyte) in solution and be used to determine the concentration of the species. CMEs have been used to fabricate such devices [44]. The molecules used to prepare such electrodes can only interact with the analyte of interest. This technique has been employed in the manufacture of biosensors such as the glucose sensor [45]. Biosensors detect organic and biological species or other chemical species in biological systems. The basic principle behind their fabrication is to

immobilize biologically sensitive molecules, for example DNA, antigen/antibody, or an enzyme, on the electrode surface that can recognize and interact with a particular biological analyte and produce an electrochemically detectable signal in the process [35, pp 587]. The glucose sensor, for example, is based on the enzyme glucose oxidase that catalyzes the oxidation of glucose to gluconolactone, releasing two electrons in the process [45]. Hence, because enzymes are themselves selective (they recognize and bind specific biological molecules) electrodes modified with enzymes become selective to the specific molecules recognized by the enzyme adsorbed on their surfaces.

Also, electrodes coated with thin film of Nafion help solved a problem of dopamine and ascorbate determination in neurophysiology [46]. Adams and co-workers [46] showed that dopamine can be detected in the brains of living rats by surgically embedding an electrode in the rat's brain. However, ascorbate present in the cerebral fluid that was analyzed is oxidized at almost the same potential as dopamine and hence interferes with the determination of dopamine. The electrode was made to be selective by coating it with a thin Nafion film [47]. Nafion is a cation exchange polymer that detects cations and rejects anions. Because dopamine is a cation and ascorbate an anion at physiological pH values, the Nafion-modified electrode could detect only dopamine. This led to the use of Nafion-coated electrodes for *in vivo* analysis of dopamine and other cationic neurotransmitters, and as standards for these kinds of investigations.

Electrocatalysis

Electrocatalysis at a modified electrode surface refers to a redox reaction between an analyte in solution and the electrode that when mediated by a redox couple (mediator) immobilized at the electrode surface, occurs at a lower overpotential than would otherwise occur at the bare electrode surface [1]. Redox reactions of some important analytes at bare electrode

surfaces are slow and require potentials that are higher than their formal redox potentials for the reactions to take place at desirably higher rates. When such electrodes are modified by immobilizing a redox couple (mediator) at their surfaces, the rates of the redox reactions are accelerated and occur at lower potentials near the formal potential of the mediator [48].

Several redox polymer films have been coated (immobilized) on electrode surfaces and used for electrocatalysis, that is, the redox polymers are used to catalyze electrochemical reactions [49]. The immobilized redox couple serves both as catalyst for the redox reaction and a charge carrier. Two types of catalysis, redox catalysis and chemical catalysis can occur as a result of reactions between a charged mediator and an analyte.

Research Objective

The objective of this research was to study desorption of platinum nanoparticles adsorbed on chemically modified Au nanometer-sized electrodes. This was done by studying the decrease in the electrocatalytic current produced as a result of proton reduction at the surfaces of the PtNPs. The work done was comprised of three important steps. First was the fabrication of nanometer-sized bare Au electrodes. For this, the laser assisted Puller method was used. The electrodes fabricated were in the range 100 to 250 nm in radius. Second, the bare Au electrodes were modified by soaking in a solution of cysteamine, which formed monolayers on the Au electrodes. Last, the electrodes were soaked in a solution of PtNPs. PtNPs were adsorbed on the monolayer, and the Au/cysteamine/PtNPs electrodes then scanned in sulfuric acid solution, and the resulting catalytic current monitored with increasing potential cycles.

CHAPTER 2

EXPERIMENTAL SECTION

Chemicals

The following chemicals were purchased from the suppliers indicated and were used as received: Potassium Nitrate (KNO_3), technical grade Sulfuric Acid (H_2SO_4, Fischer Scientifics), Sodium Borohydrite ($NaBH_4$, 96+%, Fluka), hydrogen hexachlorolatinate (IV) (Pt 30%, Alfa Aesar), trisodium citrate dihydrate (99+%, Aldrich), ferrocenemethanol (97%, $FeCH_2OH$, Aldrich), USP grade Ethanol (CH_3CH_2OH) obtained from Pharmaco Products Inc, and Cysteamine ($C_2H_7NS.HCl$) from Tokyo Chemical Industry CO. LTD. Aqueous solutions were prepared using deionized water (Milli-Q, Millipore Corp).

Instruments

Nanometer-sized Au electrodes were prepared using a P-2000 laser based micropipette puller (Sutter Instrument Co) and were polished using a Microelectrode Beveler (model BV-10, Sutter instrument Co). An optical microscope (Nikon) was used to observe electrodes. CV experiments required the use of a preamplifier (BAS PA-1).

Au microwires (25.00um in diameter), Ag wire, and borosilicate glass capillary tubings (1.0 mm o.d, 0.58 mm i.d), were obtained from Sutter Instruments.

Fabrication of Gold (Au) Nanoelectrodes

Chemically modified nanometer-sized Au electrodes were prepared by a two- step process shown schematically in Figure 4. First, bare nanometer-sized Au electrodes were fabricated using a laser-assisted pulling method [15] as follows: Annealed Au microwire (about 1cm long) was inserted and sealed in borosilicate glass capillary tubing and then pulled into two ultrasharp Au nanowire tips using a P-2000 Laser based micropipette puller. The tips of the capillary tubing were sealed by heating and mechanically polished by means of a Microelectrode Beveler, exposing a disk shaped Au nanosurface. The electrodes were observed using the

reflection model of an optical microscope at 1000 magnification. Only electrodes for which a

tiny, shiny, disk-shaped spot (Figure 7) was observed were used for the rest of the experiment.

(b1)

Laser Pulling

Anneal

Polish &
connect

(b2)

(a)

(c)

(d)
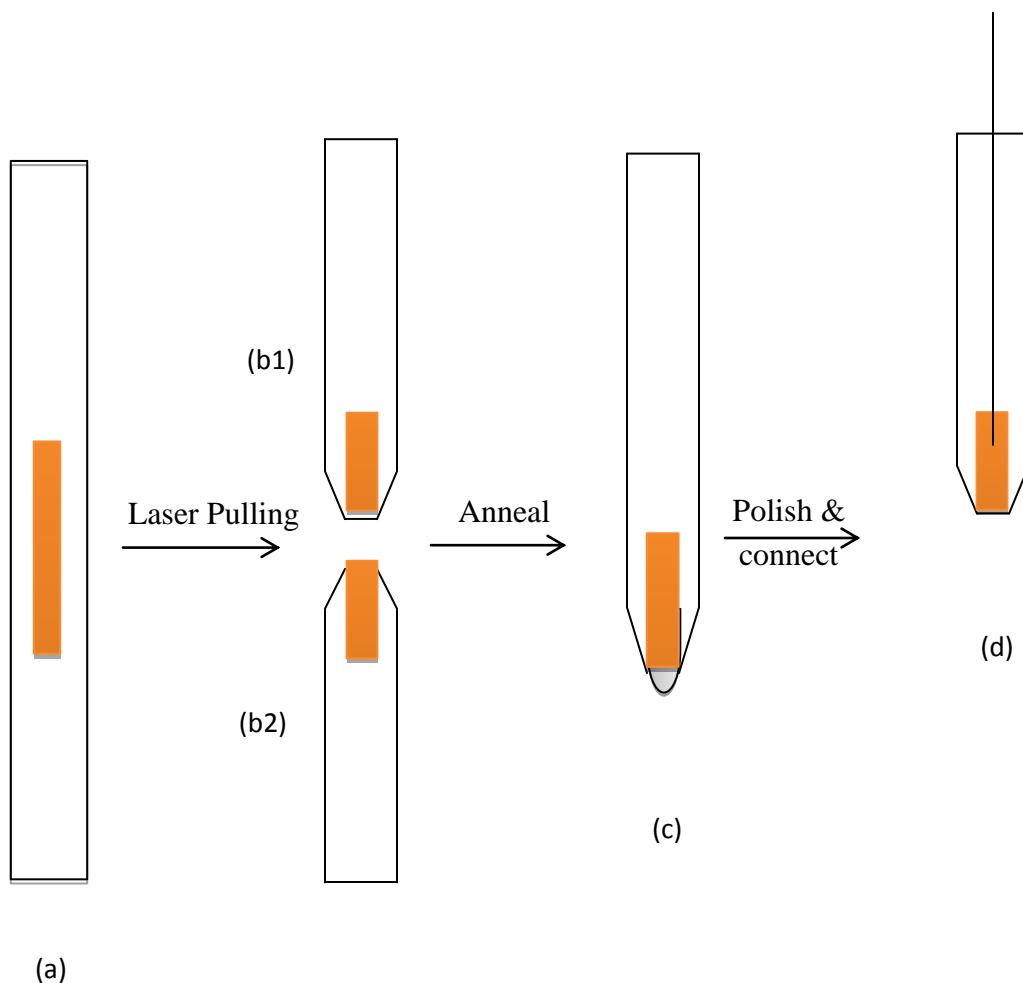
Figure 4: Schematic of the laser assisted Puller method for the fabrication of nanometer-sized

Gold electrode; (a) Au microwire inserted in glass pipette, (b1) Recessed electrode, (b2) Protruded

electrode, (c) annealed electrode, and (d) polished and connected electrode

A conducting microwire was inserted at the open end of the capillary tubing to make

contact with the Au wire and then sealed.   In some cases where there was little or no contact

between the two wires, a small amount of silver powder was inserted at the open end of the

capillary tubing before inserting the conducting wire to ensure good contact between the two

wires.

Characterization and Modification with SAMs

After preparation of nanometer-seized bare electrodes, they were thoroughly rinsed with deionized water and scanned in 1.0 mM $FcCH_2OH$ (with 0.1 mM KNO_3 as supporting electrolyte) until a stable cyclic voltammogram with almost no perturbations was obtained. A one-compartment, two electrode cell system and a preamplifier in a Faraday cage was used, with a Ag silver wire (0.25 mm in diameter) serving as a quasi- reference electrode (AgQRE). The cleanliness of electrodes was ensured by scanning in 0.5M H_2SO_4 to obtain the characteristic peaks of a clean Au electrode. In cases where the peaks were not observed, the electrodes were heated for about 3 or 4 seconds in a hot coil (at about 150 ^0C), rinsed thoroughly with deionized water, and scanned in acid again. This was repeated until the characteristic peaks were obtained. Only electrodes that exhibited the characteristic peaks of clean Au were used for further experiments.

Modification of the nanometer-sized electrodes (Figure 5) was done by immersing in a 0.1M cysteamine/ethanol solution for at least 3 hours.
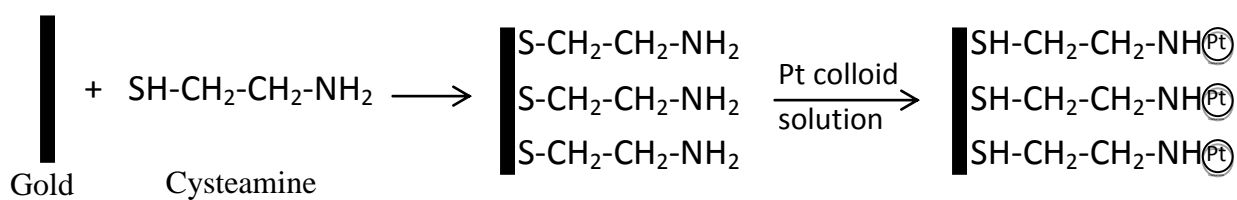
Figure 5: Modification of gold electrode with Cysteamine and then Pt nanoparticles

After soaking electrodes were removed from cysteamine solution, they were rinsed with ethanol first and then thoroughly again with deionized water. They were scanned in ferrocenemethanol (FcMeOH) and then sulfuric acid to obtain background current, followed by soaking in Pt

nanoparticles solution for about three hours and overnight in some cases. After removal from the

PtNP solution, they were scanned in sulfuric acid. Figure 6 shows the experimental set-up.
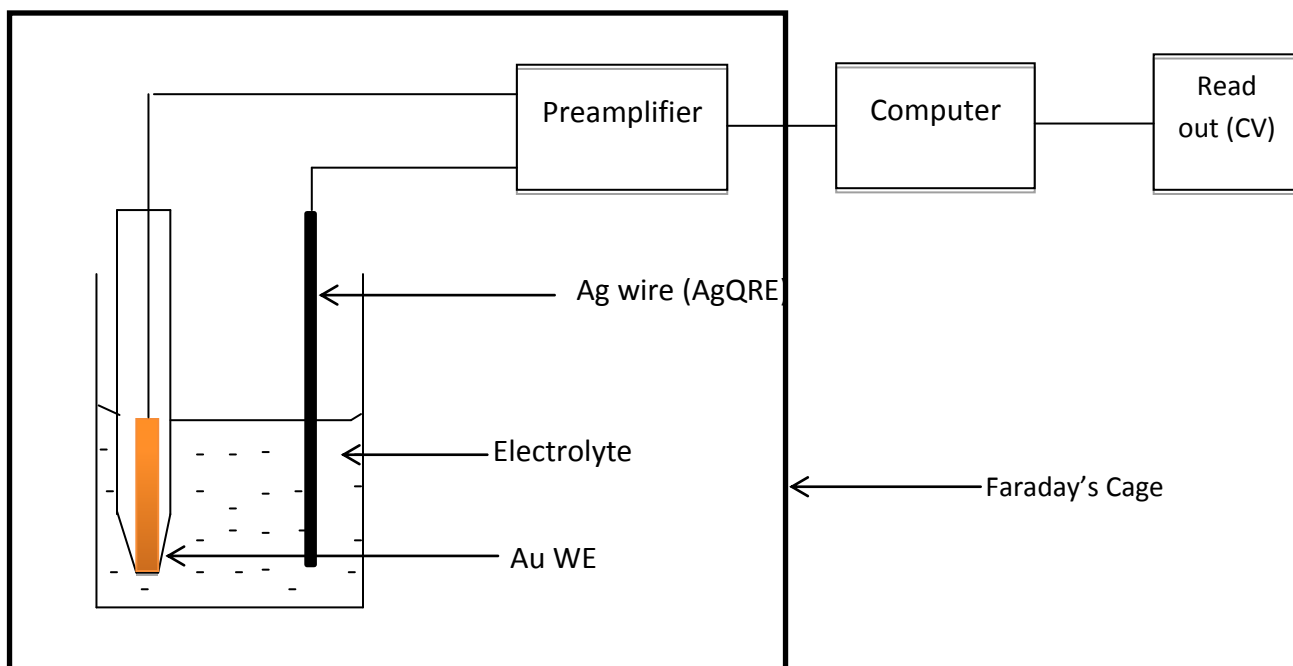
Figure 6: Schematic diagram for cyclic voltammetry experiment. The electrolyte depends on the stage of

the experiment and is either 1Mm Ferrocenemethanol (with 0.1M KNO_3 as supporting electrolyte), or

0.5 M H_2SO_4, or Pt particles solution

<u>Preparation and Characterization of Pt Nanoparticles</u>

Pt nanoparticles were synthesized as reported in reference 17. Briefly, to 100 mL of 0.4

mM aqueous H_2PtCl_6 was added 50 mL of 2.8 mM trisodium citrate dihydrate aqueous solution.

The mixture was stirred vigorously with a magnetic stirrer while adding 10 mL of 12 mM

$NaBH_4$ drop wise. A pale yellow solution was formed that turned dark brown in about 5

minutes. The solution was continuously stirred vigorously for 4 hrs and stored in a refrigerator.

The sizes of the Pt NPs prepared by this method ranges from 2 to 6 nm in diameter, most of them at 4 ± 0.8 nm in diameter [18].

CHAPTER 3

RESULTS AND DISCUSSION

Cleanliness of Gold Nanoelectrodes

Cleanliness of fabricated gold electrodes was ensured by scanning in 0.5 M sulfuric acid.
Figure 7 shows the optical microscopic image (magnification of 1000) of the top view of a well-
polished nanometer-sized electrode prepared by the Puller method. The disk-shaped shiny spot
at the middle of the bright cycle of the picture is gold electrode. It shows that the surface of the
electrode is flat, hence well-polished.

Figure 7: Top view of the optical microscopic image of a well-polished nanometer-sized Au
electrode. The magnification is 1000x

Figure 9 (a) is the cyclic voltammogram (CV) of the electrode obtained by scanning in a
solution containing 1.0 mM FcMeOH (with 0.1 M KNO_3 as supporting electrolyte) vs AgQRE
before modification with cysteamine.   The shiny spot on the image, Figure 7, and the good

quality sigmoidal shaped cyclic voltammogram do not mean that the surface of the electrode is clean and clear of any impurities. Our group had shown in a previous work [13] that a nanoelectrode with a good voltammogram does not indicate its cleanliness and purity; rather, the voltammogram of the electrode in sulfuric acid, Figure 8, does.
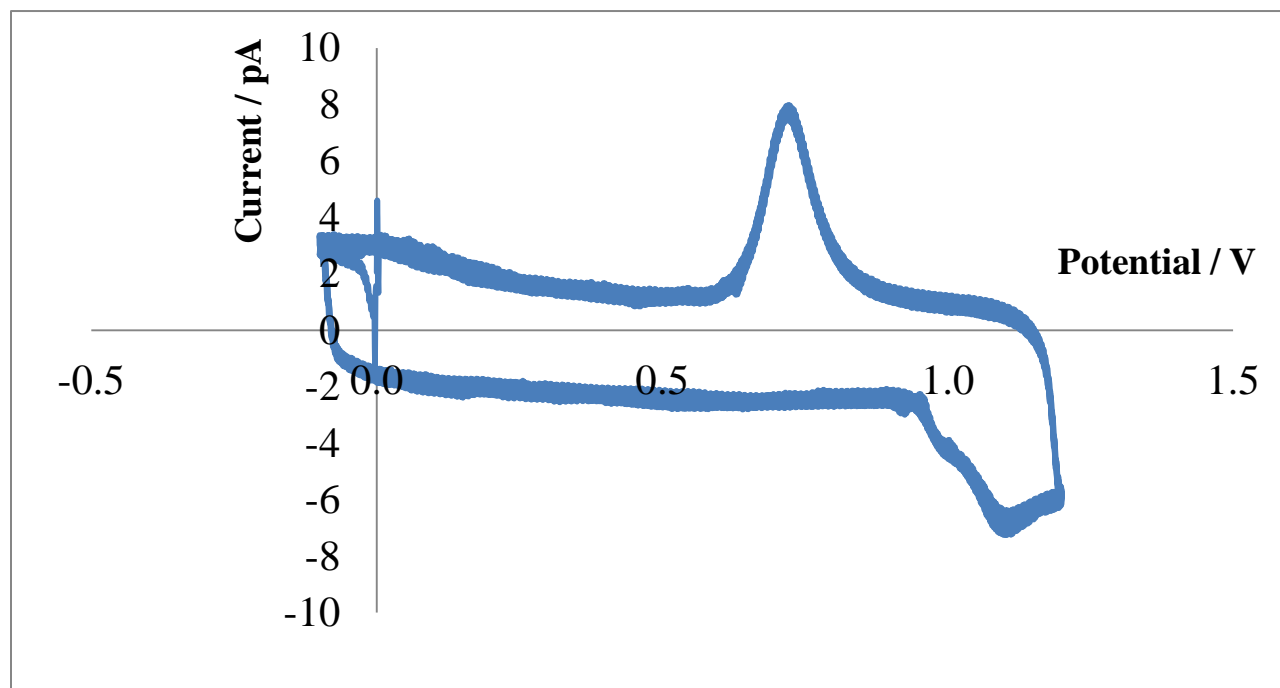
Figure 8: Cyclic voltammogram obtained at a clean Au nanometer-sized electrode recorded in a 0.5 M H_2SO_4 solution. The scan rate was 150 mV/s, and the number of scans was 15. It shows the characteristic features of clean gold electrodes, the gold oxidation formation peaks (at 1.0 and 1.1 V), gold oxide stripping peak (at 0.7 V), and the flat portion (0.2 to 0.6 V)

When scanned in H_2SO_4 between -0.1 to 1.4V, the cyclic voltammogram of a clean and well-polished nanoelectrode exhibits the characteristic gold oxidation and gold oxide stripping peaks of a clean macro gold electrode at about 1.1 to 1.4V and around 0.9V respectively, with a flat portion of the curve between the oxide stripping peak and a hydrogen evolution region found at about –0.1V. Hence, the cleanliness of each nanometer-sized electrode used for the

experiment was verified by scanning in 0.5 M sulfuric acid vs AgQRE until the CV, with the characteristic peaks, became stable (approximately 15 cycles). Figure 8 shows a cyclic voltammogram in 0.5 M sulfuric acid for one of the electrodes used in the experiment. The gold oxidation and oxide stripping peaks and flat portions of the curve are indicative of the cleanliness of the electrode.

Voltammogram at Bare Au and Au/Cysteamine Modified Electrodes

The steady state limiting current observed for the bare Au electrodes in FcMeOH solution, figure 9 (a) (red) for example, were used to calculate the effective radii of the electrodes. The diffusion coefficient of FcMeOH is 7.6×10^{-6} cm^2 s^{-1} and only one electron is transferred per mole of FcMeOH, equation (4).

$$FcMeOH \longrightarrow [FcMeOH]^{+} + e \qquad\qquad (4)$$
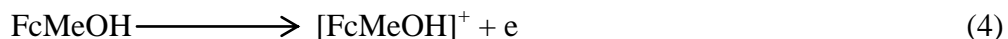
Hence, using equations (2) and (3), the effective radius for the bare Au electrode shown in Figure 9 (a) is 200 nm.

Figure 9 (b) (blue) shows the CV of the electrode in FcMeOH after modification with cysteamine. Normally, the limiting current for the oxidation of ferrocenemethanol should be unaffected by short chain SAMs [6] because such short chains do not suppress electron tunneling through them. Therefore, the limiting current for the oxidation of FcMeOH should be approximately the same before and after modification with cysteamine. However, Figure 9 shows that the limiting current decreased by about 9 pA after modification with cysteamine.
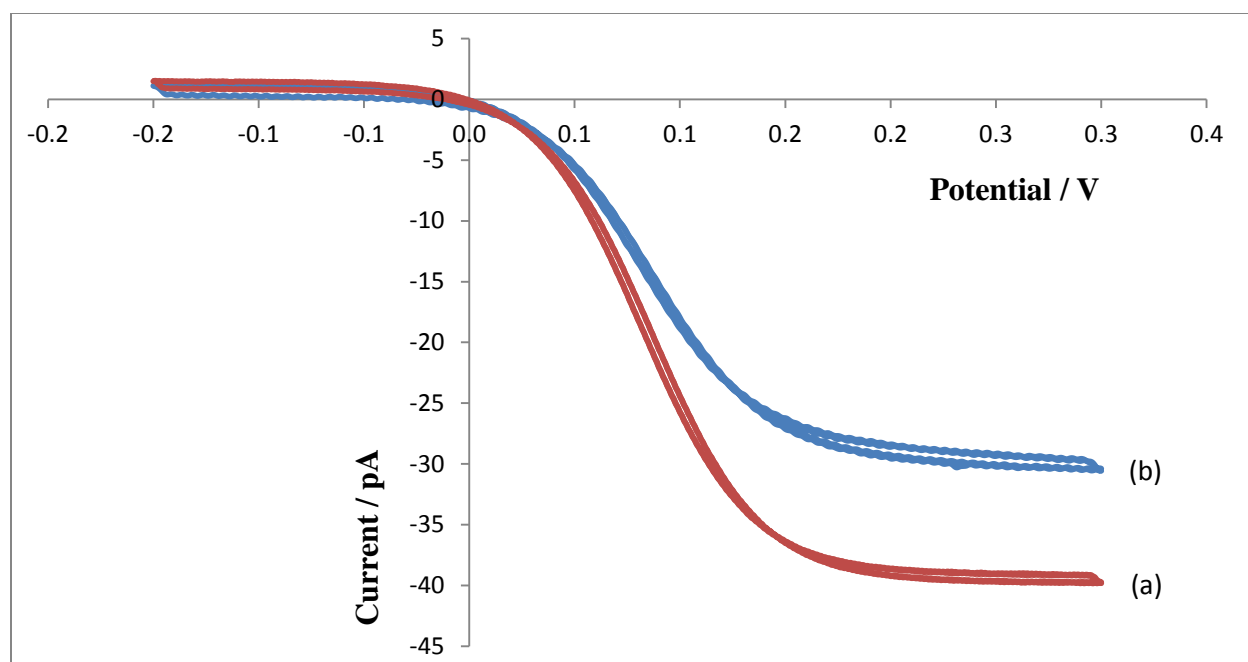
Figure 9: CV curves for bare and modified Au electrodes in a solution of 1 mM FcMeOH and 0.1 M KNO_3 (supporting electrolyte). (a) is the CV for the bare electrode (200 nm in radius) before modification with cysteamine and (b) is that after modification. The scan rates were 50 mV/s for both electrodes. The non-zero offset was probably due to instrumental drift

This was observed for over 80% of the electrodes used for experiments. This could be as a result of multilayer formed on the electrode surface. That is, some cysteamine molecules stick together at the surface of a monolayer that has been formed thus hampering electron tunneling to the surface.

<u>Cyclic Voltammetry in Sulfuric Acid after Soaking in Pt Nanoparticles</u>

In some cases, electrodes were soaked in PtNP solution for at least 2 hours 30 minutes, or overnight, and yet in others, scanned in a solution of the particles. The only difference that was observed with respect to the soaking/scanning times was that slightly higher currents were obtained for relatively longer time periods, which indicated that more Pt particles were adsorbed

on the monolayer during that time. Before soaking in Pt nanoparticles, modified electrodes were

scanned in sulfuric acid between –0.6 and 0.3 V vs AgQRE to obtain a background CV shown in

Figure 10 (red). No drastic increase in current was observed at this range. There was only a very

small increase in current at about -0.6 V. We assume this was due to some minimal proton

reduction at the Au surface or at the monolayer surface.
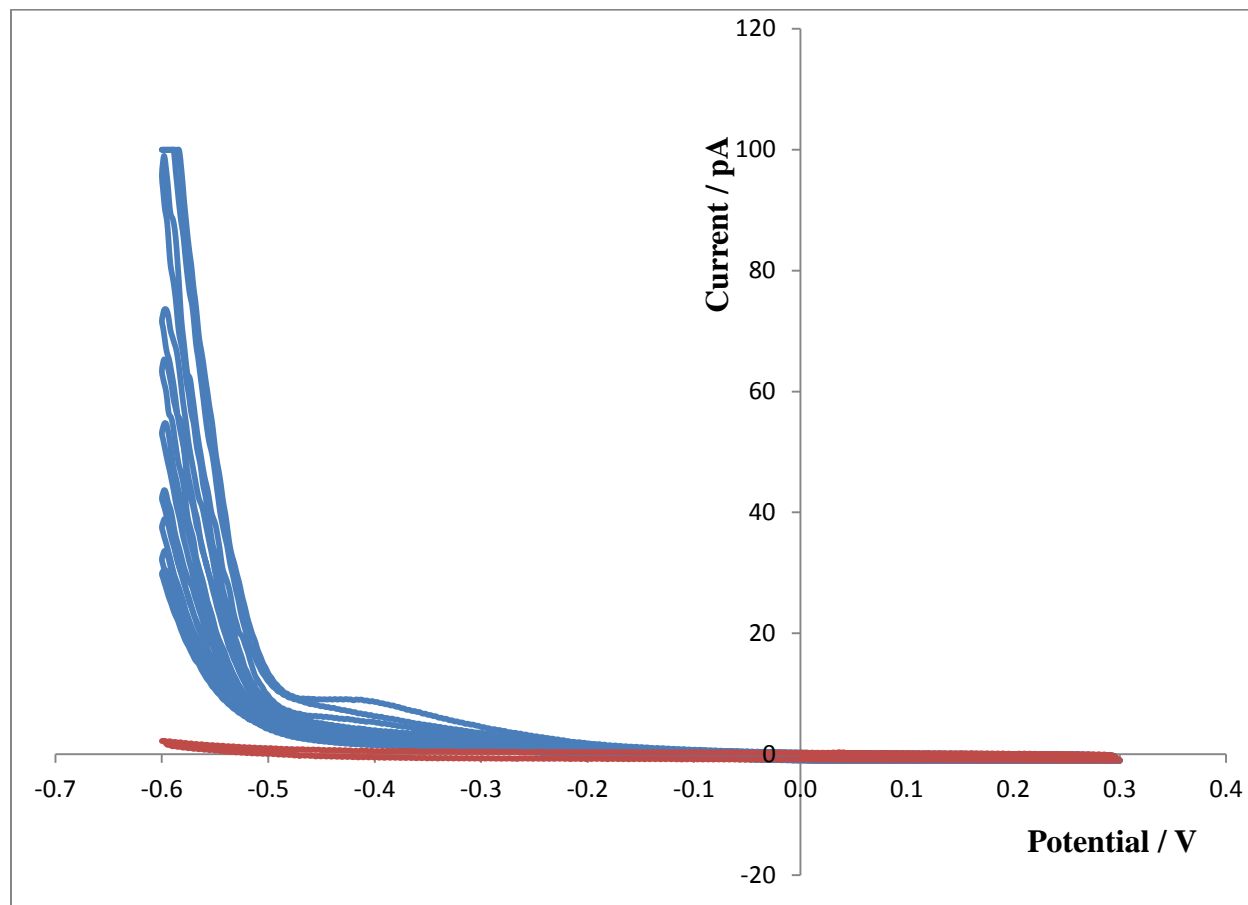

Figure 10: Electrochemical reduction of protons at Au/Cysteamine electrode without (red, blank)

and with (blue) PtNPs on the surface of the cysteamine. The electrolyte was 0.5 M H_2SO_4 and

potential sweep rate was 100 mV/s. The electrode was not rinsed after soaking in PtNPs

solution. The current for the first potential cycle was higher than the instrument limit

The blue curve in Figure 10 shows the CV for an electrode scanned in 0.5 M sulfuric acid (0.3 to -0.6 V) after soaking in Pt nanoparticles. Because there was very low current observed before soaking in particles, the sharp increase in current at about -0.6 V is an indication that PtNPs were adsorbed on cysteamine and catalyzed the reduction of proton to hydrogen. The steady-state current for the very first potential cycle shown is greater than 100 pA.   However, the current decreased uniformly in a step-wise manner with increasing number of potential cycles but did not reach the background current (the current of the modified electrode in the same potential range in acid without particles). The magnitude of the decrease of the first potential cycle was large but then degreased and became almost constant before decreasing again to some smaller value.

The current for a single PtNP is approximately between 40 to 65 pA depending on the particle size distribution [39]. Because the current observed after the first cycle (Figure 10 (blue) was very large, over 100 pA, which clearly does not represent catalysis at a single Pt NP. Hence, we assume that the high current was as a result of proton reduction at the surface of an aggregate or several aggregates of PtNPs at the surface. The Pt colloid solution was stored in a refrigerator after preparation and used continuously throughout the experiment. Although the particles were stabilized by citrate to prevent aggregation, it is possible that some of them could still have collided to form aggregates during the storage time, and the aggregates attached to the cysteamine layer when the electrode was immersed in the solution. Because the magnitude of the current decrease after the first potential cycle is large compared to the others, it is evident that some particle aggregates first desorb from the monolayer surface. We attribute the series of almost constant magnitudes of current decrements after the first potential cycle to single particles desorption from the monolayer. Some very small decrements of current shown in Table 2 that

were less than 1 pA were also observed, which presents the possibility of very small particles present. We believe that some of these decrements of current could also be as a result of adsorption of some extrinsic impurities that led to deactivation of the particles, causing decrease in current.

Figure 11 shows the result of an electrode that was rinsed slightly after soaking in PtNPs before scanning in sulfuric acid. We observed that in this case, the current for the first potential cycle was 50 pA, which is less than half that for the first potential cycle in Figure 10, where the electrode was not rinsed before scanning in acid.
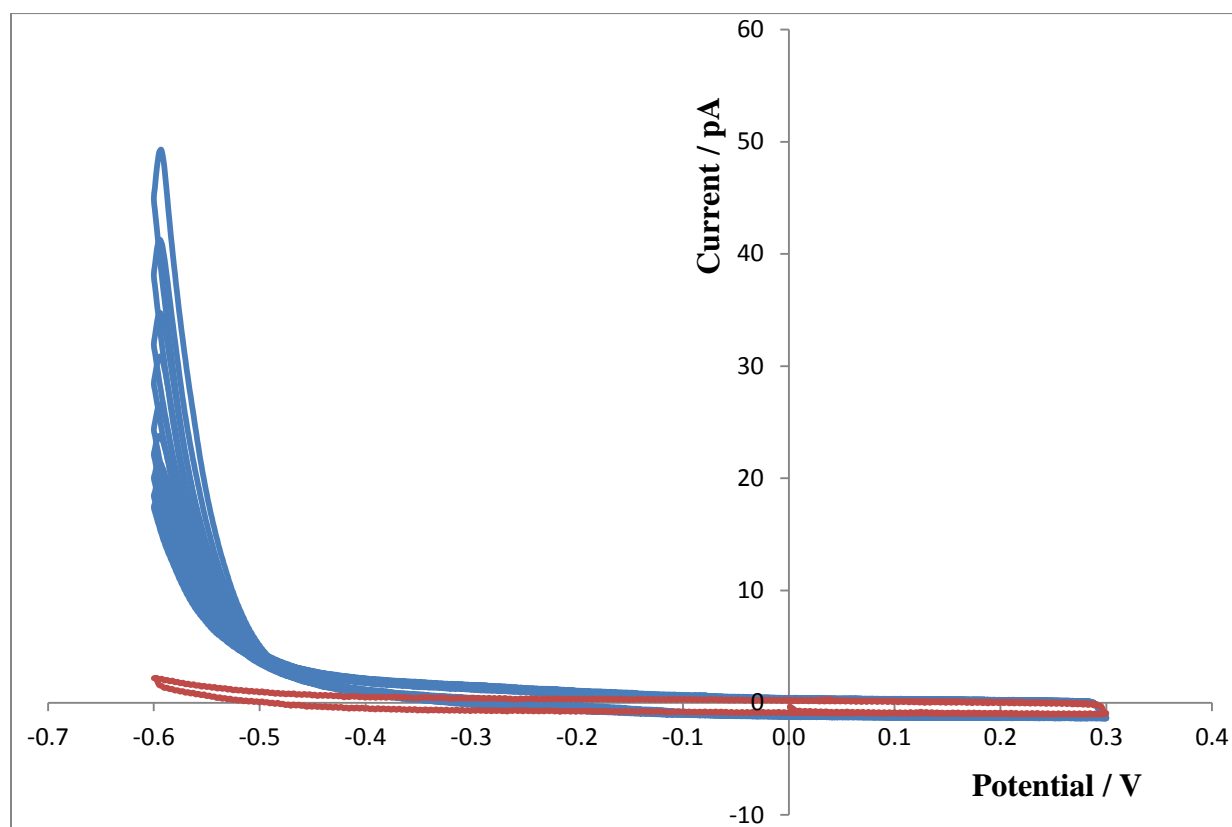

Figure 11: Electrochemical reduction of protons at an Au/Cysteamine (red) and Au/Cysteamine/PtNPs electrode rinsed slightly after soaking in PtNPs solution. Solution was 0.5 M H_2SO_4 and scan rate was 100 mV/s

This shows that light rinsing of the electrodes before scanning took off some of the PtNPs that we assume were loosely bound to the cysteamine surface. However, even after thorough rinsing, the final currents after all the stepwise decrements were still quite higher than the background currents. This was observed for all electrodes that were used. It shows that some of the PtNPs were strongly bound to the cysteamine monolayer and could not be removed even with thorough rinsing. It is also possible that some very small particles could have migrated by mass transfer into the cysteamine monolayer and were trapped at some defects within the monolayer network where they could still catalyze proton reduction, or they migrated to the Au surface and were permanently immobilized on it, and reduction still occurred at their surfaces.

The transient currents for desorption of particles from two electrode surfaces are presented in Table 2. The current observed are those we assume are as a result of depletion of some very small particles. The currents were so small and were read by zooming the current values for each potential cycle.

The very small current change values (the magnitude of the decrements) could indicate the presence of very small particles (less than 1 nm in diameter) in the particle solution. These are obviously smaller than the expected particle sizes (between 2 to 6 nm in diameter with most of them about 4.0 nm in diameter) as reported by literature for the preparation method that was used to prepare the particles. Perhaps, as suggested earlier, these very small particles penetrated the cysteamine monolayer and migrated to the electrode surface where they were immobilized on Au, accounting for the final current for each electrode being higher than the background current. Also, the electrostatic interaction between the Pt particles and the Nitrogen atoms of the cysteamine could be very strong that thorough rinsing will not take off some of the particles.

The table also confirms that currents decrease with increasing number of cycles (steps), with the magnitude of decrease for the various steps of each electrode being very small and close.

Table 2: Currents observed as a result of desorption of PtNPs from two electrode surfaces after thorough rinsing.

	Electrode 1		Electrode 2	
Step	Current(pA)	Current Change (pA)	Current(Pa)	Current Change (pA)
1	14.38	0.37	10.71	0.05
2	14.01	0.31	10.66	0.14
3	13.70	0.35	10.52	0.12
4	13.35	0.45	10.40	0.17
5	12.90	-	10.23	-

Conclusion

Nanometer-sized Au electrodes of effective radii between 100 to 250 nm have been fabricated using the laser assisted Puller method and were chemically modified with cysteamine. We have demonstrated that Pt nanoparticles are absorbed on the surface of the CMEs after soaking or scanning in a solution of the particles. The Au/Cysteamine/PtNPs electrodes were characterized using steady-state cyclic voltammetry. We showed that the PtNPs on the modified electrodes catalyze proton reduction, characterized by a high current that was extremely low at the bare Au electrodes. The observed current decreased with increasing potential cycles. We attribute these decrements to desorption of Pt particles form the cysteamine surface. Further

examination of the magnitudes of current decrements indicates that they depend on the particle sizes desorbed from the surface between scanning cycles. We conclude that particle aggregates, single particles, and even particles smaller than the estimated particle sizes desorbed from the electrode surfaces as the electrodes were continuously scanned in acidic solution.

Future Work

The reported work focused on the adsorption and desorption of PtNPs from the surfaces of CMEs.   Changes in the monolayer network resulting from adsorption and desorption of the particles have not been studied due to lack of instrumentation. In the future, this work can be completed by using surface techniques to study the changes in the structure of the monolayers and the particle distribution on them at the beginning of experiments and progressively as the particles desorb from the electrode surfaces. Surface techniques like AFM and ellipsometry can be used to examine the nature of the particle aggregates on the electrode surface and the changes in monolayer. This will provide valuable information that can lead to approximation of the amount of particles on the electrode surface and either reinforce the observations of this research or bring forth new ideas for further research.

Also, these same studies can be carried out on nanometer-sized electrodes whose effective radii are approximately the same to those of the particles to observe if there will be any major differences in the observed current pattern.

REFERENCES

1) Durst. R. A.; Baumner, A.; Murray. R.; Buck. R.; Andrieux. C. *Pure & Appl. Chem.* **1997**, *69*, 1317-1323.

2) Krings, N.; Strehblow, H.; Kohnert, J.; Martin, H. *Electrochim. Acta.* **2003***, 49*, 167-174.

3) Kodama, C.; Hayashi, T.; Nozoye, H. *Appl. Surf. Sci.* **2001***, 169-170*, 264-267.

4) Esplandiu, M.; Hagenström, H.; Kolb, D. *Langmuir.* **2001***, 17*, 828-838.

5) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987***, 109*, 3559-3568.

6) Xiaoyin, X.; Pan, S.; Jum, J.; Fu-R, F.; Bard, A.; J. Phys. Chem. C. **2009**,113, 14978-14982.

7) Chen, S.; Kucernak, A. *J. Phys. Chem B.* **2004***, 108*, 3262-3276.

8) Li, Y.; Cox, J. T.; Zhang, B. *J. Am. Chem. Soc.* **2010***, 132*, 3047-3054.

9) Xiao, X.; Bard, A. J. *J. Am. Chem. Soc.* **2007***, 129*, 9610-9612.

10) Bain, C. D.; Troughton, E. B.; Tao, Y. T.; Evall, J.; Whitesides, M. G.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321-335.

11) Fischer, L. M.; Tenje, M.; Heiskanen, A. R.; Masuda, N.; Castillo, J.; Bentien, A.; Émneus, J.; Jakobsen, M. H.; Boisen, A. *Microelectr. Eng.* **2009***, 86*, 1282-1285.

12) Widrig, C. A.; Chung, C.; Porter, M. D. *J Electroanal. Chem* **1991***, 310*, 335-359.

13) Lakbub, J.; Kady, I.; Sun, P. *Electroanalysis* **2011***, 23*, 2205-2211.

14) Sun, P.; Laforge, F. O.; Abeyweera, T. P.; Rotenberg, S. A.; Carpino, J.; Mirkin, M. V. *Proceedings of the National Academy of Sciences U.S.A.* **2008***, 105*, 443-448.

15) Sklyar, O.; Treutler, T. H.; Vlachopoulos, N.; Wittstock, G. *Surf. Sci.* **2005***, 597*, 181-195.

16) Fan, F. R.; Bard, A. J. *Science* **1995**, *267*, 871-874.

17) Penner, R. M.; Heben, M. J.; Longin, T. L.; Lewis, N. S. *Science* **1990**, *250*, 1118-1121.

18) Lakbub, J.; Poliwe, A.; Kamasah, A.; Yang, C.; Sun, P. *Electroanalysis* **2011**, *23,* 2270-2274.

19) Mandler, D.; Turyan, I. *Electroanalysis* **1996**, *8*, 207-213.; Malem, F.; Mandler, D. *Anal. Chem.* **1993***, 65*, 37-41.; Giz, M.; Duong, B.; Tao, N. *J. Electroanal. Chem* **1999***, 465*, 72-79.

20) Notoya, T.; Polling, G. *Corrosion* **1979***, 35*, 193-200.

21) Shao, Y.; Mirkin, M. V.; Fish, G.; Kokotov, S.; Palanker, D.; Lewis, A. *Anal. Chem.* **1997***, 69*, 1627-1634.

22) Conyers Jr, J. L.; White, H. S. *Anal. Chem.* **2000***, 72*, 4441-4446.

23) Lee, S. K.; Yoon, Y. H.; Kang, H. *Electrochemistry Communications* **2009***, 11*, 676-679.

24) Baykul, M. *Mat. Sci. and Eng. B*. **2000**, *74*, 229-233.

25) Jena, B. K.; Percival, S. J.; Zhang, B. *Anal. Chem.* **2010**, *82*, 6737-6743.

26) Bigelow, W. C.; Pickett, D.L.; Ziesman, W.A. *J. Colloid Interface Sci*. **1946**, *1*, 513-538.

27) Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983***, 105*, 4481-4483.

28) Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100,* 465−496

29) Zen, J. M.; Senthil Kumar, A.; Tsai, D. M. *Electroanalysis* **2003***, 15*, 1073-1087.

30) Sur, U. K.; Lakshminarayanan, V. *J. Electoanal. Chem.* **2004**, 565, 343-350.

31) Jiang, C.; Elliott, J. M.; Cardin, D. J.; Tsang, S. C. *Langmuir.* **2008***, 25*, 534-541.

32) Ganesh, V.; Pal, S. K.; Kumar, S.; Lakshminarayanan, V. *Electrochim. Acta.* **2007***, 52*, 2987-2997.

33) Xiao, X.; Fan, F. R. F.; Zhou, J.; Bard, A. J. *J. Am. Chem. Soc.* **2008***, 130*, 16669-16677.

34) Kind, M.; Wöll, C. *Prog. Surf. Sci.* **2009***, 84*, 230-278.

35) Bard, A. J.; Faulkner, L. R. *Electrochemical methods: Fundamentals and Applications;* 2nd ed.; Wiley & Sons: New York, 2001, pp 581-587.

36) Cossaro, A.; Mazzarello, R.; Rousseau, R.; Casalis, L.; Verdini, A.; Kohlmeyer, A.; Floreano, L.; Scandolo, S.; Morgante, A.; Klein, M. *Science.* **2008***, 321*, 943-946.

37) Mehring, P.; Beimborn, A.; Westphal, C. *Appl. Surf. Sci.* **2010***, 256*, 7265-7269.

38) Chen, J. C. *Introduction to Scanning Tunneling Microscopy*, 2nd ed.; Oxford University Press: New York, 1993, pp 24.

39) Schott, J. H.; Arana, C. R.; Abruna, H. D.; Petach, H. H.; Elliott, C.; White, H. S. *J. Phys. Chem.* **1992***, 96*, 5222-5224.

40) Seeger, D.; Kowalchyk, W.; Korzeniewski, C. *Langmuir.* **1990***, 6*, 1527-1534.

41) Martin, C. R.; Foss. C. A. Chemically modified electrodes. In *Laboratory techniques in electroanalytical chemistry*; Kissinger, P. T.; Heineman, W. R., Ed.; Marcel Dekker: New York, 1996, pp 403-439.

42) Wirde, M.; Gelius, U. *Langmuir* **1999***, 15*, 6370-6378.

43) Watkins, B. F.; Behling, J. R.; Kariv, E.; Miller, L. L. *J. Am. Chem. Soc.* **1975***, 97*, 3549-3550.

44) Stoecker, P. W.; Yacynych, A. M. *Sel. Electr. Rev*. **1990**, *12*, 137-160.

45) Guilbault, G. G.; Lubrano, G. L. *Anal. Chem. Acta*. **1973**, *64*, 439-455.

46) Gerhardt, G. A.; Oke, A. F.; Nagy, G.; Moghaddam, B.; Adams, R. N *Brain Res.* **1984***, 290*, 390-395.

47) Nagy, G.; Gerhardt, G.; Oke, A.; Rice, M.; Adams, R.; Szentirmay, M.; Martin, C. *J. Electroanal. Chem.* **1985***, 188*, 85-94.

48) Wzodzimierz, K.; Wang, J.; L'Her, M.; Buck, R. P. *Pure and Appl. Chem.* **1998**, *70*, 1301-1318.

49) Andrieux, C.; Saveant, J.; Murray, R. *Molecular Design of Electrode Surface*; Wiley & Sons: New York, 1992, pp 208.

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Lakbub, J.; Pouliwe, A.; Kamasah, A.; Yang, C.; Sun, P*. Electrochemical Behaviors of Single Gold Nanoparticles. *Electroanalysis* **2011***, 23*, 2270-2274.