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ULTRA-HIGH PERFORMANCE SENSOR MODIFIED WITH NANO GOLD PARTICLES, HEMOGLOBIN AND BOVINE SERUM ALBUMIN FOR CYANIDE DETECTION

By

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DEDICATION

I dedicate my thesis work to my family. A special feeling of gratitude to my loving Grandmother, Mother, Father and Aunt whose words of encouragement and push for tenacity ring in my ears. My sister and brothers Morsali, Mohammamdmehdi and Ali have never left my side and are very special. I dedicate this thesis to my lovely Shahab, who has supported me throughout the process and

without whom I could not have come to its

completion.

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Chapter I

1.1. Statement of Problem

Cyanide molecule is made of a carbon atom triple bonded to nitrogen atom and is named the Cyano Group [1]. The cyano group can react with several organic and non-organic materials, such as sodium, potassium, hydrogen, methyl and so on. Depending on how the bonding occurs and what is the material it binds to, it could show as a colorless gas or in a crystal form. Solid cyanides like potassium cyanide or sodium cyanide might or might not have a bitter almond smell when reacting with solutions. Cyanide is known as a "rapidly acting, deadly chemical" [2]. Due to researches done by the Center for Disease Control and Prevention (CDC) and Food and Drug Administration (FDA), cyanide poisoning could be fast and fatal, even in very small amounts. Cyanide can happen in many forms. It is found in nature, bounded to a sugar molecule in fruits like apples and peaches. It is also produced by actions of fungi and bacteria. Cyanide may also be produced as a side product of combustion reaction. Hydrogen cyanide, a very common form of cyanide is also producible through the Andrussow Process, which follows the proceeding reaction:

 $CH4 + NH3 + 1.5 O2 \rightarrow HCN + 3 H2O [3]$

What is of most interest for us in this project is potassium cyanide. Potassium cyanide is a white/colorless crystalized salt, which is close to table salt or sugar in appearance. The reason we chose this form of cyanide to work with is first because it's more soluble than the other forms of cyanide, having the solubility of 71.6g/100 ml of water. This number gives us the chance to choose a wide range of concentrations for our experimentations. Potassium cyanide is produced by treating hydrogen cyanide with a 50% aqueous solution of potassium hydroxide, followed by evaporation of the solution in a vacuum [4]:

 $HCN + KOH \rightarrow KCN + H_2O$

Or by treating formamide with potassium hydroxide:

 $HCONH_2 + KOH \rightarrow KCN + 2H_2O$

Second reason of why we chose this element is because it is a common form of cyanide compounds being produced in gold mining, electroplating, chemical gliding and buffing in jewelry and also organic synthesis. It gives us the chance to study its effects under realistic conditions in which actual human or environmental contact might happen with it.

Potassium cyanide's chemical product is mostly used in one of the following industries in US [5]:

- Widely used in organic synthesis of Chemical and Pharmaceutical Intermediates

In this case, most of its disposals would be through water and soil, if not complied with the hazardous waste regulations. Specifically in pharmaceutical companies, it might be simply washed off during the last process of production. Adding these washes in a large scale nationwide, would add up to an enormous number of cyanide concentration in swage water. Many of the wastewater treating plants provides removing of hazardous material in micro scales. But only a few have the technology to detect these materials in nano-scale. For cyanide, even in very low concentrations, consuming the water including it could be carcinogenic.

- Recycling of precious metals

In the process of recycling, if it's not in a large-scale automated factory, people will be in direct contact with the potassium cyanide and its gases produced during the reactions. However, its worth mentioning that most of these recycling companies are regulated by EPA and are forced to comply with F001-F009, D001-D004, and D006-D011 hazardous waste regulations. But adding even more safety in the work place is always recommend, which helps with the prevention of future possible effects of hazardous material, in terms of cancer, allergies or other health problems.

- Electroplating

Electroplating is the process of plating one metal onto another by hydrolysis, most commonly for decorative purposes or to prevent corrosion of a metal. It might not be as dangerous as the ones we had before, since mostly it's in small scales, but the same hazards applicable to organic synthesis will apply for this situation as well.

Cyanide compounds can affect both human beings and the environment. As mentioned above, inhaling potassium cyanide gases could be fatal immediately. Cyanide interferes with the body's ability to bind oxygen molecules to blood's hemoglobin. This will cause the hemoglobin to be saturated with cyanide molecule rather than oxygen, because it has a higher affinity for it and the victim will suffocate within minutes. It also could affect agricultural products and plants if sprayed on a field or is contained in the water feeding the field. All species requiring oxygen to survive will be affected with this poisonous substance.

Due to CDC, potassium cyanide releases hydrogen cyanide gas, a highly toxic chemical asphyxiant that interferes with the body's ability to use oxygen. Exposure to potassium cyanide can be rapidly fatal. It has a whole-body (systemic) effects, particularly affecting those organ systems most sensitive to low oxygen levels: the central nervous system (brain), the cardiovascular system (heart and blood vessels), and the pulmonary system (lungs).

1.2. Research Goals

According to the Toxic Exposure Surveillance System, there were 3165 human exposures to cyanide from 1993 to 2002, of which 2.5 percent were fatal [6]. This fatality could be reduced if more safety protocols are added to work environment. Cyanide is produced in large scales on mining sites and metal processing plants and is disposed in their sewage flows. This disposal could result in build up of cyanide crystals in soils and treated water, if not well treated. This is where new and advanced protocols come in and if regulated and worked with, could save some from their future health issues.

In this research we tried to overcome some boundaries for detecting cyanide ion to be used both in environmental and biomedical purposes using a metallic sensor. The assumption is with a right-formed protocol in a work place associated with cyanide gas production, we can decrease the risk of exposure. Electrochemical sensors are faster, cheaper and more sensitive than the other possible procedures currently used in most sites to detect biomarkers or substances of interest.

Our experimentation combined the use of electrochemical cell and Gamry Frameworks software for analysis of data. The electrodes coating procedure required multiple solutions. Each experiment was run in different voltage ranges to find the best range for a detector peak. Several cyanide solution concentrations were used to find a good fit for both environmental and biomedical purposes.

Chapter II

ULTRA-HIGH PERFORMANCE SENSOR MODIFIED WITH GOLD NANO PARTICLES, HEMOGLOBIN AND BOVINE SERUM ALBUMIN FOR CYANIDE DETECTION

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ABSTRACT:

Cyanide is one of the most toxic materials reported by the Center of Disease Control (CDC). It has higher affinity than oxygen does for body hemoglobin as well as organelles in need of oxygen to thrive. In long-term exposure, it could result in diseases like the Chronic Obstructive Pulmonary Disease (COPD). To date, researchers have accomplished detecting cyanide down to 1*10⁻⁸ mol/lit, employing electrochemical sensors. We used a new design for our glassy carbon, gold and platinum electrode for their measurements with a cyclic voltammogram. We coated the electrode with melamine, gold nanoparticles, hemoglobin and Bovine Serum Albumin (BSA). Gold and platinum electrode showed excellent stability and reproducibility. Cyclic voltammetry measurements showed a detection limit of 1*10⁻¹⁸ mol/lit for platinum electrode. This limit could be applied to multiple biomedical or environmental purposes, such as early detection of diseases biomarkers to avoid harsh treatments.

Key words: electrochemical sensors, cyanide detection, toxicity, nanoparticles

2.1. Introduction

Cyanide is known as a very toxic substance. The lethal dose of cyanide in human body is an amount equivalent to 1.5mg/kg body weight. Because of its extreme high affinity for hemoglobin and an electron transport system close to oxygen atom, it will substitute oxygen on relevant binding sites in human body, which constitutes of mitochondria, hemoglobin, nervous system, etc.

Researchers and scientists have conducted significant researches to establish different procedures and methods for detecting toxic agents for regulating air and water quality, one of which was cyanide. A boron doped diamond electrode combined with electrochemical method based on cytochrome c biosensor was used to detect possibly all the harmful pollutants in the environment, such as cyanide, arsenic and mercury [7]. They achieved satisfactory sensitivity and detection limits with this method. Various methods like cyclic voltammetry, electrochemical impedance spectroscopy, UV-vis absorption spectroscopy and sequence wave voltammetry were used to confirm the affinity of electrode for different analytes. Orlanducci et al. used Surface Enhanced Raman Spectroscopy (SERS) and deposited gold nanoparticles on carbon nanotubes to make a new form of electrochemical detector system for nitrile-based substances, which as said, are highly toxic [8]. Main purpose of CNT was to increase gold deposition and the size of gold nanoparticles is controlled this way. Gold increases the affinity of nitrile groups, and enhance the Raman signal for their plasmonic effect. This procedure is very selective, reversible and sensitive. Turek et al. reported for the first time the simultaneous detection of cyanide ion and heavy metals in a solution with the use of silicon based calcogenide glass muISEs [10]. They've performed the simultaneous measurement of CU2+, Cd, Pb and CN. With the use of electrochemical characterization, it showed good sensitivity and low

detection limits of 0.2-3.8 umol/lit for heavy metals and 0.5 umol/lit for cyanide ion. Liu et al. studied the toxicity of KCN via two procedures, first one using the Vibrioqinghaiensis sp. Nov. Q67 luminous bacteria and a fluorescent spectroscopy, second using a nano PbO₂ electrode as a working electrode of an electrochemical system [14]. Wang et al. made and optimized a submersible electrochemical biosensor for on the site monitoring of free cyanide [17]. The probe uses a microdialysis sampling tube, which has 5 cellulose hollow fibers, a glassy carbon working electrode, an Ag/AgCl reference electrode and a platinum wire counter electrode. This sensor can remotely detect free cyanide. Siontorou et al. incorporated hemoglobin/ methemoglobin into a metal supported self-assembly bilayer lipid membrane (s-BLM) to detect cyanide ion [18]. Drawback was that a whole new senor needed to be prepared for each new unknown or new experiment. Methemoglobin was chosen because of its stable product when reacted with cyanide ions. The detection limit for cyanide was decreased five fold when using methemoglobin. Table 2.1 summarizes the information for all the detection limits and agents of run for the reviewed literature.

All studies were in agreement of detecting cyanide down to 1e-6 mol/lit using diverse detection methods, majorly electrochemical cells. All methods differ in their preparation time and schemes, as their choice of material and electrodes vary a lot. All been said, the literature is absent of lower detection limits, which could be applied to biomedical fields of study. Also performance of the electrodes against time is vague and needs more investigation.

Substances	Method	Detection limit	Year	Source	
detected					
Arsenic and Cyanide compounds	Cytochrome C biosensor with electrochemical method	4.3-9.1 mu M.	2012	Fuku et al. (7)	
Nitrile-Based Organic Solvents and cyanide groups	Hybrid Au/CNT Systems with electrochemical deposition	Good sensitivity	2011	Orlanducci et al. (8)	
Organophosphates (cyanide ions)	Silicon-based microsensor with a Teflon nanoporous membrane supported on silicon	Great sensitivity	2011	Sayyah et al. (9)	
Cyanide and heavy metals	miniaturized silicon based sensor system	-	2010	Turek et al. (10)	
Cyanide	hydroxyapatite nanowires array (HANWA) biosensor performed by template-assisted electrode-position	0.6 ng/ml	2010	Wang et al. (11)	
Cyanide	Silver doped silica nanocomposite synthesized via a sol-gel technique combined with a nanoparticle preparing method	1.4 x 10(-8) mol/lit	2009	Taheri et al. (12)	
Cyanide	Fused indoline and benzooxazine fragment chemosensor	1 mu M in 30 seconds	2008	Ren et al. (13)	
Cyanide and tetramine	luminescent bacteria and PbO2 electrochemical sensor	38.38 and 0.60 mu g/mL for cyanide, 0.24 and 0.02 mu g/mL for tetramine	2007	Liu et al. (14)	
Cyanide in blood	Amperometric test and an electrochemical sensor	4 mu mol dm(-3)	2006	Lindsay et al. (15)	
Hydrogen cyanide gas	Simple electrochemical method (three electrode concept)	0.66 mg/m ³	1999	Rao et al. (16)	
Cyanide	Internal delivery of microliter enzyme and substrate solutions coupled to an in situ microdialysis sampling of the toxin, and an amperometric detection of the enzymatically generated product	2 x 10(-6) M	1998	Wang et al. (17)	
Cyanide	Electrochemical minisensor: methemoglobin incorporated into self- assembled bilayer lipid membranes (s-BLMs) on a metal support	4.9 nM or 0.317 mu g/L	1997	Siontorou et al. (18)	
Hydrazine compounds	Cyclic voltammetry on a nafion/ruthenium(III) modified glassy carbon	1x10(-7) M	1998	Casella et al. (19)	
Cyanide	A photoelectrochemical	-	1996	Licht et al.	

Table 2.1.Summary of Literature Search

	sensor, sensing element			(20)
	consists of an n-CdSe			
	electrode immersed in			
	solution, with the open-			
	circuit potential			
	determined under			
	illumination			
Carbon dioxide,	Simple electrochemical	10(-6) M	1997	Nikolelis et
triazines, or cyanide	method (three electrode			al. (21)
ions	concept)			
SCN-, SeCN-	A carbon paste electrode	250 mu mol/L and	1994	Cookeas et
	(CPE) modified with	0.8 mu mol/L (at pH		al. (22)
	cobalt phthalocyanine	2.0) for SCN-, and		
	(CoPC-CPE) was used as	0.2-20 mu mol/L		
	an amperometric flow	and 0.1 mu mol/L		
	sensor	(at pH 7.0) for		
		SeCN-		

2.2. Material and Methods

2.2.1. Material characteristics

Gold, Platinum and Glassy Carbon Electrodes (Au, Pt and GCE) with a diameter of 0.2 cm used in the potentiometric tests were bought from Tianjin Aida Heng Sheng Co, Tianjin, China. The counter electrode with a platinum metallic component has a diameter of 0.1 cm and a length of 0.5 cm. Hemoglobin (Hb), Melamine, Bovine Serum Albumin (BSA), AuCl3HCl•4H2O (Au %> 48 %) and cyanide were bought from Sigma-Aldrich Chemicals Co, St. Louise, MO, USA. The main instrument used for running the electrochemical cell was a Gamry 600 potentiostat.

2.2.2. Instrumentation

The main instrument used for running the electrochemical cell is bought from Gamry Instruments and the Echem Analyst Software was used to analyze the data.

2.2.3. Sample Testing

Potassium Cyanide (KCN) was tested with gold, platinum and glassy carbon electrodes in multiple different ranges of concentration. The durability of each electrode was also explored through having runs weekly after the first day experiment.

2.3. Results

2.3.1. Glassy Carbon Runs with Cyanide

In these sets of experiments no specific peak points were found. After multiple experiments using different glassy carbon electrodes to explore its potential for cyanide detection, we decided to not move on with this electrode, as it does not give us a good distinct peak in low/high concentrations. The reason could be glassy carbon's specific nature in terms of connection to Melamine and gold nanoparticles. Previous works showed that it has good stability and reproducibility for detecting NO₂ and H_2O_2 if the coating starts with Cystamine.

2.3.2. Gold Electrode Runs with Cyanide

The results of this run is separated in two different ranges, one is in ultra low detections from $1*10^{-14}$ to $1*10^{-5}$ mol/lit and the other set covers $1*10^{-5}$ to $1*10^{-2}$ mol/lit, which is the high concentration range. It should be emphasized that in higher ranges the peaks for oxidative reaction shifts about 250 mV from 600 to 350 (Fig. 2.1B).

The peaks' magnitude for $1*10^{-14}$ to $1*10^{-5}$ is not substantial. Cyanide is detectable with gold electrode in very low limits but the difference between the detection limits is small (Fig. 2.1A and 2.2B). However, the delta current found in higher concentrations, from $1*10^{-5}$ to $1*10^{-2}$, is pretty high with gold, but is unstable in the reductive peak (Fig. 2.1B and 2.2C). At the oxidative peaks for high concentrations, the peaks shift to the left as the concentration increases, for which the reason should be investigated more. The shift starts at $1*10^{-4}$ to $1*10^{-1}$ and is 250 mV in magnitude. We explored the potential of our electrodes against time; their

durability and reproducibility were proven to be very satisfactory. After 82 days past the first coating, the magnitude of the electrode's detection is still high (Fig 2.2 D).

The effect of BSA was also investigated in gold electrode's runs with cyanide. Our findings suggest that there is not a considerable difference between electrodes coated with an extra layer of BSA and the ones with no BSA. The assumption was that BSA would fill in binding sites of hemoglobin and leaving the more specific sites open for cyanide to bind, therefore increasing the detection limit and selectivity of the electrode.







Figure 2.1 voltammogram result of Gamry framework for running the gold electrode with CN. A) low concentrations (1e-14 to 1e-5. B) High concentrations (1e-5 to 1e-2).



B

A





D



Figures 2.2 Data analysis for gold electrode in low and high concentration. A) Gold Electrode Ran With CN From Concentration 1e-14 to 1e-5, at 460 mV reductive peak. B) Gold Electrode Ran With CN From Concentration 1e-14 to 1e-5, at 600 mV

oxidative peak. C) Gold Electrode Ran With CN From Concentration 1e-5 to 1e-2, at 460 reductive peaks. D) Gold Electrode Ran With CN From Concentration 1e-5 to 1e-2, at 600 shifting to 350 mV oxidative peaks.

2.3.3. Platinum Electrode Runs with Cyanide

The results of this run is also separated in two different ranges, one is in ultra low detections from $1*10^{-18}$ to $1*10^{-6}$ mol/lit and the other set is covering $1*10^{-6}$ to $1*10^{-1}$ mol/lit, which is the high concentration range (Fig. 2.3A and 2.3C). The peaks over 850 mV were not detectable for low detection ranges of concentration, but the results for detection on -25 mV had an excellent magnitude with great stability over time and high durability (Fig. 2.4A).

Platinum electrode showed the most promise in detecting cyanide, both in high and low limits. In high concentrations, there were two major peaks detected, oxidative at 850 and reductive at -25 mV (2.4B and 2.4C). Both peaks showed great linearity and high magnitudes in detection. The results for the current output of these electrodes were stable over time and decrease in very small μ Amps. At low concentrations, from 1*10⁻¹⁸ to 1*10⁻⁶, platinum electrode had a current detection limit of 6-7 μ Amps, which is much lower than what has been reported previously (Fig. 2.4A).









Figure 2.3 voltammogram result of Gamry framework for running the platinum electrode with CN. A) From Concentration 1e-18 to 1e-6, No BSA Coating. B) From Concentration 1e-18 to 1e-6, With BSA Coating. C) From Concentration 1e-6 to 1e-1, No BSA Coating. D) From Concentration 1e-6 to 1e-1, With BSA Coating.





B





С

Figures 2.4 Data analysis for platinum electrode in low and high concentration. A) Platinum Electrode Ran With CN From Concentration 1e-18 to 1e-6, at -25 mV reductive peaks. B) Platinum Electrode Ran With CN From Concentration 1e-6 to 1e-1, at 850 mV oxidative peaks. C) Platinum Electrode Ran With CN From Concentration 1e-6 to 1e-1, at -25 mV reductive peaks.

2.4. Discussion

We reached a very low detection limit with our design for sensor coating, which is 10^6 orders of magnitude lower than what has been done before.

Our work is in good alignment with Fuku et al. trial in 2012 [7]. They used a Boron-doped diamond electrode, which will make the preparation process harder and more expensive. With our different design, the detection limit decreases 10¹² orders of magnitude, which readies the electrodes for biomedical purposes. Orlanducci et al. used CNTs to stabilize the size of gold nanoparticles for their specific targeted properties [8]. Their results were in good agreement with ours, however, preparing a CNT is time consuming and makes the coating design more expensive. Our tests prove that the electrode is working properly and consistently after 31 days and in some cases 82 days. This suggests that even without the use of carbon nanotubes, the size of gold nanoparticles are stabilized with its previous melamine coating. Also, hemoglobin is a stable substance, which takes a while to degrade. Therefore, the extra coating layer of hemoglobin helps the sensors survive a longer time if properly sustained. The electrodes offer the results of their first day run even after a month past the coating.

Turek et al.'s multiple detection system, which detected CN^{-} , Pb, Cd and CU^{2+} simultaneously, detected a limit of $(0.2-3.8)*10^{-6}$ mol/lit [10]. This design is excellent for environmental purposes. However, setting the electrode up for detecting multiple heavy materials will exhaust all the binding sites and erode the electrode faster, therefore decreasing the sensitivity and selectivity of the electrode. That resulted in their detections to be 10^{12} orders of magnitude higher than what has been detected in this study, which again emphasizes the use of our electrodes in biomedical and health sciences.

Liu et al. used the idea of blocking cyanide molecules in place with the high affinity they have with PbO₂ molecules [14]. Although their focus was majorly on the second method they used rather than electrochemical, they achieved satisfactory results of $9.2*10^{-6}$ mol/lit of detection. The affinity of cyanide for hemoglobin is much higher than that of PbO₂, and the results of our experiment is in excellent agreement with this statement. Siontorou et al. made a break through with detecting cyanide in low detections of $4.9*10^{-9}$, by using methemoglobin as their binding agent for cyanide [18]. But still, with the higher affinity that cyanide has for hemoglobin, it makes it possible for the detection to go as low as $1*10^{-18}$ mol/lit, as has been detected in our study.

Wang et al. accomplished a detection limit of 2*10⁻⁶ mol/lit for cyanide, using glassy carbon electrode and a micro dialysis sampling tube with 5 cellulose hollow fibers in 1998 [17]. This is a perfectly suitable sensor for the environment but there has been no specific data on how stable their sensor is. The sensor's stability is important in means that for an on-site analysis of air quality, you shouldn't be forced to recoat a new system every week. The design presented in our study is suitable for a long-term use of each electrode, with great reproducibility and stability.

2.5. Conclusion

In conclusion, between three major electrodes tested with an electrochemical system in this study, glassy carbon electrode was proven to not react preferably with cyanide, presumably because of its melamine coating, in its detections. Gold and platinum electrodes both showed great potential in detecting cyanide for high ranges of concentration in $1*10^{-6}$ to $1*10^{-2}$ mol/lit. Platinum electrode with our design of the electrode coating system proved to be an excellent matter for detecting cyanide in ultra-low detections in $1*10^{-18}$ to $1*10^{-6}$ mol/lit, which are at least 10^{6} orders of

magnitude lower than what has been detected before in the literature. Both gold and platinum electrodes showed good stability and reproducibility with respect to time. Gold electrode at one set of coating showed to be viable for high limit detections up to 82 days after the coating. The results showed that gold peaks reside between 460 mV for reductive and 600 mV for oxidative peaks. However, in high concentrations, going from $1*10^{-4}$ to $1*10^{-1}$, the oxidative peaks shift to lower voltages from 600 to 350 mV and there appear another oxidative peak at 318 mV, in the return peak, which is supposed to be site of reduction reaction. In the adding of BSA, the results showed that BSA could be slightly beneficial in detection purposes. However, it is not necessary to include it in the implementation of coating procedure, since the difference between the current detected was less than 1 μ Amp. It should be mentioned that during some runs with the BSA coated electrodes, new peaks show up at 150 mV for lower concentrations, but they weren't consistent in several experiments.

Platinum electrode showed the most promise in detecting cyanide, both in high and low limits. At low concentrations, from $1*10^{-18}$ to $1*10^{-6}$, platinum electrode had a current detection limit of 6.2 µAmps. We also concluded that the electrode's sensitivity doesn't decrease when ran in human blood serum and the detection is still consistent with PBS runs. This could be an excellent potential for further biomedical researches and healthcare use, for fast and cheap detection of cyanide trace in human blody.

Further investigation is needed to study the effect of different sizes of gold nanoparticles on the electrodes and how they can increase or decrease the stability, sensitivity and reproducibility of electrodes. More research should be conducted on nano-molecular level reactions happening at the surface of electrodes at the time of run, possibly using an AFM microscope, to explore the nature of electrode's returning peaks in gold electrode for high concentrations. Also, using the same design for detecting other biomarkers, which possibly have a high affinity for hemoglobin, could replace other electrochemical methods, which have a higher detection.

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APPENDIX A ADDITIONAL TEST RESULTS

Log Concentration	AU1/ 19th	AU1/26	Au1/3rd	AU1 / 11	AU1/ 6.3	AU1/6.28	AU1/ 9.9	AU1/ 9.15	AU1/ BSA/ 12.11	AU1/ BSA / 12.27
-5	0	0	0	0	-	0	-	-	0	0
-4.698970004	-	-	-	0.014	-	0.01	-	-	0.105	0.045
-4.397940009	0.277	0.172	0.043	0.167	-	0.051	-	-	0.171	0.11
-4.22184875	0.309	0.276	0.09	0.293	-	0.075	-	-	0.241	0.177
-4.096910013	-	-	-	0.406	-	0.081	-	-	0.264	0.254
-4	0.31	0.365	0.175	0.503	0	0.1115	0	0	0.304	0.339
-3.698970004	-	-	-	0.796	0.584	0.359	0.509	0.287	0.64	0.696
-3.397940009	1.338	1.17	0.648	1.094	1.052	0.596	0.815	0.406	0.906	1.065
-3.22184875	2.52	1.933	1.054	1.368	1.468	0.843	1.09	0.656	1.117	1.318
-3.096910013	-	-	-	1.628	1.862	1.073	1.313	0.694	1.273	1.539
-3	3.549	2.547	1.481	1.865	2.184	1.129	1.426	0.709	1.352	1.689
-2.698970004	-	-	-	3.9	5.744	6.348	3.786	2.552	1.554	4.562
-2.397940009	4.702	7.8	6.608	6.625	8.732	9.229	5.515	6	3.684	6.505
-2.22184875	14.779	13.21	11.243	7.994	10.902	11.449	6.884	7.695	5.846	8.008
-2.096910013	-	-	-	8.867	12.802	13.529	8.041	9.646	6.439	9.241
-2	20.529	19.47	15.093	9.53	13.732	14.199	12.018	10.856	6.511	10.181

Table A.1Echem Analyst Data For Gold Electrode I Ran With CN From Concentration 1e-5 to 1e-2 M at 600 mV
Log Concentration	AU1/ 19th	AU1/26	Au1/3rd	AU1/11	AU1/ 6.3	Au1/6.28	AU1/ 9.9	AU1/ 9.15	AU1/ BSA/ 12.11	AU1/ BSA / 12.27
-5	0.12	2.37	2.67	0.587	-	0.84	-	-	0.41	2.15
-4.698970004	-	-	-	0.361	-	0.15	-	-	0.171	1.831
-4.397940009	0.06	1.65	1.22	0.183	_	0	_	-	0.088	1.341
-4.22184875	0.01	0.77	0.17	0.071	-	0.02	_	_	0.029	0.894
-4.096910013	_	_	-	0.016	_	0.04	_	_	0	0.392
-4	0	0	0	0	0	0.14	0	0	0.071	0
-3.698970004	_	-	-	0.041	0.02	0.87	0.54	0.08	0.373	0.069
-3 397940009	1 25	4 53	0.62	0.1	0	1 47	0.77	0 161	0.536	0.178
-3 22184875	2.16	5.91	0.52	0.153	0.19	2.03	1.21	0.26	0.718	0.28
-3.096910013	2.10	5.91	0.52	0.199	0.34	2.03	1.592	0.20	0.879	0.434
-5.090910015	2 70	6.00	1 12	0.199	0.5	2.30	2.02	0.47	0.005	0.425
-3	2.19	0.99	1.12	0.241	1.29	2.71	2.03	1.022	1.17	1.754
-2.698970004	-	-	-	0.902	1.28	0.95	2.397	1.033	1.17	1.734
-2.397940009	3.19	10.51	3.81	1.549	1.44	8.46	2.8	1.78	2.975	2.089
-2.22184875	4.47	11.2	4.86	2.115	1.56	9.24	3.1367	2.143	3.83	2.182
-2.096910013	-	-	-	2.585	1.71	9.73	3.52	2.213	4.068	2.169
-2	3.9	11.27	5.47	3.006	1.75	9.85	3.902	2.311	4.061	2.097

Table A.2Echem Analyst Data For Gold Electrode I Ran With CN From Concentration 1e-5 to 1e-2 M at 460 mV

Log Concentration	AU2/19th	AU2/ 26th	Au2/3rd	Au2/ 11th	AU2/ 6.3	AU2/ 6.28	AU2/ 9.9	AU2/ 9.15	AU2/ BSA / 12.27
-5	0.191	0	1.168	0.006	-	0	-	-	0
-4.698970004	-	-	-	0	-	0.04	-	-	0.098
-4.397940009	0.009	0.085	0.45	0.043	-	0.044	-	-	0.141
-4.22184875	0	0.121	0.092	0.09	-	0.074	-	-	0.205
-4.096910013	-	-	-	0.124	-	0.101	_	_	0.292
-4	0.242	0.207	0	0.154	0.903	0.124	0	0	0.371
-3.698970004	-	-	-	0.403	0.021	0.346	0.504	0.287	0.77
-3.397940009	1.201	0.771	0.421	0.68	0	0.583	0.702	0.364	1.165
-3.22184875	2.29	1.374	0.574	0.958	0.193	0.795	0.845	0.606	1.486
-3.096910013	_	_	_	1.223	0.252	1.036	1.012	0.694	1.737
-3	3.407	1.995	0.611	1.733	0.857	1.089	1.032	0.532	1.768
-2.698970004	_	_	_	4.56	4.08	6.157	3.69	2.773	5.161
-2.397940009	4.518	8.888	8.392	8.847	6.763	9.045	5.767	6	7.23
-2.22184875	13.755	13.181	12.527	10.843	8.492	11.421	7.516	7.806	8.676
-2.096910013	_	_	_	12.403	9.772	13.311	8.321	9.646	9.88
-2	22.325	17.121	15.907	13.653	10.822	13.531	11.033	10.856	10.15

Table A.3Echem Analyst Data For Gold Electrode II Ran With CN From Concentration 1e-5 to 1e-2 M at 600 mV

Conc at 460	AU2/19th	AU2/ 26th	Au2/3rd	Au2/ 11th	AU2/ 6.3	AU2/ 6.28	AU2/ 9.9	AU2/ 9.15	AU2/ BSA / 12.27
-5	0.34	0.62	1.86	0.064	-	0.32	-	-	2.095
-4.698970004	0.16	-	-	0.21	-	0.12	-	-	1.48
-4.397940009	0.16	0.36	1.09	0.101	-	0	-	-	0.93
-4.22184875	0.04	0.15	0.5	0.024	-	0.07	-	-	0.52
-4.096910013	-	-	-	0.005	-	0.18	-	-	0.21
-4	0	0	0	0	0.87	0.12	0	0	0
-3.698970004	_	-	-	0.058	0.32	0.65	0.52	0.08	0.37
-3.397940009	1.32	0.38	0.47	0.127	0	1.04	0.84	0.161	0.58
-3.22184875	1.78	0.93	1.94	0.274	0.1	1.41	1.2933	0.247	0.74
-3.096910013	-	-	-	0.415	0.07	1.79	1.7133	0.363	0.92
-3	2.04	1.39	2.61	0.485	0.03	1.89	2.1233	0.56	0.85
-2.698970004	-	-	-	1.45	1.17	4.82	2.59	1.033	2.411
-2.397940009	2.51	2.63	4.57	2.295	0.99	5.8	2.98	1.776	2.859
-2.22184875	2.7	2.84	4.65	3.193	0.86	6.3	3.43	2.143	3.062
-2.096910013	-	-	-	4.002	1.04	6.56	3.814	2.213	3.169
-2	2.65	3	4.79	4.833	0.95	6.64	4.23	2.311	3.169

Table A.4Echem Analyst Data For Gold Electrode II Ran With CN From Concentration 1e-5 to 1e-2 M at 460 mV

	Oxidative at 600 mV			Reductive at 460 mV			
Log Concnetration (M)	AU1 / 7.7	AU1/9.9	AU1/9.15	AU1/ 7.7	AU1/9.9	AU1/9.15	
-14	0.3731	0.397	0.272	1.96	2.405	2.68	
-13.39794001		0.374	0.269		1.75	1.86	
-13.22184875		0.344	0.256		1.1	0.91	
-13	0.2931	0.302	0.252	0.92	0.546	0.5	
-12.39794001		0.294	0.249		0.277	0.22	
-12.22184875		0.282	0.237		0.204	0.05	
-12	0.2071	0.246	0.234	0	0	0	
-11.39794001		0.208	0.224		0.29	0.02	
-11.22184875		0.197	0.21		0.32	0.06	
-11	0.1571	0.169	0.205	0.71	0.355	0.15	
-10.39794001		0.158	0.192		0.391	0.33	
-10.22184875		0.137	0.183		0.482	0.45	
-10	0.1021	0.114	0.173	1.27	0.601	0.72	
-9.397940009		0.103	0.147		0.63	0.86	
-9.22184875		0.099	0.129		0.764	1.05	
-9	0.0461	0.094	0.124	1.49	0.89	1.33	
-8.397940009		0.088	0.107		1.3	1.53	
-8.22184875		0.083	0.095		1.52	1.7	
-8	0	0.079	0.076	1.62	1.615	1.83	
-7.397940009		0.077	0.05		1.75	2.1	
-7.22184875		0.059	0.045		1.806	2.2	
-7	0.12	0.027	0.031	1.83	1.866	2.33	
-6.397940009		0	0		1.877	2.48	
-6.22184875		0.08	0.028		1.903	2.57	
-6	0.378	0.12	0.047	1.94	1.99	2.58	
-5.397940009		0.203	0.066		2.132	2.58	
-5.22184875		0.32	0.075		2.3	2.6	
-5	0.604	0.449	0.106	2.01	2.405	2.65	

Table A.5Echem Analyst Data For Gold Electrode I Ran With CN From Concentration 1e-14 to 1e-5 M at 600 and 460 mV

	Oxidative at 600 mV			Reductive at 460 mV				
Log Concentration (M)	AU1 / 7.7	AU1/9.9	AU1/9.15	AU1/ 7.7	AU1/9.9	AU1/9.15		
-14	0.65	0.344	0.484	2.401	1.37	1.42		
-13.39794001		0.34	0.455		0.52	0.54		
-13.22184875		0.327	0.455		0.2	0.19		
-13	0.471	0.29	0.449	0	0.04	0.06		
-12.39794001		0.243	0.417		0	0		
-12.22184875		0.226	0.402		0.2	0.02		
-12	0.374	0.204	0.392	0.77	0.24	0.02		
-11.39794001		0.203	0.363		0.39	0.06		
-11.22184875		0.165	0.345		0.43	0.15		
-11	0.294	0.154	0.328	1.07	0.52	0.33		
-10.39794001		0.121	0.293		0.71	0.45		
-10.22184875		0.101	0.278		0.72	0.72		
-10	0.158	0.099	0.252	1.3	0.79	0.86		
-9.397940009		0.095	0.213		0.81	1.05		
-9.22184875		0.09	0.186		0.87	1.33		
-9	0.103	0.089	0.163	1.73	0.89	1.37		
-8.397940009		0.079	0.134		0.94	1.53		
-8.22184875		0.075	0.106		0.99	1.7		
-8	0.047	0.066	0.082	1.931	1.02	1.72		
-7.397940009		0.055	0.026		1.08	1.83		
-7.22184875		0.021	0.011		1.12	2.09		
-7	0	0	0	2.173	1.18	2.1		
-6.397940009		0.05	0.028		1.31	2.2		
-6.22184875		0.12	0.029		1.37	2.33		
-6	0.471	0.2	0.065	2.35	1.42	2.48		
-5.397940009		0.27	0.174		1.59	2.57		
-5.22184875		0.3	0.207		1.71	2.58		
-5	0.208	0.34	0.269	2.428	2.19	2.58		

Table A.6Echem Analyst Data For Gold Electrode II Ran With CN From Concentration 1e-14 to 1e-5 M at 600 and 460 mV

Log Concentration (M)	8.8	8.15	8.19 A	8.19 B	12.11 BSA	12.27 BSA
-6	0	0	0.56	1.15	0	0
-5.698970004	0.23	0.033	0.51	0.79	0.01	0.31
-5.397940009	0.43	0.241	0	0	0.3	0.55
-5.22184875	0.76	0.312	0.34	0.93	0.42	1.1
-5.096910013	0.81	0.303	0.36	1.15	0.43	1.58
-5	0.92	0.616	0.43	1.22	0.56	1.95
-4.698970004	2.87	0.879	0.98	1.78	1.48	3.28
-4.397940009	3.44	1.552	1.28	2.29	1.91	3.56
-4.22184875	4.4	1.925	1.46	2.79	2.7	3.79
-4.096910013	4.55	2.036	1.56	3.19	2.78	4.11
-4	5.51	2.205	1.66	3.53	3.47	4.42
-3.698970004	5.95	2.526	2.02	3.57	3.69	4.51
-3.397940009	6.29	2.966	2.56	3.67	3.79	5.12
-3.22184875	6.5	3.286	2.69	3.7	3.91	5.13
-3.096910013	6.63	3.326	2.8	3.72	3.93	5.14
-3	6.79	3.536	3	3.78	3.99	5.33
-2.698970004		3.786	3.07	3.8	4.05	5.55
-2.397940009		4.006	3.17	3.85	4.12	5.73
-2.22184875		4.116	3.19	3.86	4.13	5.82
-2.096910013		4.266	3.28	3.87	4.15	6.15
-2		4.316	3.45	3.95	4.19	6.56
-1.698970004		4.716	3.68	4.26		
-1.397940009		4.756	3.76	4.3		
-1.22184875		5.236	3.87	4.4		
-1.096910013		5.716	3.99	4.56		
-1		5.816	4.08	4.72		

Table A.7Echem Analyst Data For Platinum Electrode I Ran With CN From Concentration 1e-6 to 1e-1 M at 850 mV

Log Concentration (M)	8.8	8.15	8.19 A	8.19 B	12.11 BSA	12.27 BSA
-6	1.03	0.41	0	0	0	1.01
-5.698970004	0.56	0.69	0.135	0.36	0.318	0.63
-5.397940009	0.43	0.28	0.238	0.44	0.455	0.22
-5.22184875	0.4	0.16	0.342	0.56	0.553	0.08
-5.096910013	0.17	0.02	0.374	0.57	0.592	0.03
-5	0	0	0.379	0.68	0.657	0
-4.698970004	0.7	0.89	0.614	0.8	0.968	0.54
-4.397940009	0.93	1.19	0.617	1.02	1.163	1
-4.22184875	1.42	1.8	0.702	1.4	1.231	1.27
-4.096910013	1.56	2.49	0.757	1.56	1.283	1.48
-4	1.9	2.77	0.787	1.72	1.218	1.63
-3.698970004	3.06	4.66	0.82	1.76	1.86	2.52
-3.397940009	3.79	5.94	0.88	2.78	2.215	3.34
-3.22184875	4.09	6.57	0.912	3.01	2.374	3.77
-3.096910013	4.17	6.91	0.969	3.15	2.509	3.98
-3	4.28	7.07	1.116	3.19	2.561	4.15
-2.698970004	-	8.19	1.343	3.825	3.16	4.88
-2.397940009	-	8.89	1.571	4.227	3.534	5.33
-2.22184875	-	9.31	1.676	4.413	3.728	5.618
-2.096910013	-	9.61	1.762	4.537	3.89	5.795
-2	-	9.71	1.992	4.559	3.953	5.932
-1.698970004	-	9.94	2.234	5.154	-	-
-1.397940009	-	10.19	2.401	5.398	-	-
-1.22184875	-	10.39	2.394	5.482	-	-
-1.096910013	-	10.41	2.257	5.436	-	-
-1	-	10.53	2.077	5.308	-	-

Table A.8Echem Analyst Data For Platinum Electrode I Ran With CN From Concentration 1e-6 to 1e-1 M at -25 mV

Log Concentration (M)	8.8	8.15	8.19 A	8.19 B	12.27 BSA
-6	0	0	0	0	0
-5.698970004	0.48	0.28	0.01	0.08	
-5.397940009	0.9	0.48	0.3	0.34	0.28
-5.22184875	0.93	0.54	0.42	0.79	1.05
-5.096910013	1.17	0.69	0.43	0.95	
-5	1.48	0.84	0.56	1.03	1.69
-4.698970004	3.33	1.48	1.48	2.12	3.74
-4.397940009	4.52	1.76	1.91	2.85	4.74
-4.22184875	5.03	2.36	2.7	3.38	5.02
-4.096910013	5.23	2.66	2.78	3.81	5.43
-4	5.93	2.86	3.47	4.08	5.49
-3.698970004	7.14	3.3	3.69	4.23	5.67
-3.397940009	7.23	3.53	3.79	4.52	5.94
-3.22184875	7.34	3.62	3.91	4.55	6
-3.096910013	7.44	3.69	3.93	4.59	6.01
-3	7.98	3.7	3.99	4.61	6.39
-2.698970004	-	3.74	4.05	4.7	6.59
-2.397940009	-	3.76	4.12	4.78	6.8
-2.22184875	-	3.82	4.13	4.82	6.89
-2.096910013		3.82	4.15	4.84	7.13
-2	-	3.84	4.19	4.95	7.35
-1.698970004	-	3.87	4.2	4.98	-
-1.397940009	-	4	4.42	4.98	-
-1.22184875	-	4.06	4.48	5.05	-
-1.096910013	-	4.13	4.5	5.21	-
-1	-	4.26	4.84	5.38	-

Table A.9Echem Analyst Data For Platinum Electrode II Ran With CN From Concentration 1e-6 to 1e-1 M at 850 mV

Log Concentration (M)	8.8	8.15	8.19 A	8.19 B	12.27 BSA
-6	2.61	2.02	0.54	0.35	0.29
-5.698970004	1.48	1.89	0.3	0.16	
-5.397940009	1.09	1.73	0.27	0.38	0
-5.22184875	0.65	1.36	0.23	0.5	0
-5.096910013	0.41	0.85	0.18	0.46	
-5	0	0	0	0	0.1
-4.698970004	0.55	2.36	0.29	0.54	1.01
-4.397940009	1.01	2.48	0.33	0.93	1.53
-4.22184875	1.29	2.69	0.46	1.01	1.9
-4.096910013	1.47	2.7	0.44	1.21	2.21
-4	1.7	2.76	0.62	1.38	2.32
-3.698970004	3.2	3.28	1.15	2.12	3.48
-3.397940009	4.43	3.55	1.68	3.02	4.23
-3.22184875	4.91	3.55	1.93	3.35	4.75
-3.096910013	5.34	3.57	2.05	3.6	5.18
-3	5.51	3.57	2.11	3.69	5.32
-2.698970004	-	4.82	2.74	4.57	6.2
-2.397940009	-	5.22	3.18	5.12	6.78
-2.22184875	-	5.43	3.42	5.43	7.15
-2.096910013	-	5.549	3.601	5.65	7.37
-2	-	5.601	3.656	5.69	7.4
-1.698970004	-	6.242	4.339	6.435	-
-1.397940009	-	6.328	4.649	6.782	-
-1.22184875	-	6.507	4.731	6.885	-
-1.096910013	-	6.512	4.683	6.817	-
-1	-	6.59	4.507	6.617	-

Table A.10Echem Analyst Data For Platinum Electrode II Ran With CN From Concentration 1e-6 to 1e-1 M at -25 mV

APPENDIX B GRAPHIC RESULTS OF CYCLIC VOLTAMMETRY ANALYSIS



Figure B.1 Voltammogram Data For Gold Electrode I Ran With CN With and Without BSA From Concentration 1e-5 to 1e-2 at 600 mV, Coated March



Figure B.2 Voltammogram Data For Gold Electrode I Ran With CN With and Without BSA From Concentration 1e-5 to 1e-2 at 600 mV, Coated June and September

Log Concentration (M)



Figure B.3 Voltammogram Data For Gold Electrode I Ran With CN With and Without BSA From Concentration 1e-5 to 1e-2 at 460 mV, Coated March



Figure B.4 Voltammogram Data For Gold Electrode I Ran With CN With and Without BSA From Concentration 1e-5 to 1e-2 at 460 mV, Coated June and September



Figure B.5 Voltammogram Data For Gold Electrode II Ran With CN With and Without BSA From Concentration 1e-5 to 1e-2 at 600 mV Coated March







Figure B.7 Voltammogram Data For Gold Electrode II Ran With CN With and Without BSA From Concentration 1e-5 to 1e-2 at 460 mV, Coated March



Figure B.8 Voltammogram Data For Gold Electrode II Ran With CN With and Without BSA From Concentration 1e-5 to 1e-2 at 460 mV, Coated June and September

0 9th day/ coat of Jun 1st day/ coat of Sep AU1, low, @600 \diamond 6th day/ coat of Sep 0.7 0.6 0 0.5 Current (micro amp) 0.4 Ľ, ġ ģ . . . 0.3 0 $\diamond_{\diamond\diamond}$ ċ

</ \diamond 0.2 \diamond \diamond_{\diamond} 0 ģ ģ 0.1 \diamond^{\diamond} $\diamond \diamond$ 0 Ş Â \diamond 0 -16 -14 -12 -10 -8 -6 -4 Log Concentration (M)

Figure B.9 Voltammogram Data For Gold Electrode I Ran With CN From Concentration 1e-14 to 1e-5 at 600 mV



Figure B.10 Voltammogram Data For Gold Electrode I Ran With CN From Concentration 1e-14 to 1e-5 at 460 mV

9th day/ coat of Jun 0 1st day/ coat of Sep \diamond 6th day/ coat of Sep AU2, low, @600 0.7 0.6 0.5 ¢ 0 d ∞_{\diamond} \diamond Current (micro amp) 0.4 \diamond ģ \sim 0.3 Ð ¢ \circ \diamond ¢٥ ф 0.2 £ \diamond \diamond \diamond Ø \diamond <u>ч</u> 0.1 Ðġ \$ \diamond \otimes 0 -16 -14 -12 -10 -8 -6 -4 Log Concentration (M)

Figure B.11 Voltammogram Data For Gold Electrode II Ran With CN From Concentration 1e-14 to 1e-5 at 600 mV



Figure B.12 Voltammogram Data For Gold Electrode II Ran With CN From Concentration 1e-14 to 1e-5 at 460 mV



Current (micro amp)

Figure B.13 Voltammogram Data For Platinum Electrode IA With and Without BSA Ran With CN From Concentration 1e-18 to 1e-6 at -25 mV



Figure B.14 Voltammogram Data For Platinum Electrode IB With and Without BSA Ran With CN From Concentration 1e-18 to 1e-6 at -25 mV



Figure B.15 Voltammogram Data For Platinum Electrode IIA With and Without BSA Ran With CN From Concentration 1e-18 to 1e-6 at -25 mV



Figure B.16 Voltammogram Data For Platinum Electrode IIB With and Without BSA Ran With CN From Concentration 1e-18 to 1e-6 at -25 mV

Figure B.17 Voltammogram Data For Platinum Electrode I With and Without BSA Ran With CN From Concentration 1e-6 to 1e-2 at 850 mV

- Day 1/coat Aug
- □ Day 7/ coat Aug
- ◊ Day 11/ coat Aug
- × Day 11/coat Aug
- + Day 1/ coat Dec/ BSA
 - Day 5/ coat Dec/ BSA





Figure B.18 Voltammogram Data For Platinum Electrode I With and Without BSA Ran With CN From Concentration 1e-6 to 1e-2 at -25 mV





Figure B.19 Voltammogram Data For Platinum Electrode II With and Without BSA Ran With CN From Concentration 1e-6 to 1e-2 at 850 mV



Figure B.19 Voltammogram Data For Platinum Electrode II With and Without BSA Ran With CN From Concentration 1e-6 to 1e-2 at -25 mV

APPENDIX C PICTORIAL RESULTS OF CYCLIC VOLTAMMETRIES

Figure C.1 Glassy Carbon Electrode I Ran With NO₂ From Concentration 1e-9 to 1e-3, 01.27.2014



Figure C.2 Glassy Carbon Electrode II Ran With NO₂ From Concentration 1e-9 to 1e-3, 01.27.2014



Figure C.3 Glassy Carbon Electrode I Ran With NO₂ From Concentration 1e-8 to 1e-3, [-1.0, 1.2] V, 02.01.2014



Figure C.4 Glassy Carbon Electrode II Ran With NO₂ From Concentration 1e-8 to 1e-3, [-1.0, 1.2] V, 02.01.2014



Figure C.5 Glassy Carbon Electrode I Ran With H₂O₂ From Concentration 1e-8 to 1e-3, [-1.0, 1.2] V, 02.01.2014



Figure C.6 Glassy Carbon Electrode II Ran With H₂O₂ From Concentration 1e-8 to 1e-3, [-1.0, 1.2] V, 02.01.2014



Figure C.7 Glassy Carbon Electrode I Ran With NO₂ From Concentration 1e-8 to 1e-3, [-1.0, 1.2] V, 02.02.2014



Figure C.8 Glassy Carbon Electrode II Ran With NO₂ From Concentration 1e-8 to 1e-3, [-0.4, 1.2] V, 02.02.2014



Figure C.9 Glassy Carbon Electrode I Ran With H₂O₂ From Concentration 1e-8 to 1e-3, [-1.0, 1.2] V, 02.02.2014



Figure C.10 Glassy Carbon Electrode II Ran With H₂O₂ From Concentration 1e-8 to 1e-3, [-1.0, 1.2] V, 02.02.2014


Figure C.11 Glassy Carbon Electrode I Ran With NO₂ From Concentration 1e-8 to 1e-4, [-0.4, 1.2] V, 02.23.2014



Figure C.12 Glassy Carbon Electrode II Ran With NO₂ From Concentration 1e-8 to 1e-4, [-0.4, 1.2] V, 02.23.2014



Figure C.13 Glassy Carbon Electrode I Ran With H₂O₂ From Concentration 1e-8 to 1e-3, [-0.4, 1.2] V, 02.23.2014



Figure C.14 Glassy Carbon Electrode II Ran With H₂O₂ From Concentration 1e-8 to 1e-3, [-0.4, 1.2] V, 02.23.2014



Figure C.15 Glassy Carbon Electrode I Ran With NO₂ From Concentration 1e-8 to 1e-4, [-0.4, 1.2] V, 03.03.2014



Figure C.16 Glassy Carbon Electrode II Ran With NO₂ From Concentration 1e-8 to 1e-4, [-0.4, 1.2] V, 03.03.2014



Figure C.17 Glassy Carbon Electrode III Ran With NO₂ From Concentration 1e-8 to 1e-4, [-0.4, 1.2] V, 03.03.2014



Figure C.18 Glassy Carbon Electrode I Ran With H₂O₂ From Concentration 1e-8 to 1e-3, [-0.4, 1.2] V, 03.03.2014



Figure C.15 Glassy Carbon Electrode I Ran With NO₂ From Concentration 1e-6 to 1e-3, [-0.4, 1.2] V, 03.09.2014



Figure C.16 Glassy Carbon Electrode II Ran With NO₂ From Concentration 1e-6 to 1e-3, [-0.4, 1.2] V, 03.09.2014





Figure C.17 Glassy Carbon Electrode III Ran With NO₂ From Concentration 1e-6 to 1e-3, [-0.4, 1.2] V, 03.09.2014

Figure C.18 Glassy Carbon Electrode I Ran With H₂O₂ From Concentration 1e-6 to 1e-3, [-0.4, 1.2] V, 03.09.2014



Figure C.19 Glassy Carbon Electrode I Ran With CN From Concentration 1e-10 to 1e-3, [-0.4, 1.2] V, 03.15.2014



Figure C.20 Glassy Carbon Electrode II Ran With CN From Concentration 1e-10 to 1e-3, [-0.4, 1.2] V, 03.15.2014



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Figure C.21 Glassy Carbon Electrode I Ran With CN From Concentration 1e-10 to 1e-3, [-0.4, 1.2] V, 04.13.2014

Figure C.22 Glassy Carbon Electrode II Ran With CN From Concentration 1e-10 to 1e-3, [-0.4, 1.2] V, 04.13.2014



Figure C.23 Gold Electrode I Ran With NO₂ From Concentration 1e-6 to 1e-3,

[-0.4, 1.2] V, 03.09.2014



Figure C.24 Gold Electrode II Ran With NO₂ From Concentration 1e-6 to 1e-3, [-0.4, 1.2] V, 03.09.2014



Figure C.25 Gold Electrode I Ran With H₂O₂ From Concentration 1e-6 to 1e-3, [-0.4, 1.2] V, 03.09.2014



Figure C.26 Gold Electrode II Ran With H_2O_2 From Concentration 1e-6 to 1e-3, [-0.4, 1.2] V, 03.09.2014



Figure C.27 Gold Electrode I Ran With CN From Concentration 1e-10 to 1e-4, [-0.4, 1.2] V, 03.15.2014



Figure C.28 Gold Electrode II Ran With CN From Concentration 1e-10 to 1e-4, [-0.4, 1.2] V, 03.15.2014



Figure C.29 Gold Electrode II Ran With CN From Concentration 1e-10 to 1e-3, [-1.0, 1.0] V, 03.20.2014



Figure C.30 Gold Electrode I Ran With CN From Concentration 1e-10 to 1e-4, [-0.4, 1.2] V, 04.13.2014



Figure C.31 Gold Electrode II Ran With CN From Concentration 1e-10 to 1e-4, [-0.4, 1.2] V, 04.13.2014



Figure C.32 Gold Electrode I Ran With CN From Concentration 1e-10 to 1e-3, [-1.0, 1.0] V, 04.13.2014



Figure C.33 Gold Electrode II Ran With CN From Concentration 1e-10 to 1e-3, [-1.0, 1.0] V, 04.13.2014



Figure C.34 Gold Electrode I Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 04.19.2014



Figure C.35 Gold Electrode II Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 04.19.2014



Figure C.36 Gold Electrode I Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 04.26.2014



Figure C.37 Gold Electrode II Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 04.26.2014



Figure C.38 Gold Electrode I Ran With CN From Concentration 1e-5 to 1e-1, [-0.4, 1.2] V, 05.03.2014



Figure C.39 Gold Electrode II Ran With CN From Concentration 1e-5 to 1e-1, [-0.4, 1.2] V, 05.03.2014



Figure C.40 Gold Electrode I Ran With CN From Concentration 1e-5 to 1e-1, [-0.4, 1.2] V, 05.11.2014



Figure C.41 Gold Electrode II Ran With CN From Concentration 1e-5 to 1e-1, [-0.4, 1.2] V, 05.11.2014



Figure C.40 Gold Electrode I Ran With CN From Concentration 1e-5 to 1e-1, [-0.4, 1.2] V, 06.03.2014



Figure C.41 Gold Electrode II Ran With CN From Concentration 1e-5 to 1e-1, [-0.4, 1.2] V, 06.03.2014



Figure C.42 Gold Electrode I Ran With NO₃ From Concentration 1e-10 to 1e-2, [-0.4, 1.2] V, 06.05.2014



Figure C.43 Gold Electrode II Ran With NO₃ From Concentration 1e-10 to 1e-2, [-0.4, 1.2] V, 06.05.2014



Figure C.44 Gold Electrode I Ran With CN From Concentration 1e-18 to 1e-5, [-0.4, 1.2] V, 07.07.2014



Figure C.45 Gold Electrode II Ran With CN From Concentration 1e-18 to 1e-5, [-0.4, 1.2] V, 07.07.2014



Figure C.46 Gold Electrode I Ran With CN From Concentration 1e-14 to 1e-5, [-0.4, 1.2] V, 09.09.2014



Figure C.47 Gold Electrode II Ran With CN From Concentration 1e-14 to 1e-5,





Figure C.48 Gold Electrode I Ran With CN From Concentration 1e-4 to 1e-1, [-0.4, 1.2] V, 09.09.2014



Figure C.49 Gold Electrode II Ran With CN From Concentration 1e-4 to 1e-1,





Figure C.46 Gold Electrode I Ran With CN From Concentration 1e-14 to 1e-5, [-0.4, 1.2] V, 09.14.2014



Figure C.47 Gold Electrode II Ran With CN From Concentration 1e-14 to 1e-5,

[-0.4, 1.2] V, 09.14.2014



Figure C.48 Gold Electrode I Ran With CN From Concentration 1e-4 to 1e-1, [-0.4, 1.2] V, 09.14.2014



Figure C.49 Gold Electrode II Ran With CN From Concentration 1e-4 to 1e-1,





Figure C.50 Gold Electrode I Ran With CN From Concentration 1e-14 to 1e-5, [-0.4, 1.2] V, 10.09.2014



Figure C.51 Gold Electrode II Ran With CN From Concentration 1e-14 to 1e-5, [-0.4, 1.2] V, 10.09.2014



Figure C.52 Gold Electrode I Ran With CN From Concentration 1e-5 to 1e-1, [-0.4, 1.2] V, 10.09.2014



Figure C.53 Gold Electrode II Ran With CN From Concentration 1e-5 to 1e-1, [-0.4, 1.2] V, 10.09.2014



Figure C.54 Gold Electrode I +BSA Ran With CN From Concentration 1e-12 to 1e-6, [-0.4, 1.2] V, 10.27.2014



Figure C.55 Gold Electrode II +BSA Ran With CN From Concentration 1e-12 to 1e-6, [-0.4, 1.2] V, 10.27.2014



Figure C.56 Gold Electrode I +BSA Ran With CN From Concentration 1e-5 to 1e-2, [-0.4, 1.2] V, 10.27.2014



Figure C.57 Gold Electrode II +BSA Ran With CN From Concentration 1e-5 to 1e-2, [-0.4, 1.2] V, 10.27.2014



Figure C.58 Platinum Electrode I Ran With NO₂ From Concentration 1e-10 to 1e-3, [-0.4, 1.2] V, 04.07.2014



Figure C.59 Platinum Electrode II Ran With NO₂ From Concentration 1e-10 to 1e-3, [-0.4, 1.2] V, 04.07.2014



Figure C.60 Platinum Electrode I Ran With H₂O₂ From Concentration 1e-10 to 1e-3, [-0.4, 1.2] V, 04.07.2014



Figure C.61 Platinum Electrode II Ran With H₂O₂ From Concentration 1e-10 to 1e-3, [-0.4, 1.2] V, 04.07.2014



Figure C.62 Platinum Electrode I Ran With NO₂ From Concentration 1e-10 to 1e-3, [-1.0, 1.0] V, 04.07.2014



Figure C.63 Platinum Electrode II Ran With NO₂ From Concentration 1e-10 to 1e-3, [-1.0, 1.0] V, 04.07.2014



Figure C.64 Platinum Electrode I Ran With H₂O₂ From Concentration 1e-10 to 1e-3, [-1.0, 1.0] V, 04.07.2014



Figure C.65 Platinum Electrode II Ran With H₂O₂ From Concentration 1e-10 to 1e-3, [-1.0, 1.0] V, 04.07.2014



Figure C.66 Platinum Electrode I Ran With CN From Concentration 1e-10 to 1e-3, [-0.4, 1.2] V, 04.07.2014



Figure C.67 Platinum Electrode II Ran With CN From Concentration 1e-10 to 1e-3, [-0.4, 1.2] V, 04.07.2014



Figure C.68 Platinum Electrode I Ran With CN From Concentration 1e-10 to 1e-3, [-1.0, 1.0] V, 04.07.2014



Figure C.69 Platinum Electrode II Ran With CN From Concentration 1e-10 to 1e-3, [-1.0, 1.0] V, 04.07.2014



Figure C.70 Platinum Electrode I Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 04.19.2014



Figure C.71 Platinum Electrode II Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 04.19.2014



Figure C.72 Platinum Electrode I Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 04.26.2014


Figure C.73 Platinum Electrode II Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 04.26.2014



Figure C.74 Platinum Electrode I Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 05.03.2014



Figure C.75 Platinum Electrode II Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 05.03.2014



Figure C.76 Platinum Electrode I Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 05.1.2014



Figure C.77 Platinum Electrode II Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 05.11.2014



Figure C.78 Platinum Electrode I Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 06.03.2014



Figure C.79 Platinum Electrode I Ran With NO₃ From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 06.05.2014



Figure C.79 Platinum Electrode II Ran With NO₃ From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 06.05.2014



Figure C.80 Platinum Electrode I Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 06.28.2014



Figure C.81 Platinum Electrode II Ran With CN From Concentration 1e-10 to 1e-1, [-0.4, 1.2] V, 06.28.2014



Figure C.82 Platinum Electrode I Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 07.07.2014



Figure C.83 Platinum Electrode II Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 07.07.2014



Figure C.84 Platinum Electrode I Ran With CN From Concentration 1e-18 to 1e-1, [-0.4, 1.2] V, 07.15.2014



Figure C.85 Platinum Electrode II Ran With CN From Concentration 1e-18 to 1e-1, [-0.4, 1.2] V, 07.15.2014



Figure C.84 Platinum Electrode I Ran With CN From Concentration 1e-18 to 1e-1, [-0.4, 1.2] V, 07.21.2014



Figure C.86 Platinum Electrode I Ran With CN From Concentration 1e-18 to 1e-8, [-0.4, 1.2] V, 07.25.2014



Figure C.87 Platinum Electrode II Ran With CN From Concentration 1e-18 to 1e-8, [-0.4, 1.2] V, 07.25.2014



Figure C.88 Platinum Electrode I Ran With CN From Concentration 1e-8 to 1e-1, [-0.4, 1.2] V, 07.25.2014



Figure C.89 Platinum Electrode II Ran With CN From Concentration 1e-8 to 1e-1, [-0.4, 1.2] V, 07.25.2014



Figure C.90 Platinum Electrode I Ran With CN From Concentration 1e-18 to 1e-8, [-0.4, 1.2] V, 07.31.2014



Figure C.91 Platinum Electrode II Ran With CN From Concentration 1e-18 to 1e-8, [-0.4, 1.2] V, 07.31.2014



Figure C.90 Platinum Electrode I Ran With CN From Concentration 1e-8 to 1e-1, [-0.4, 1.2] V, 07.31.2014



Figure C.91 Platinum Electrode II Ran With CN From Concentration 1e-8 to 1e-1, [-0.4, 1.2] V, 07.31.2014



Figure C.92 Platinum Electrode I Ran With CN From Concentration 1e-18 to 1e-8, [-0.4, 1.2] V, 08.05.2014



Figure C.93 Platinum Electrode II Ran With CN From Concentration 1e-18 to 1e-8, [-0.4, 1.2] V, 08.05.2014



Figure C.94 Platinum Electrode I Ran With CN From Concentration 1e-8 to 1e-1, [-0.4, 1.2] V, 08.05.2014



Figure C.95 Platinum Electrode II Ran With CN From Concentration 1e-8 to 1e-1, [-0.4, 1.2] V, 08.05.2014



Figure C.96 Platinum Electrode I Ran With CN From Concentration 1e-6 to 1e-3, [-0.4, 1.2] V, 08.08.2014



Figure C.97 Platinum Electrode II Ran With CN From Concentration 1e-6 to 1e-3, [-0.4, 1.2] V, 08.08.2014



Figure C.98 Platinum Electrode I Ran With CN From Concentration 1e-8 to 1e-1, [-0.4, 1.2] V, 08.08.2014



Figure C.99 Platinum Electrode II Ran With CN From Concentration 1e-8 to 1e-1, [-0.4, 1.2] V, 08.08.2014



Figure C.100 Platinum Electrode IA Ran With CN From Concentration 1e-4 to 1e-3, [-0.4, 1.2] V, 08.13.2014



Figure C.101 Platinum Electrode IIA Ran With CN From Concentration 1e-4 to 1e-3, [-0.4, 1.2] V, 08.13.2014



Figure C.102 Platinum Electrode IB Ran With CN From Concentration 1e-4 to 1e-3, [-0.4, 1.2] V, 08.13.2014



Figure C.103 Platinum Electrode IIB Ran With CN From Concentration 1e-4 to 1e-3, [-0.4, 1.2] V, 08.13.2014



Figure C.104 Platinum Electrode I Ran With CN From Concentration 1e-6 to 1e-1, [-0.4, 1.2] V, 08.13.2014



Figure C.105 Platinum Electrode II Ran With CN From Concentration 1e-6 to 1e-1, [-0.4, 1.2] V, 08.13.2014



Figure C.106 Platinum Electrode IA Ran With CN From Concentration 1e-6 to 1e-1, [-0.4, 1.2] V, 08.19.2014



Figure C.107 Platinum Electrode IIA Ran With CN From Concentration 1e-6 to 1e-1, [-0.4, 1.2] V, 08.19.2014



Figure C.108 Platinum Electrode IB Ran With CN From Concentration 1e-6 to 1e-1, [-0.4, 1.2] V, 08.19.2014



Figure C.109 Platinum Electrode IIB Ran With CN From Concentration 1e-6 to 1e-1, [-0.4, 1.2] V, 08.19.2014



Figure C.110 Platinum Electrode IA +BSA Ran With CN From Concentration 1e-13 to 1e-6, [-0.4, 1.2] V, 12.27.2014



Figure C.111 Platinum Electrode IIA +BSA Ran With CN From Concentration 1e-13 to 1e-6, [-0.4, 1.2] V, 12.27.2014



Figure C.112 Platinum Electrode IB +BSA Ran With CN From Concentration 1e-6 to 1e-2, [-0.4, 1.2] V, 12.27.2014



Figure C.113 Platinum Electrode IIB +BSA Ran With CN From Concentration 1e-6 to 1e-2, [-0.4, 1.2] V, 12.27.2014



Figure C.114 Platinum Electrode IA +BSA Ran With CN From Concentration 1e-18 to 1e-14, [-0.4, 1.2] V, 01.06.2015



Figure C.115 Platinum Electrode IB +BSA Ran With CN From Concentration 1e-18 to 1e-14, [-0.4, 1.2] V, 01.06.2015



Figure C.116 Platinum Electrode I +BSA Ran With CN From Concentration 1e-13 to 1e-6, [-0.4, 1.2] V, 01.06.2015



Figure C.117 Platinum Electrode I +BSA Ran With CN From Concentration 1e-5 to 1e-4, [-0.4, 1.2] V, 01.06.2015



Figure C.118 Platinum Electrode I Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 01.27.2015



Figure C.119 Platinum Electrode II Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 01.27.2015



Figure C.120 Platinum Electrode I +BSA Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 01.28.2015



Figure C.121 Platinum Electrode II +BSA Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 01.28.2015



Figure C.122 Platinum Electrode I +BSA Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 02.01.2015



Figure C.123 Platinum Electrode II +BSA Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 02.01.2015



Figure C.124 Platinum Electrode I Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 02.02.2015



Figure C.125 Platinum Electrode II Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 02.02.2015



Figure C.126 Platinum Electrode I +BSA Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 02.09.2015



Figure C.127 Platinum Electrode II +BSA Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 02.09.2015



Figure C.128 Platinum Electrode I Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 02.10.2015



Figure C.129 Platinum Electrode I +BSA Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 02.16.2015



Figure C.130 Platinum Electrode I +BSA Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 03.02.2015



Figure C.131 Platinum Electrode II +BSA Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 03.02.2015



Figure C.132 Platinum Electrode I Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 03.03.2015



Figure C.133 Platinum Electrode II Ran With CN From Concentration 1e-18 to 1e-6, [-0.4, 1.2] V, 03.03.2015



Figure C.134 Gold Electrode I +BSA Ran With CN From Concentration 1e-6 to 1e-2, [-0.4, 1.2] V, 01.27.2015



Figure C.135 Gold Electrode II +BSA Ran With CN From Concentration 1e-6 to 1e-2, [-0.4, 1.2] V, 01.27.2015



Figure C.136 Gold Electrode I +BSA Ran With CN From Concentration 1e-6 to 1e-2, [-0.4, 1.2] V, 02.01.2015



Figure C.137 Gold Electrode II +BSA Ran With CN From Concentration 1e-6 to 1e-2, [-0.4, 1.2] V, 02.01.2015



Figure C.138 Gold Electrode I +BSA Ran With CN From Concentration 1e-6 to 1e-2, [-0.4, 1.2] V, 01.09.2015



Figure C.139 Gold Electrode I +BSA Ran With CN From Concentration 1e-6 to 1e-2, [-0.4, 1.2] V, 03.02.2015



Figure C.140 Gold Electrode II +BSA Ran With CN From Concentration 1e-6 to 1e-2, [-0.4, 1.2] V, 03.02.2015
