FORMATION OF PLATINUM THIN FILMS BY ELECTROCHEMICAL ALD AND 2D NETWORKS OF CARBON NANOTUBES FOR ELECTROCHEMICAL APPLICATIONS

by

DEEPA VAIRAVAPANDIAN

(Under the direction of Marcus Lay)

ABSTRACT

The main topic of this dissertation is the formation nanostructures for catalysis applications by electrochemical methods. First part of the thesis deals with the formation of Pt thin films by electrochemical atomic layer deposition method (EC-ALD). The electrochemical deposition techniques are advantageous over the vacuum phase techniques because of low cost involved and temperature (ambient) used to make thin films. However the bulk electrodeposition method doesn't offer atomic level control to the formation of thin films. The thin films growth ends up 3 dimensional leading to rough Pt films. Hence we propose a modification in the electrodeposition technique using surface limited redox replacement method. In this method, a sacrificial layer of less noble metal such as copper is deposited on the gold substrate at under potential (UPD). The resultant monolayer of copper is replaced by Pt by flowing Pt at open circuit potential. Since UPD results in one atomic

layer of copper, we expect to get one atomic layer of Pt formed by the SLRR process. Copper forms UPD on Pt as well as Au. So the SLRR process is repeated any number of times depending on the thickness of Pt film needed. Home made flow cell system is used for this study. In the second part of the thesis, we focus on fabricating carbon nanotube networks as support for catalyst materials. In order to make efficient use of carbon nanotubes as catalyst support, control on the density and defects on the carbon nanotubes need to be controlled. We propose using novel room temperature deposition method called 'Laminar flow depoosition' (LFD) method. In this method carbon nanotube is deposited on silane coated glass slides by coating the slides with carbon nanotube/surfactant solution and then drying in the presence of nitrogen. The amount of tubes deposited is controlled by concentration of solution and time of deposition. We show the possibility of making carbon nanotube electrodes with varying electrochemical behavior by controlling the density. Cyclic voltammetry studies show the evolution of micro or macro electrode behavior depending on the density of network. Also the amount of Pt deposition depends on the defects on the carbon nanotubes. We show that acid treatment can be used to engineer the extent of defect formation. Raman studies show the formation of defects by acid treatment. By combining the LFD and acid treatment, we are able to tailor the carbon nanotube networks.

INDEX WORDS: Electrochemical atomic layer deposition, Surface limited redox replacement, Single walled carbon nanotubes, Laminar flow deposition, Atomic force microscopy, cyclic voltammetry

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DEEPA VAIRAVAPANDIAN

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DEEPA VAIRAVAPANDIAN

Major Professor: Marcus D. Lay

Committee: John L. Stickney
Jonathan Amster

Electronic Version Approved:

Maureen Grasso

Dean of the Graduate School

The University of Georgia

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DEDICATION

To all my teachers and my family

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CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

Making advanced nanoscale materials with novel properties has become the focus of research in many areas especially electronics, renewable energy sources, sensors, catalysis etc[1, 2] . The unique electronic, chemical, optical properties of nanomaterials are tunable based on their size and shape [3].This dissertation work focuses on the preparation of nanoscale materials (Particularly Pt thin films and Pt nanoparticles) by electrochemical deposition techniques. One of the biggest challenges of present century is meeting the energy needs. Electrochemical energy devices such as batteries (for energy storage) and fuel cells (for energy production) are being explored as possible solution to our energy needs. Nanoscale materials have unique properties that can be harnessed for electrode, electrolyte or catalyst for these energy devices [4, 5]. Platinum has been most commonly used as catalyst in fuel cells[6-9]. In order to make fuel cells viable for energy production, the cost involved should be reduced. Since Pt is expensive noble metal and its availability is limited, many researchers focus on lowering Pt catalyst loading and improving utility [10-13].

Thin film catalyst layers with ultra low Pt loading has been under investigation to make high performance catalyst layers[14-16]. It has been demonstrated that the crystal surface, atomic arrangement and surface morphology of Pt has a significant effect on its catalytic

properties[17, 18]. Hence there is a need to gain better control over the formation of these Pt films. Smooth films of platinum is essential to use the limited resources of Pt, furthermore small amount of Pt deposited onto metal electrodes improve their catalytic property. Controlled growth of Pt thin films has been accomplished by vacuum phase techniques such as molecular beam epitaxy, ion beam sputtering etc[19]. Electrochemical deposition method is advantageous over the vacuum phase techniques because of low cost involved and ambient temperature used. However in electrodeposition techniques, layer by layer growth has been possible only upto initial few layers of Pt[20]. The thin film growth resulted in 3D growth and roughening, hence ideal atomic level control could not be achieved. We employed the electrochemical analogue of atomic layer deposition (ALD) called electrochemical ALD to grow atomically Pt thin films. ECALD had been used to form compound semiconductor films[21]. The basic principle of ECALD involves using surface limited reactions (Under Potential Deposition) to grow one atomic layer at a time. In order to make elemental thin films, we propose using novel method 'surface limited redox replacemen (SLRR)' in ECALD cycle using flow cell. In chapter 2, the formation of Pt films using SLRR is demonstrated. Using current time traces and cyclic voltammetry studies, it is shown that we gain atomic level control in the formation of Pt thin films. Studies using electrochemical quartz crystal microbalance and electron probe microscopy are discussed in detail.

In the second part of the dissertation, fabrication of carbon nanotube network to be used as catalyst support for Pt nanoparticles is explored. Carbon nanotube networks showed

promise as catalyst support[22-24]. In chapter 3, the structural and electrochemical properties of carbon nanotubes and their use as catalyst support are discussed in detail. There is a need to control density and distribution of Pt nanoparticles in order to achieve excellent catalytic efficiency. The fabrication of CNT networks that act as support hence becomes significant. We investigated a new method to make CNT networks with varying density by 'Laminar Flow Deposition (LFD)' method[25]. The room temperature depositions of carbon nanotubes on glass slides enable control over their density and electrochemical behavior. This is discussed in detail in the chapter 4. AFM studies and cyclic voltammetry studies are used as evidence for the advantages that the LFD method offers. In order to control the distribution of Pt nanoparticles, engineering of defect sites on the carbon nanotubes is done by acid treatment. The results of acid treatment and its effects on Pt nanoparticle electrodeposition were also demonstrated.

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CHAPTER 2

FORMATION OF PLATINUM FILMS BY ELECTROCHEMICAL ATOMIC LAYER DEPOSITION (ALD) VIA REDOX REPLACEMENT OF CU UPD: FLOW CELL STUDIES

ABSTRACT

An initial investigation about the development of Surface Limited Redox Replacement (SLRR) for Platinum nanofilm formation is described in this paper. SLRR included forming a Cu UPD on Au substrate and then replacing it spontaneously by Pt, at Open Circuit Potential (OCP). This reaction was incorporated into an Electrochemical Atomic Layer Deposition cycle using Flow cell and repeated to form thicker Pt films. The use of both Pt (II) and Pt (IV) were investigated. The OCP changes during the exchange process were monitored and showed that exchange was complete in about 3 minutes. The flow rate of Pt and use of the type of Pt ions used had an effect on the exchange time. The charge for Cu deposition increased from cycle to cycle rapidly in the first few cycles and then slowly after 10-15 replacement cycles. The increase in charge and also the cyclic voltammetry showed that the deposition was not ideal layer by layer. However the extent of roughening reduced after the surface was completely covered by Pt as is evident from the copper deposition charge. Attempts to use electrochemical annealing by Iodine showed that

the exchange efficiency decreased to greater extent in presence of Iodine. Higher driving force (for eg. Use of Lead as sacrificial element) was proposed to increase the exchange efficiency. The results from SLRR of Pb UPD by Platinum and using electrochemical annealing showed surface roughening could be greatly reduced and near ideal layer by layer growth of Pt could be achieved. The resultant films were analyzed by EPMA and they have nearly uniform composition across deposit and no significant amount of copper or lead was present.

INTRODUCTION

Metal thin films find significant applications in many areas such as catalysis, electronics, magnetic data storage, MEMS (Micro Electro Mechanical Systems), and nanodevice construction[1, 2]. One major objective of electrodeposition is to grow 2D thin films. Many physical and chemical properties of metal nanoparticles and nanofilms are dependant on the size and morphology[3]. This has led to lot of research being done in this area. However the area of thin film growth is presently controlled by vacuum phase deposition techniques such as CVD, MBE [4-6]. Electrodeposition provides simple, cost effective, room temperature processes as alternative for growing thin films. However, most electrodeposition of metal films results in 3-D growth and surface roughening, the result of nucleation and growth as a deposition mechanism.Recently there have been a number of studies attempting to grow metal films electrochemically layer by layer. Sieradzki et al. proposed the ideas of Electrochemical Defect Mediated Growth (DMG)[7] and also Surfactant Mediated Growth

(SMG) [8] . Interlayer transport of deposited atoms must be rapid to prevent 3D growth. In DMG and SMG, either co-deposition of the metal of interest with a reversibly deposited metal or predeposition of a sub monolayer of a surfactant metal on top of depositing metal was used (to make the interlayer transport faster). In some more special cases, electro deposition has been used to grow epitaxial metal layers up to few monolayers. Magnussen et al. showed that epitaxial layer by layer growth of Ni on Au (111) could be obtained up to 5ML.

Formation of epitaxial films of noble metals like platinum has proven even more difficult to deposit layer by layer because of cluster formation, the result of their high cohesive energy. A large amount of research has been devoted to the formation of platinum nanoparticles and films because of their importance as electro catalysts and in magnetic data storage application. Uosaki *et al.*showed that it is possible to make quasi two dimensional layer by layer growth of platinum on Au (111) by electrochemical reduction of $PtCl_6^{2-}$ complexes [9]. But growth of optimal 2D platinum films has been difficult. Adzic *et al.* showed atomic level control in the formation of platinum films by using a predeposited Cu UPD layer as a sacrificial layer to subsequently be exchanged for a Pt atomic layer [10]. Copper UPD formed on Au (111) was exchanged for Pt, in a platinum ion solution, at open circuit. This process is referred to as Surface Limited Redox Replacement (SLRR). Subsequent studies have shown that the SLRR can be repeated any number of times, essentially using it in an electrochemical atomic layer deposition (ALD) cycle. The concept

of using SLRR in a cycle was first investigated by Weaver et al., where up to 8 cycles of SLRR were performed in the growth of Pt films on Au [11]. Similar studies were performed to grow Ag films[12]. Electrochemical ALD cycles have been previously developed for the growth of a number of compound semiconductors[13-16] . In the formation of semiconductor compounds, UPD of one element on the other forms an atomic layer and this can be alternated to get films of desired thickness[17]. However, in order to form elemental deposits UPD alone can't be used in an EC-ALD cycle since a metal doesn't UPD on itself. Therefore the concept of galvanic displacement referred to here as Surface Limited Redox Replacement (SLRR) has been incorporated in EC-ALD cycle for the formation of Platinum thin films. This method has been used by our group earlier for UHV studies of Cu nanofilm formation[18] and STM studies of Pt nanofilm formation[19]. The intent of this article is to report some initial studies in the formation of platinum nanofilms, by employing SLRR an electrochemical ALD cycle, using Flow cell. In these studies Cu UPD was used as the sacrificial layer.

EXPERIMENTAL

The electrochemical flow cell system used in these studies was similar to the systems previously described[20] . The experimental setup employed consisted of standard peristaltic pumps (Cole Parmer) and solenoid actuated Teflon valves for solution selection. The pumps, valves and applied potential were controlled by computer using either Lab view or Auto lab program. In order to avoid oxygen problems, solutions were extensively purged with

nitrogen gas. Also, since most tubing is permeable to oxygen, solution delivery tubes along with the valves and solution reservoirs were placed inside a nitrogen purged Plexiglas box.

The flow cell consisted of a planar substrate held away from a counter electrode by a 1mm thick silicone gasket. The deposition area was 3.8 cm^2. Glass microscope slides coated with 5nm of titanium, as an adhesion layer, and 300nm of Au, deposited by vapor deposition, were used as substrates. The glass slides were initially etched in 15% HF for 60 seconds and then rinsed with ultra pure water prior to insertion in vapor deposition chamber. These substrates were annealed at 400°C for 12 hours after deposition. Gold wire was used as the counter electrode and a Ag/AgCl (Bioanalytical Systems, Inc., West Lafayette, IN) was used as reference electrode. All potentials are reported with respect to this reference electrode. Solutions used include 1mM K_2PtCl_4 , 1mM H_2PtCl_6,50mM $HClO_4$, 1Mm $PbClO_4$, 0.5M H_2SO_4 and 1mM KI.

The electrochemical ALD cycle consisted of the following steps: Cu solution was pumped through the cell at chosen under potential for fixed time to get one monolayer of Cu. Monolayer in this paper refers to one adsorbate atom for every substrate atom. The Pt ion solution was then pumped through the cell for 180 seconds, at OCP, to allow for the replacement of Cu UPD. Rinsing with the blank solution (Sulfuric acid) completed the cycle. The above steps constitute one ALD cycle. The Cu UPD resulted in a coverage of 0.67 monolayer (ML), defined with respect to the number of Au surface atoms on the substrate. Ideally, 100% of the electrons in the Cu would end up in Pt atoms on the surface, or Pt

coverage of 0.67 ML every cycle, When Pt (II) ions were used and a Pt coverage of about 0.33ML every cycle when Pt (IV0 ions were used. As Cu UPD is formed on both gold and platinum , this process can be repeated any number of times to obtain platinum films of desired thickness. Characterizations of the films were done by cyclic voltammetry, EPMA, Atomic Force Microscopy and ellipsometer.

RESULTS AND DISCUSSIONS

The electrochemical ALD of Platinum thin films was accomplished by utilizing Surface Limited Redox Replacement of a sacrificial element, Copper in this case. Each EC-ALD cycle comprised of depositing a Monolayer of the sacrificial element Cu and then replacing it with Pt ions at Open circuit potential; the difference in electrode potential of Cu UPD and Pt ion reduction being the driving force. The schematic of ideal Pt film formation is shown in Fig 2.1. Gold was chosen as substrate because of its stability and well-studied electrochemistry. Copper deposition potentials were determined from Cu cyclic voltammetry on Au. Copper Cyclic voltammetry on polycrystalline gold resembled the ones from literature (Fig 2.2). Two deposition potentials for Cu UPD 0.05V, 0.1V were investigated. Then Cu UPD was replaced using Pt (II) / Pt (IV) ion solutions. Cu being less noble was oxidized in the presence of Pt cations and Pt ions were simultaneously reduced and deposited on the substrate as shown by the reactions [I] and [II].

$$Cu_{UPD} + Pt^{2+} \longrightarrow Cu^{2+} + Pt \qquad [I]$$

$$2Cu_{UPD} + Pt^{4+} \longrightarrow Cu^{2+} + Pt \qquad [II]$$

The Platinum reduction is dependant on the electrons provided by copper oxidation. Therefore when Pt (+2) was used each ECALD cycle should result in one monolayer of Pt and when Pt (+4) was used each cycle result only in half monolayer of Pt. EC-ALD cycle involving SLRR is shown in figure 2.3. Fig 2.3 shows the current and potential vs. time for third and fourth replacement cycles. First, Cu UPD was formed at 0.05V for 15 seconds and then Pt (+4) solution was flowed for 3 minute. Rinse with blank solution completed the cycle.

The Copper deposition charge was calculated for each cycle by integrating the current time trace. The amount of Cu deposited was calculated in monolayer with respect to Au. The amount of Cu was expected to be the same in all the cycles since UPD potential was applied. However the amount of copper deposited increased a lot in the first few cycles and then increased at lower rate after that. The increase in copper deposition charge was an indication that Pt film surface area was increasing as the cycle number increased. The growth was hence not ideal layer by layer. However the increase in Cu deposition charge became reduced after certain number of cycles. Figure 2.4 shows the copper deposition charge vs. cycle number when Cu was deposited at 50mV. When Pt (+4) was used the charges reached a steady value after about 15 cycles whereas when Pt (+2) was used the charge reached steady value after about 8 cycles. This pattern leads us to believe that once the surface becomes completely covered by Platinum, the surface roughening was reduced though not completely eliminated.

It is a well established fact that sufficient surface mobility and interlayer mass transport are critical in 2D growth of thin films[21].The surface diffusion rate of Platinum atoms have been found to be slower than other metal elements[9].Slower lateral growth rate is a hindrance in obtaining a continuous layer of Pt from one deposition cycle. When considering the interlayer transport; the high potential energy barrier controls the movement of atoms as they land on top of an island. The atoms have to cross the barrier to reach lower level from top of island. Hence when the Platinum ions are entered in the flow cell; the Pt atoms tend to deposit on top of already formed island. These atoms need to overcome the barrier to hop off the island. The presence of Cu UPD was expected to act like a surfactant and help improve the mobility of depositing atoms with respect to already formed islands resulting in layer by layer growth. However the SLRR could not completely overcome the slower diffusion rate and the cohesive energy of Pt. In order to increase the surface mobility of Pt Electrochemical annealing using Iodine was proposed[19]. Under the present conditions the exchange efficiency of SLRR reduced to a large extent in the presence of Iodine as is evident from EPMA, EQCM and Cyclic voltammetry data and is discussed in later section.

The change in the OCP was monitored during the exchange, providing an idea of how much time was required for the exchange. The OCP changed from the potential used for Cu deposition, positive to one corresponding to a Pt surface, generally above 0.6V within three minutes, as shown in Figure 2.2 .No Cu was expected to be present on the surface at such positive potentials, as based on Cu voltammetry on Au, under those conditions. However few

experiments tried with holding the Pt solution instead of flowing for entire 3 minutes showed that Pt (+2) needed more time for completely replacing Cu. The EPMA data also showed lower amount of Pt present in the film when solution was not flowed during entire exchange time. Extended exchange time of about 5 minutes was needed in case of holding Pt (+2).

Platinum surface area after 25 cycles was determined by cyclic voltammetry (shown in Figure 2.5). This shows that the surface area of Pt increased to about 7 times the original surface area. The cyclic voltammetry obtained in case of either Pt (+2) or Pt (+4) shows the same extent of roughening. Initially it was expected that use of Pt (+2) will give less rough surface since each replacement cycle gives one monolayer of Pt. In case of Pt (+4) two replacement cycles were needed to get one monolayer. At the end of the first cycle, half monolayer of Pt is formed and during the second cycle the depositing Cu can deposit either on gold or Pt and hence resulting in 3D growth. However from the charge calculations and cyclic voltammetry, Pt (+2) and Pt (+4) behave the similar way. The charge for copper deposition also correlates to this increase in area. The Cu deposition charge stays about 3-3.5ML after initial cycles. Considering the fact that Cu UPD covers the surface only partially (about 0.6 ML), these numbers seem to match. Surface area was also determined from the Hydrogen adsorption/desorption charge (Figure 2.6) and Pt Oxide reduction charge (Figure 2.7) after every five cycles. The pattern of increase in surface area in both cases matched with that of the surface area measured by Cu deposition charge,

The exchange efficiency could not be calculated from coulometry since there is no current measured during exchange process and also Pt stripping form Au is difficult. Electrochemical Quartz Crystalline Microbalance (EQCM) studies were also done to compare the mass changes during exchange process and hence can be utilized to investigate the efficiency of exchange process. Figure 2.8 shows the Copper deposition charge and Pt mass change calculated in Monolayer with respect to Au for the first ten cycles. The calculated Cu deposition charge matched with the mass change for Pt deposition. This proved that the exchange efficiency was almost 100%. In order to increase the surface mobility of Pt atoms, Iodine solution was flowed in the cell after each replacement cycle and held in the cell for 2 minutes. Figure 2.9 shows the mass change in frequency and the current time trace in the SLRR cycle. The Cu deposition charge didn't increase from cycle to cycle as shown in Figure 2.10. However the mass changes calculated during the exchange process showed that exchange efficiency was reduced to almost 50%. The use of Iodine was also examined for more number of replacement cycles in the Flow cell (25 cycles). The cyclic voltammetry showed prominent Au peak present even after 25 cycles. The EPMA data also proved this fact. Though other studies have showed that presence of Iodine did not affect metal deposition, in this case the redox replacement could not be as efficient in presence of Iodine. The redox replacement occurs due to the difference in redox potentials of Pt and Cu UPD as already mentioned. In the presence of Iodine more driving force had to be applied.

The study presently being done in this group focuses on using Pb as a sacrificial layer and using Iodine for electrochemical annealing.

CONCLUSION

The above studies have shown that EC-ALD can be employed to form Pt films by surface limited redox replacement. The exchange process was investigated by monitoring the open circuit potential and also studying the effect of flow rate. EQCM showed that the exchange was almost 100% efficient and all the Cu atoms were replaced by Pt. This fact was also supported by the EPMA data that showed that an insignificant amount of Cu was present in the Pt films. However the amount of time needed for the complete exchange depended on the type of Pt ion used, the cycle number and also the flow rate. The charge calculations and cyclic voltammetry showed that the Pt film growth is not ideal layer by layer in the initial cycles. Though atomic level control was achieved, the behavior of Platinum showed that in order to overcome the kinetic issues further improvement need to be done and detailed investigation of Electrochemical annealing is proposed.

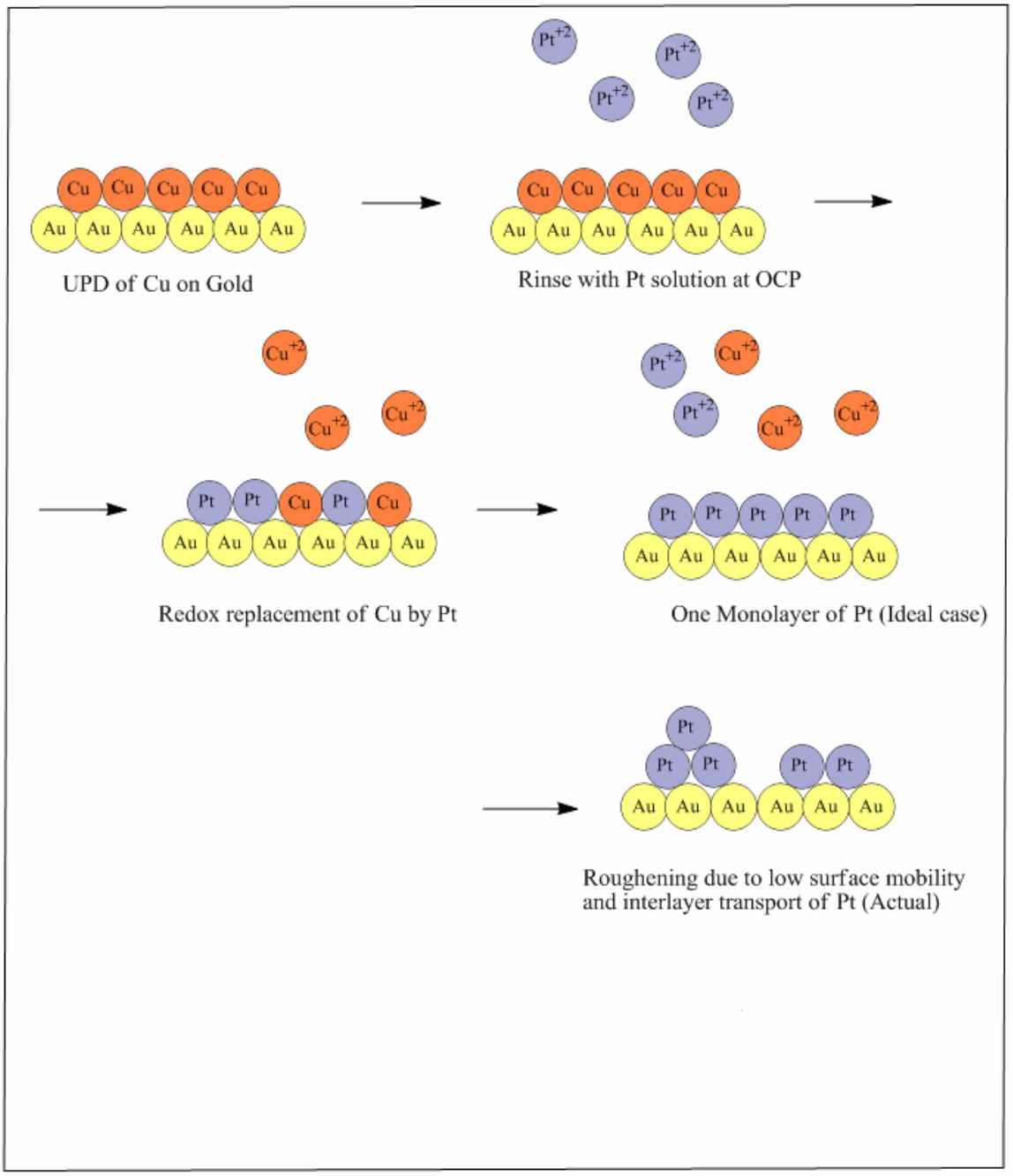

Figure 2.1 Schematics of Surface Limited Redox Replacement

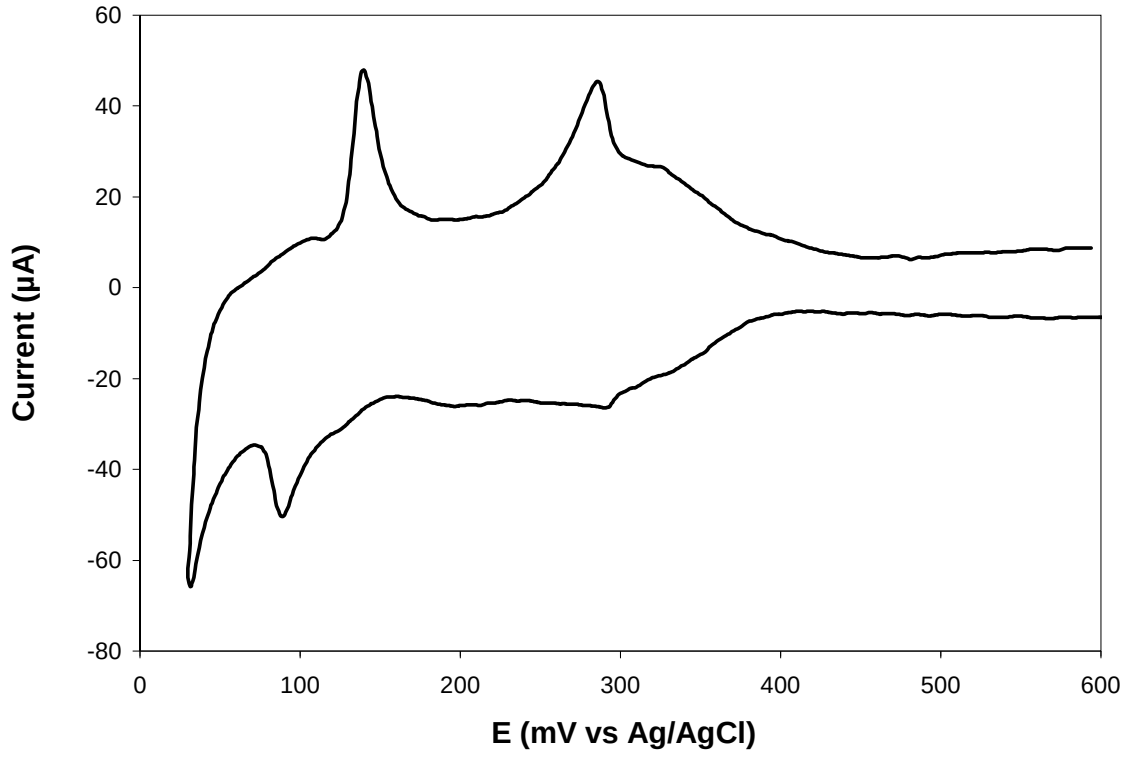

Figure 2.2 This figure shows the cyclic voltammetry of Cu on Gold vapor deposited on Glass.

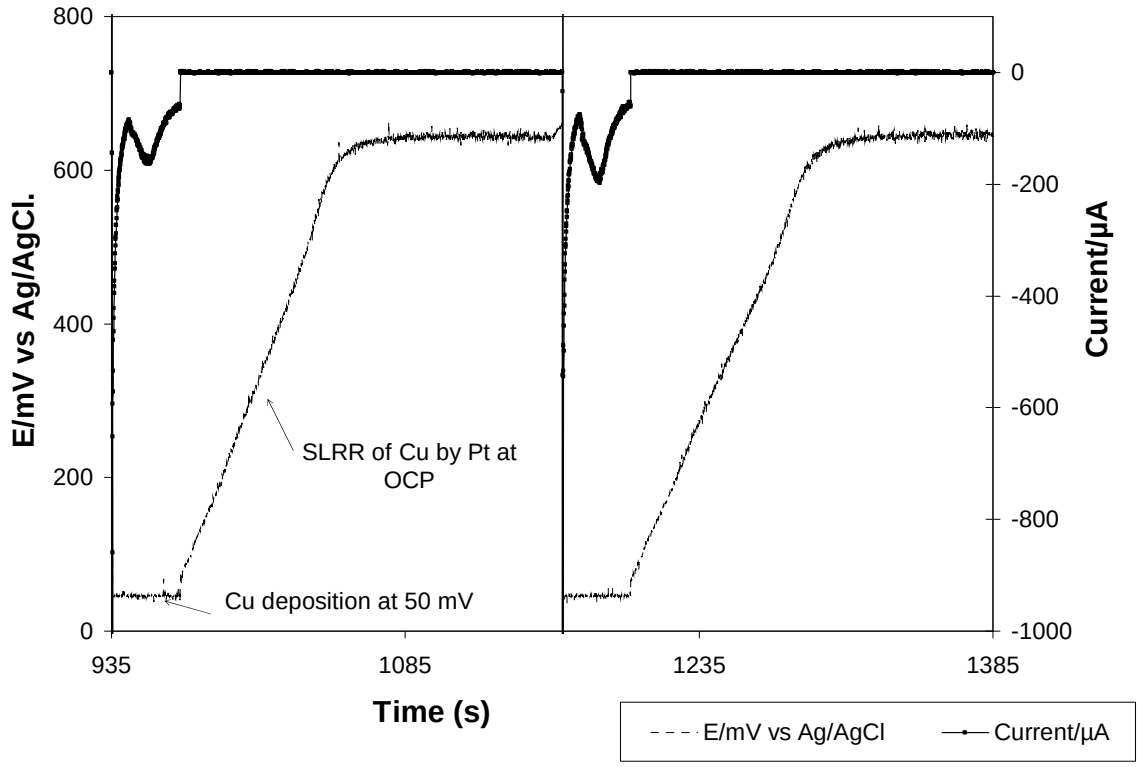

Figure 2.3 Current and potential vs. time for one SLRR Cycle

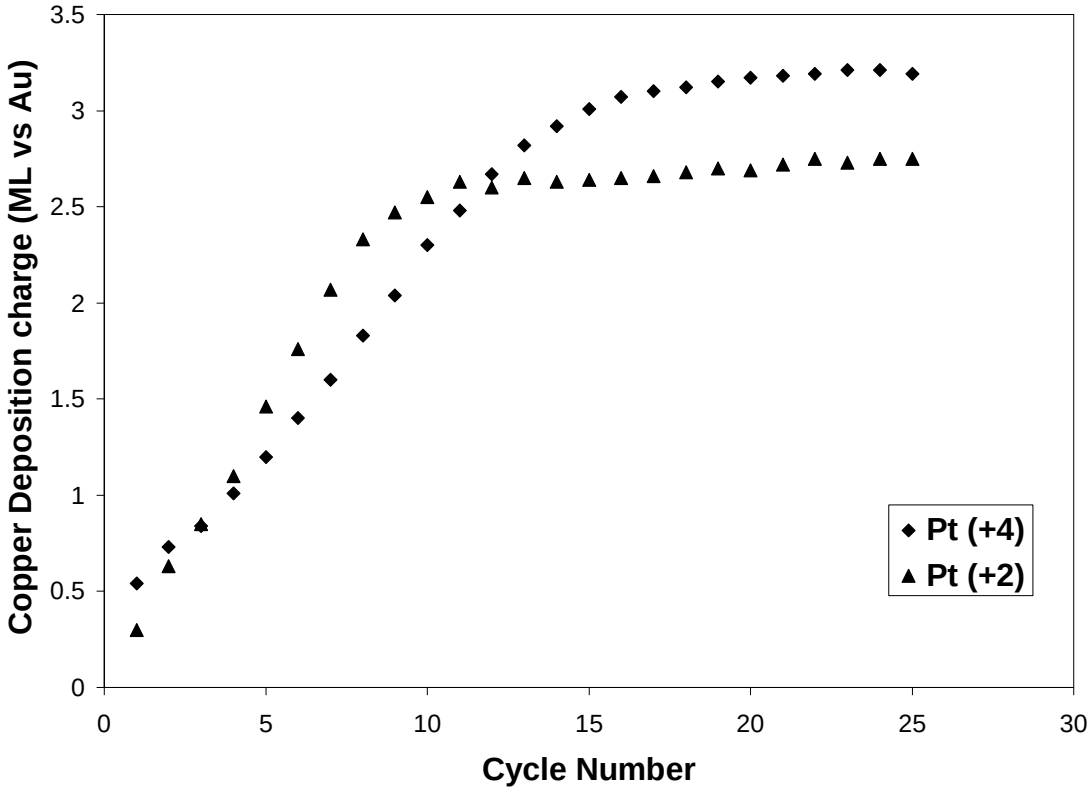

Figure 2.4 Copper deposition charge vs cycle number.

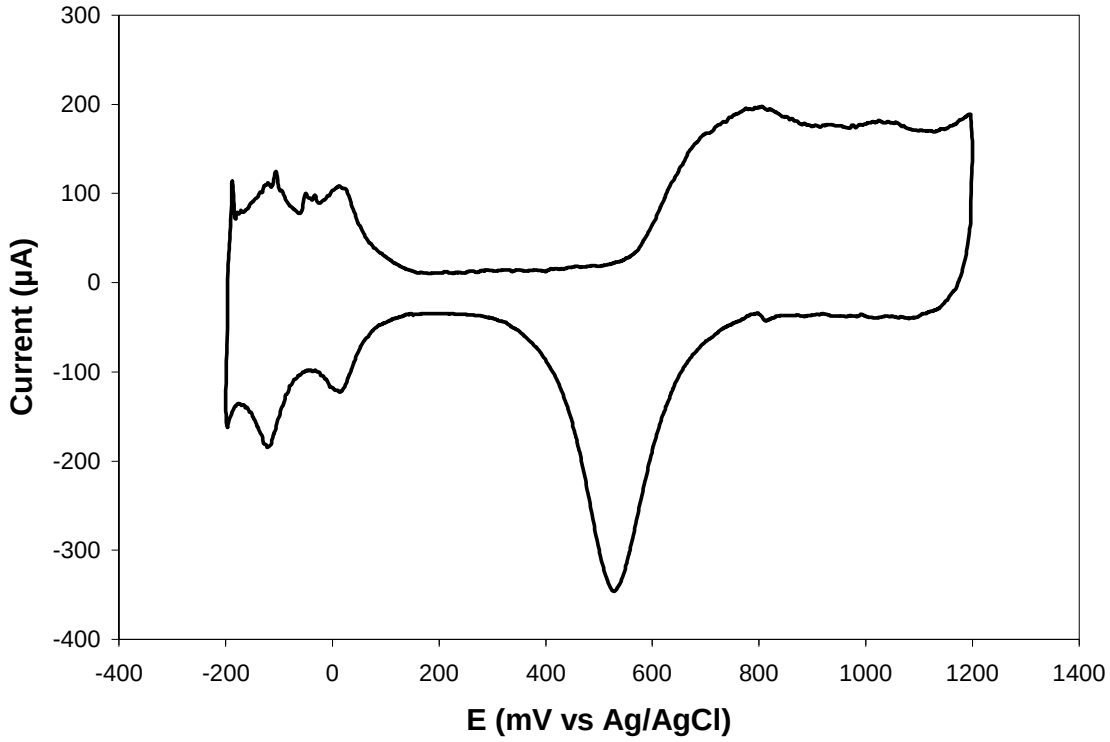

Figure 2.5 Cyclic voltammetry of the Platinum film formed by SLRR (25 cycles) in 0.5M Sulfuric acid

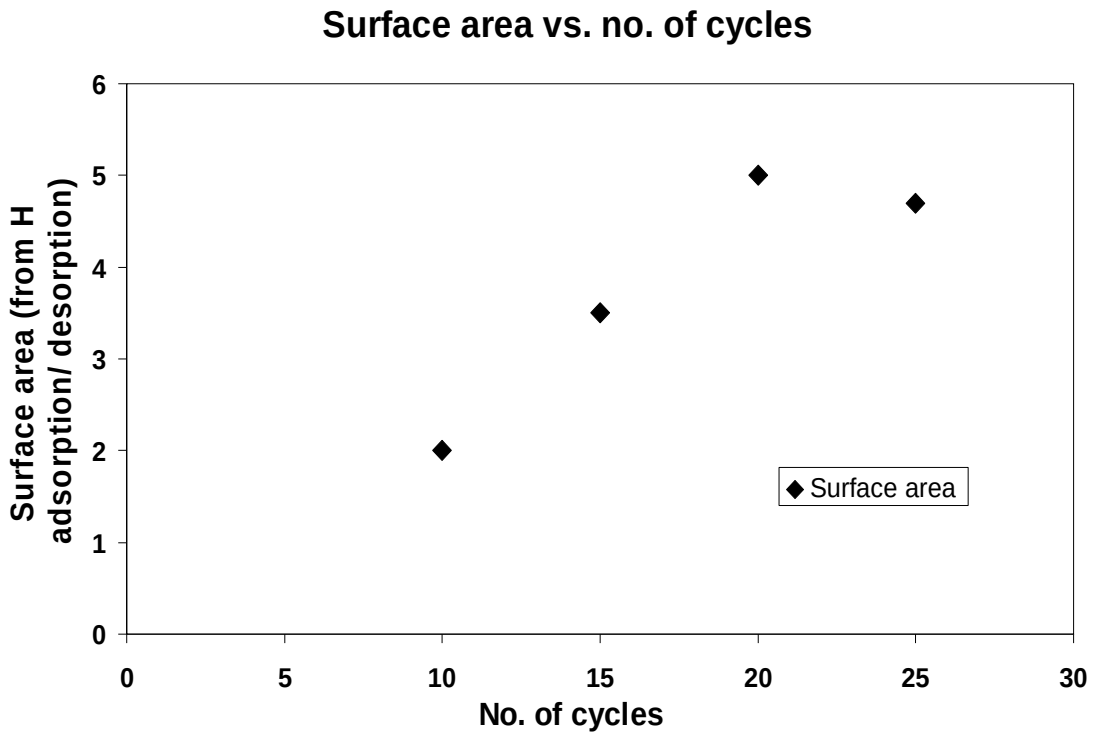

Figure 2.6 Surface area determined from the Hydrogen adsorption/desorption charge

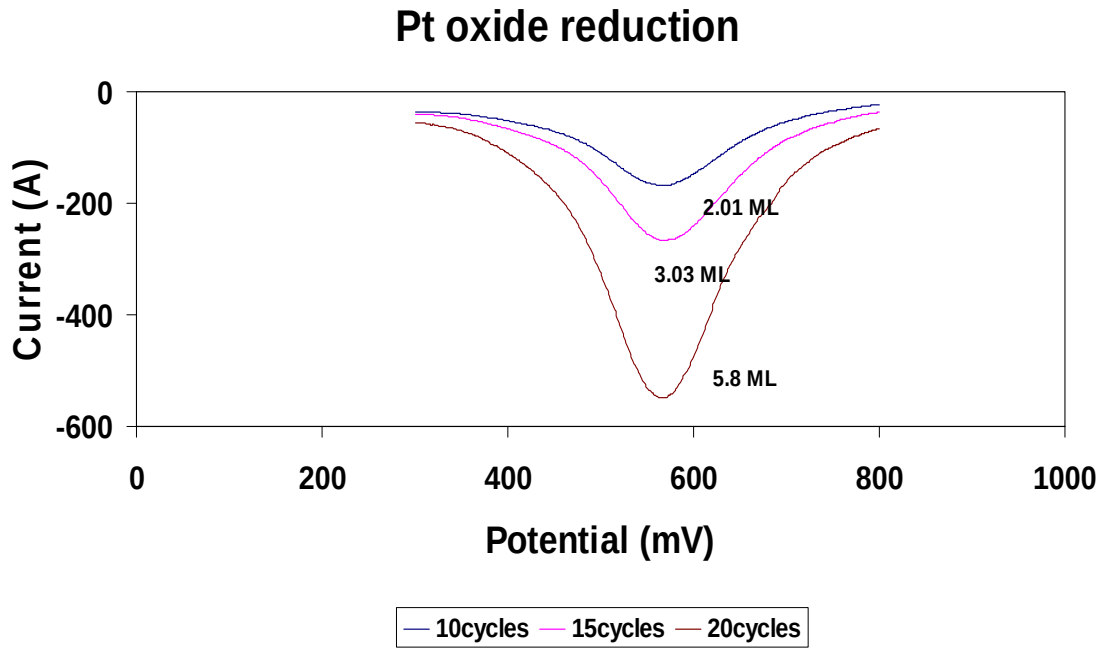

Figure 2.7 Surface area determined from the Pt Oxide reduction charge

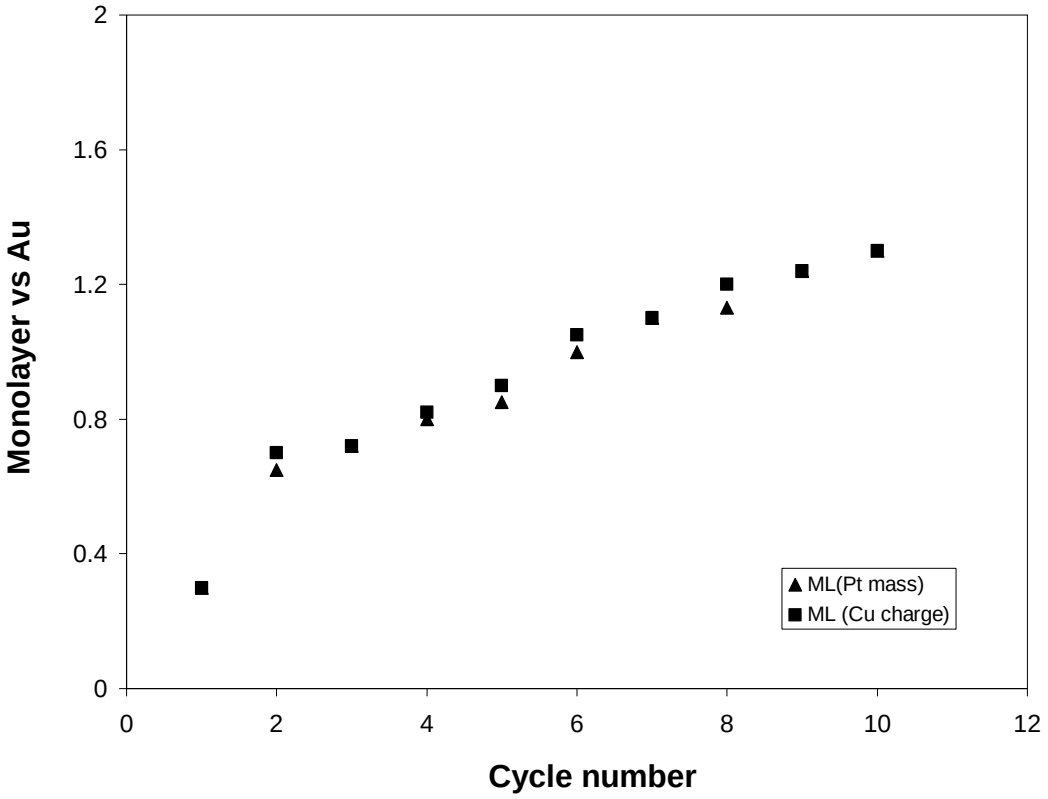

Figure 2.8 Copper deposition charge and Pt mass change calculated in Monolayer with respect to Au for the first ten cycles. Pt mass change was determined by the frequency change of the Quartz crystal Microbalance.

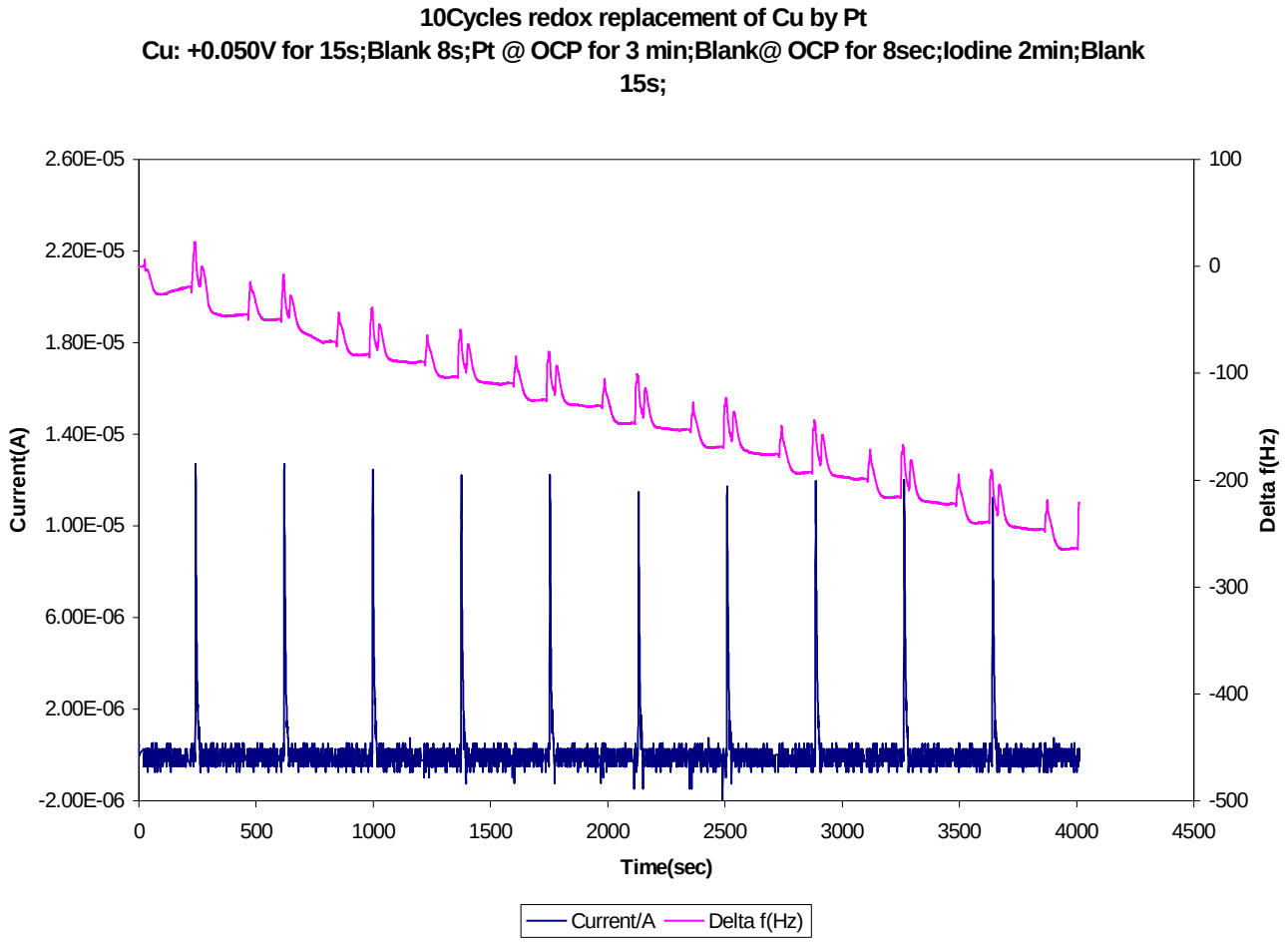

Figure 2.9 Current and frequency change for SLRR of Cu UPD by Pt measured in EQCM.

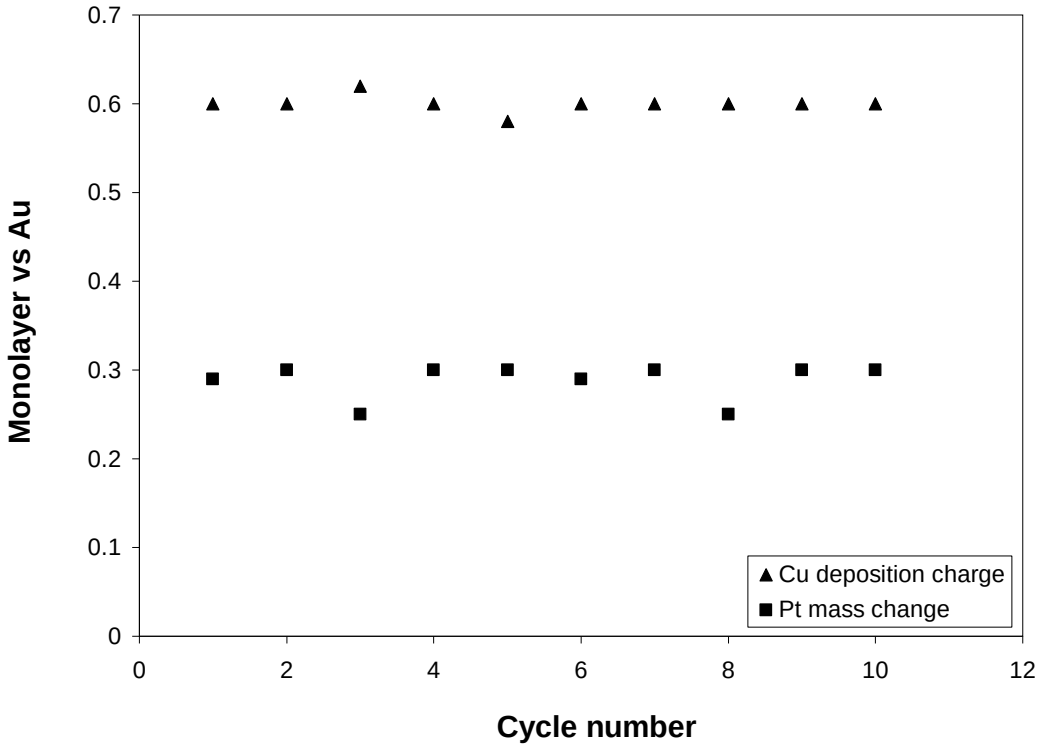

Figure 2.10 Copper deposition charge and Pt mass change calculated in Monolayer with respect to Au for the first ten cycles. Iodine was flowed after every replacement cycle. Pt mass change was determined by the frequency change of the Quartz crystal Microbalance.

EPMA data:

Experiment	Pt ion Solution	Pt (+4) Flowed		Pt(+2) Flowed		Pt (+4) No flow	
conditions	Iodine	No		No		No	
Spot no. ↓	Atomic % →	Pt %	Cu %	Pt %	Cu %	Pt %	Cu %
1.		12.29	0.10	27.9	0.92	8.28	0.37
2.		13.35	0.53	26.89	0.71	8.47	0.36
3.		12.25	0.45	27.8	0.49	8.24	0.0
4.		13.01	0.33	29.57	1.05	9.21	0.45
5. (Inlet)		36.45	0.94	87.22	1.10	14.91	0.80

Table 2.1 lists the atomic % of Pt and Cu as measured with EPMA for deposits formed with different Pt ions and also different flow conditions. When Pt (+4) was used for exchange, the films have ~ 13 % of Pt after 25 cycles whereas the films have ~ 27% when Pt (+2) was used. When solution was not flowed during the entire 3 minutes, the films showed lower Pt %.

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CHAPTER 3

CARBON NANOTUBES IN ELECTROCHEMISTRY

A new era of interest within the field of nanotechnology began with the identification of carbon nanotubes (CNTs) in 1991[1-3].Iijima reported microtubules of graphitic carbon with concentrically arranged cylinders that constitute the Multi Walled Carbon Nanotubes (MWNTs)[4]. In 1993, single walled carbon nanotubes (SWNTs) were reported by Bethune and Iijima separately[5, 6].The reports of this new type of carbon fiber triggered intense research focused on harnessing the unique properties of these nanostructures.

CARBON NANOTUBES AND ELECTRONIC STRUCTURE

Carbon Nanotube (CNT) is a sheet or sheets of graphene rolled around a central axis and the center of the CNT is hollow[7].They belong to the family of fullerenes. CNTs are either Single walled or Multiwalled. Single walled carbon nanotubes (SWNTs) consist of a single sheet of graphene seamlessly wrapped into a cylinder with diameter on the order of 1.4nm[8]. Multiwalled nanotubes (MWNTs) consist of concentric array of such nanotubes with diameter on the order of 10-20nm[8].

In our group, we focus on the electronic and electrochemical behavior of SWNT networks. Therefore the properties and applications of SWNT are discussed in detail in this section. The figure 1 shows the schematic of a two dimensional graphene sheet with

hexagonal array of carbon atoms that can be rolled into a cylinder to form SWNT. Though the SWNTs are structurally similar to graphite which is a semiconductor with zero band gap, SWNTs have different electronic properties. The unique relationship between structure and electronic properties of SWNTs has been well established[9].The SWNTs are either metallic or semi conducting depending on the diameter and helicity of the graphitic ring[10-12]. The diameter and helicity are characterized by roll up vector C_h= na1 + ma2 that connects equivalent sites on a 2D grapheme sheet. In this equation, a1 and a2 are the graphene lattice vectors as denoted in the figure and n, m are integers. The SWNTs fall into 3 different categories: armchair type (n=m) or zigzag type (m=0 or n=0) or chiral type (any other n,m). Armchair type SWNTs are metallic, for the other two types (chiral and zigzag) they are metallic if n-m = 3*l* where *l* is an integer or semi conducting if n-m ≠ 3*l*[13].

SYNTHESIS AND PURIFICATION

There are three common methods for growing SWNTs: laser ablation,[14] electric arc discharge,[15, 16] and CVD[17-20].Laser ablation involves the creation of SWNTs during condensation of laser-vaporized carbon/metal mixtures at 1200 °C. An electric arc discharge method, a spark strikes between carbon cathode and anode electrodes in the presence of metal catalyst. CVD involves the catalytic decomposition of a carbon containing gas at nanoparticles of a transition metal, which act as a catalyst. Today, variations on the CVD method are commonly used to form SWNTs[21-27].

Regardless of the growth method, there is always a significant amount of impurities present (graphitic debris, catalyst particles and fullerenes). These impurities often interfere with the desirable properties of SWNTs. Therefore, there has been extensive recent investigations in removal of impurities and several highly effective purification methods, resulting minimal damage to SWNTs: flocculation[28], microfiltration[29, 30], chromatographic procedures[31-33] and centrifugation[34, 35].Multiple centrifugation cycles has proven to be an effective method of purifying SWNT soot, without modifying the SWNTs significantly[36].2-Dimensional networks formed from SWNTs that were purified by this method showed the electrical response typical of undamaged SWNTs in electrical devices.

The solubility of SWNT material may be improved without covalent modification or with various surfactants. This method preserves the structure and properties of SWNTs to a much greater extent. Surfactants that show promise in this process include DNA[37, 38], polymers[39], and various soaps[40]. Sodium dodecyl sulfate (SDS) is one of the most common surfactants used to form aqueous suspensions of SWNTS. SDS coats SWNTs with micelles, forming a hydrophobic core and hydrophilic surface, thus assisting in homogenization in water. After the addition of the surfactant, sonication (bath or cup-horn) is used to disperse SWNTs in the solution. The micelles can then be removed in subsequent steps.

The low solubility of SWNTs is another major challenge to mass production of SWNT-based devices. This insolubility is due in large part to strong Van der Waals interactions between nanotubes, which results in aggregation. Further, harsh methods of

purification involve oxidation with a strong oxidizing acid, hydrothermal treatment along with extraction and oxidation[41] and annealing at high temperature in the presence of O_2. Many studies show combinations of these protocols are often required for effectively increasing SWNT solubility and removing impurities from as-produced (AP) SWNT material[42-48].In most cases, oxidative purification protocols have the side effect of increasing aqueous solubility due to formation of sidewall defects. Excessive defect formation may limit the use of SWNTs in many applications; introduction of a single defect along the sidewall of a pristine metallic SWNT was found to increase its electrical resistance and cause semiconductive behavior[49]. Acid treatment typically involves use of a strong oxidizing agent[41].SWNTs have been refluxed with HNO_3, H_2SO_4, HCl or mixtures of these acids[41, 43, 47]. Many groups have varied many parameters for this treatment such as duration, concentration, and repeated cycles. It is known that use of these processes can cause defects and/or shortening of SWNTs. Oxidation usually results in formation of the carboxylate group on the surface of the tube.

ELECTROCHEMICAL PROPERTIES OF CNTS

Nanoelectrodes offer various interesting properties that can be put to use in a number of electrochemical, biological, chemical applications[50, 51]. The fact that carbon nanotubes are nanoscaled electrodes makes them an interesting system to study in order to obtain a better understanding of the effect of the various types of diffusion in an electrochemical system.

Therefore, understanding the basic electrochemical properties of SWNTs is the key to making improved electrodes for a wide variety of applications.

The diameter of SWNTs can range from 0.4 to 2 nm. SWNTs can be either conducting or semi conducting based on their chirality and diameter. Studies have shown that SWNTs are comprised of a mixture of two-thirds semi conducting and one-third metallic tubes[8, 52-54]. Electrochemical studies have shown that semi conducting and metallic SWNTs exhibit similar electrochemical behavior[55].

The electrochemical behavior of graphite yields some insight into SWNTs. In case of graphite, electrode kinetics are faster at the edge-plane than at the basal plane[56]. Electrochemical pretreatment of glassy carbon electrodes produces various functional groups such as quinoid, carbonyl and carboxylate sites[57, 58]. In SWNTs, such functional groups serve as axial ligands for metal deposition. Others researchers have observed a similar behavior for SWNTs[59]. Further, the presence of oxygenated functionalities at the ends of the SWNTs facilitates electron transfer. Pretreatments done for either purification, or to introduce oxygen functionalities, play a significant role in determining the electrochemical activity of SWNTs. SWNTs that have been treated to open the ends by oxidizing the tips have the various aforementioned defects. Therefore, oxidatively treated carbon nanotubes have two distinct regions that contribute to their electrochemical behavior: the walls of the nanotubes that are comparable to the basal planes of graphite (largely un-reactive) and the ends are comparable to the edge planes of graphite (highly reactive). Both the regions have distinct

electrochemical properties due to the difference in chemical bonding; the defect sites at the ends of SWNTs provide electrochemically active sites for redox reactions.

Jun Li et al recently reported the electrochemical study of SWNT paper[60]. They concluded that the packing density of SWNTs and pretreatment define the performance of electrodes. The $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ couple was used to demonstrate that the redox reaction takes place not only at the outer surface of SWNTs but also at the interior of nanotube ensembles. Hence, they behave as three-dimensional electrodes. The same group compared two different densities of MWNT arrays[61]. The high-density arrays (~ 3 x 10^9 SWNTs cm^{-2}) behaved like a macro-scaled electrode because of overlapping of diffusion fields between SWNTs, and displayed peaks typical of diffusion at a conventional macroscopic electrode. However, for low density samples (~ 1 x 10^8 SWNTs cm^{-2}), the electrodes displayed behavior indicative of a mix of radial and laminar diffusion. However, the CV for low-density network also indicates the presence of diffusion limited behavior, as the network has mixed micro and macro electrode properties.

ELECTRODEPOSITION OF METAL NANOPARTICLES ON CNTS

Electrodeposition offers many advantages over high-temperature metal deposition for metal nanoparticle formation on SWNTs. One of the most significant advantages of electrochemical deposition is the ability to control size and distribution of nanoparticles by varying potential, time or solution concentration. Most studies involving metal nanoparticle electrodeposition focus on noble metals such as Ag, Au, Pt and Pd, [62-68] with a few

exceptions Ni, Cu,[69-71] primarily due to the need for components of alternate energy sources. Electrodeposition of metal nanoparticles on carbon nanotubes depends on various parameters, such as pretreatments, method of manufacturing for SWNTs, type of SWNTs, distance of the nanotubes from contact electrode, density of SWNTs in network etc.

As mentioned in the previous section, oxygen functionalities serve as axial ligands for metal nanoparticle precursors to bind to the SWNTs. Therefore, the most common pretreatment method involves treating them with strong acids or oxidizing agents such as H_2SO_4/HNO_3, H_2SO_4/H_2O_2, HNO_3, O_3, and $KMnO_4$. This is essentially a controlled method of damaging the tubes[72-74].

An alternative pretreatment method, involving a more gentle electrochemical oxidation, was studied by Guo and Li [59, 64]. Oxide functional groups at defect sites on the ends and sidewalls of SWNTs were produced by cycling electrochemical potential in 0.5M sodium sulfate, following a similar procedure used for activating glassy carbon electrodes[58]. They employed a three-step process to deposit Pd and Pt nanoparticles on the SWNTs: 1) pretreatment by potential cycling 2) formation of octahedral complexes of Pt(IV) or Pd(IV) 3) conversion of surface complexes to metal atoms by additional potential cycling. The density of Pt nanoparticles was higher on the thicker bundles than on thinner bundles because of the presence of a higher number of carboxylic acid groups on thicker bundles.

Dekker and coworkers have studied the electrodeposition of Au, Pt and Pd on SWNT nanoelectrode arrays deposited on non-conductive supports[66]. Electrical contact to the

SWNT network was made through vapor deposited Ti contacts. The average nanoparticle size could be controlled by varying the applied potential and metal salt concentration. Uniform sized nanoparticles were obtained at sufficiently negative potentials. The results also illustrated that even when the SWNTs were far from the Ti contact electrode; they were plated equally well showing that the nanotube-nanotube junction was not a source of significant potential loss. However, subsequent reports by other researchers have indicated that there is some loss of potential, due to inter-nanotube junctions, for larger networks[75].

Day et al have investigated the electrodeposition of Ag and Pt on high density SWNT networks,[75] forming either dispersed nanoparticles, or continuous metal nanowires on these networks, depending on the distance from contact electrode. The driving potential for electrodeposition decreased with increased distance from the metal contact electrode. Therefore, the rate of nanoparticle nucleation and growth increased at close proximity to the contact electrode, resulting in continuous nanowires, rather than separate nanoparticles, near the contact electrode. Day and coworkers have also investigated the parameters controlling nanoparticle number density, size and distribution in the case of Pd and Pt deposition on SWNT networks[67]. Pd and Pt were deposited at various potentials and demonstrated that deposition potential and time are important factors in determining nanoparticle size and density. One interesting observation they made was that when Pd deposition was done at very low deposition overpotentials, nucleation took place preferentially at defect sites on

SWNTs. However, when higher deposition overpotential was applied, nanoparticle deposition at pristine regions of the SWNTs was also initiated.

Chen et al proposed changing the size of Pt nanoparticles by changing the viscosity of the electrolyte and adjusting the number of potential pulses[76]. Aqueous solutions of H_2PtCl_6 were used as electrolyte and viscosity of the solution was varied by adding different quantities of glycerol. Tuning the viscosity was proposed as a means to control the growth of Pt nanoclusters due to controlling the diffusion of Pt (IV) ions. The shape of a nanoparticle is significant because catalytic and sensing properties depend on the arrangement of surface atoms. Studies to control the shape of the Pd nanoparticles electrodeposited on SWNTs have indicated that smooth and flat facets of Pd nano-cubes were electrodeposited on SWNTs on porous anodic alumina templates at sufficiently lower current densities 1.0 mA cm^{2}-[77].

Arai and coworkers have reported electrodeposition of Cu and Ni on carbon nanotubes[69, 70]. For the case of Ni deposition, they demonstrated selective deposition of Ni on the ends and defect sites of MWNTs. This has been attributed to the high electrical conductivity of MWNT in the axial direction and easy electron transfer in defect sites. Ni-coated SWNT nanowires were also made by electrodeposition on SWNTs supported on alumina membranes[78]. This work demonstrated the efficacy of the use of MWNTs in formation of the types of nanoscaled electrical contacts necessary for molecular computing applications.

In the application of carbon nanotubes as field-effect transistors, reduction of the contact resistance between metal electrodes and SWNTs is crucial. Electroplating of Au on semi conducting SWNTs was found to reduce the contact resistance between semi conducting SWNTs and Pd electrodes on which the nanotubes were fabricated[79].

CHEMICAL DEPOSITION OF NANOPARTICLES ON CARBON NANOTUBES

Electrodeposition offers good control over the density and size of nanoparticles formed on CNT support, however several other methods to make CNT/Nanoparticle hybrid using chemical, electroless methods had also been investigated in detail. The spontaneous reduction of metal ions on the side walls of SWNTs was shown by Dai et al[80]. Deposition of nanoparticles took place as a result of direct redox reactions between CNTs and metal ions. SWNT samples grown on silica substrate were immersed in metal salt solution (Pt/Au). Spontaneous oxidation / reduction takes place due to the difference in redox potentials between SWNT and metal ion. Metal ions get reduced and deposit on the side walls of the SWNT. This group was able to show that metal nanowires could be formed using this templating method. Surface modification of CNTs using silane derivatives were done to incorporate sulfonic acid-silicate groups that act as anchors for metal ions[81].Pt nanoparticle deposition was accomplished by reducing platinum precursor using glacial acetic acid. Pt particles were shown to deposit homogeneously with size range of 1-2nm. Noncovalent functionalisation of CNTs using silane derivatives (3-aminopropyl triethoxy silane) had been employed by other researchers to form metal nanoparticle/CNT hybrid[82, 83]. Dong et al,

showed that noncovalent functionalisation could be achieved through embedding the CNTs in polysiloxane shells. The 3-Aminopropyl triethoxy silane molecules adsorbed onto the nanotube surface could be polymerized by acid catalysis and form thin polysiloxane shells.Negatively charged gold nanoparticles are anchored to the nanotube surface by electrostatic interaction with the protonated amino groups[83]. Insitu preparation of palladium nanoparticles by reducing palladium acetate with the aid of surfactant like Sodium Dodecyl Sulfate (SDS), and subsequent deposition onto CNTs was demonstrated by Tagmatarchis et al[84]. SDS played dual role: it helped in solubilization of CNTs as well as reduction of palladium acetate to Pd nanoparticle.

APPLICATIONS OF NANOPARTICLE/CNT IN CATALYSIS AND SENSING

One of the most significant applications of SWNT/nanoparticle materials is in the area of catalysis[85, 86]. The nanometer scale dimensions of metal nanoparticles facilitate enhanced diffusion rates and fast electron transfer kinetics; these two properties have the potential to revolutionize the field of catalysis. Therefore, various research groups have done extensive studies on the effect of using carbon nanotube as catalyst.

Pt nanoparticles supported on SWNT electrodes have shown improved catalytic properties for both methanol oxidation and oxygen reduction reaction[87]. SWNTs deposited on optically transparent electrodes (OTEs) were used as substrates and Pt nanoparticles were electrodeposited on these SWNTs. Methanol oxidation currents were about 10 times higher when Pt nanoparticles were supported on SWNTs compared to the same amount of Pt

deposited on OTEs. The current values measured for oxygen reduction reaction were higher by a factor of 1.5 for Pt nanoparticles supported on SWNT compared to unsupported Pt particles.

Use of bimetallic catalysts such as Pt-Ru has been commonly accepted in order to improve catalytic efficiency and to protect Pt from CO poisoning. One of the first few studies done on electrodeposition of Pt-Ru on SWNTs was done by He et al[88]. Uniform distributions of catalyst nanoparticles were obtained, with size ranging from 60-80nm by potentiostatic method from 0.5M H_2SO_4 aqueous solutions with ruthenium chloride and chloroplatinic acid at -0.25 V. Investigation of the effect of the Pt/Ru ratio on the electrocatalytic activity on methanol oxidation was done. Maximum current density was obtained at the Pt/Ru ratio of 4:3. The Pt-Ru particles thus showed higher catalytic activity and stability than that of pure Pt nanoparticles. Therefore, modification of SWNTs with crystalline nanoparticles is a promising route to creation of enhanced catalytic materials.

Highly dispersed Pd nanoparticles on SWNT bundles prepared by electrodeposition have exhibited high catalytic activity for hydrazine oxidation and implied that if SWNTs are used as a support, the loading of precious metal catalysts could be minimized[59]. Use of MWNT paper as a Pt catalyst support was investigated by Wang et al[89]. They concluded that with smaller sized Pt particles (2.5 nm), the performance of fuel cells could be improved. Most of the studies involved the use of random networks, bundles, or SWNT paste electrodes.

Aligned networks of SWNTs will enable better control of the density and distribution of nanoparticles. An interesting liquid-phase deposition technique to align carbon nanotubes have been proposed by Lay et al[36, 90]. The directional solution drying procedure presently used by our group to make SWNT electrodes for metal NP supports involves depositing SWNT solutions on a prepared surface via nitrogen propelled drying. SWNTs align parallel to the direction of nitrogen flow.

Another significant application of carbon nanotube supported nanoparticles is in the area of chemical sensing. One of the most common methods of sensing is the chemiresistive type, in which signal transductions occur through change in resistance upon analyte adsorption or desorption. SWNTs show potential for use in such sensors because of their small size, high surface area, and high aspect ratio. This enables carbon nanotube sensors to detect smaller concentrations of gas molecules than traditional sensors[90-94]. Charge transfer between the gas molecules and semi conducting carbon nanotubes changes the electrical conductance of carbon nanotubes and thus forms the mechanism of chemiresistive sensing. Though SWNTs act as very sensitive chemiresistive sensors, they are not as selective as is necessary for practical sensing applications. Therefore, modifying SWNTs with metal nanoparticles has been investigated in order to achieve chemical selectivity [95].

SWNTs were made sensitive to hydrogen by deposition of Pd nanoparticles. Mubeen at al demonstrated fabrication of hydrogen nanosensors by electrodepositing Pd nanoparticles on SWNT networks[96]. Optimized sensors formed with baseline resistance of 10 KΩ and Pd

deposition charge of 0.05 coulombs showed excellent properties with a lower detection limit of 100 ppm and a linear response up to 1000 ppm. Low density networks of SWNTs that were electrochemically modified with Pd showed effective hydrogen sensing for even lower hydrogen concentrations, ~ 10ppm[97]. Sensor arrays composed of several functionalized SWNTs were fabricated by site selective electroplating of Pd, Pt, Rh and Au on isolated SWNTs located on a single chip[98]. Electroplated devices were tested for sensitivity to H_2, CO, H_2S, NH_3 and NO_2. Sensor response, recorded as change in conductance versus gate voltage, showed that electrodeposition of different metals on the same device offers reduction in device size and increased number of analyte specific locations; partial least square analysis of the sensor array output yielded enhanced recognition of the gases. Modification of SWNTs with crystalline nanomaterials is currently an area of great interest due to the many analytical techniques this will enable.

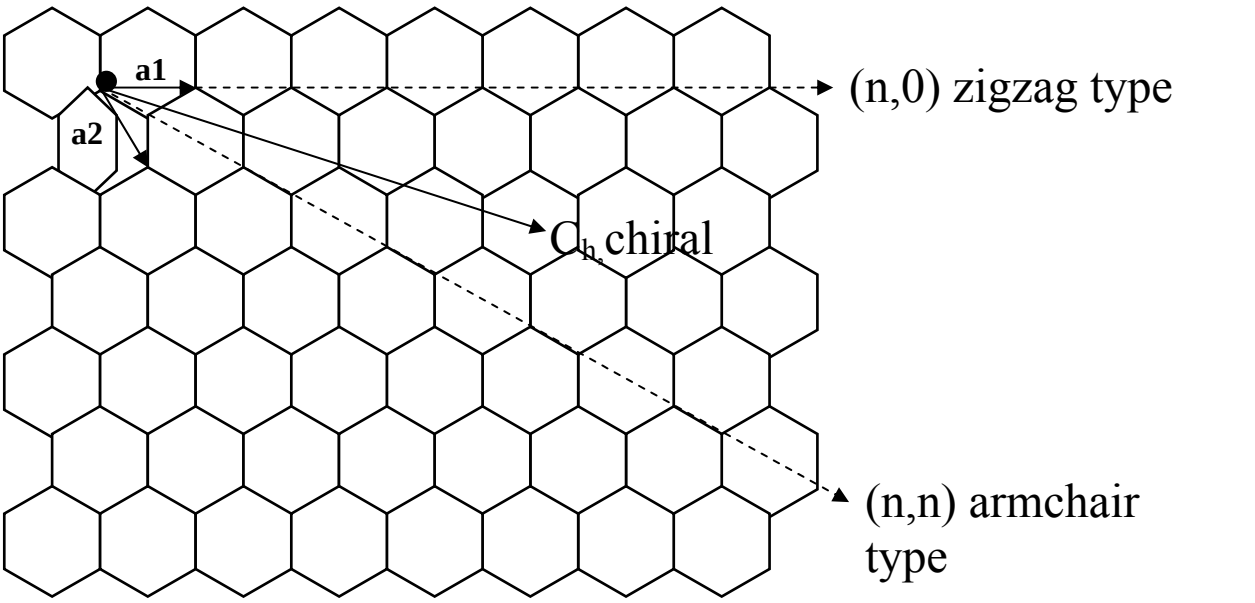

Figure 3.1 Schematic of 2 Dimensional graphene sheet that can be rolled into a SWNT

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CHAPTER 4

DEFECT ENGINEERING AND CONTROLLED DENSITY FORMATION OF CARBON NANOTUBE NETWORKS AND THEIR ELECTROCHEMICAL PROPERTIES

ABSTRACT

In this paper, we discuss the novel method we employed to make carbon nanotube networks of different densities and their electrochemical behavior. The Laminar flow method used to fabricate the 2D networks allows better control over the no. of CNTs in the network. Thus we were able to make electrodes with varying electrochemical properties based on mass transport. Also, we studied the effect of acid treatment on electrochemical properties of the as prepared carbon nantoubes. The treated carbon nanotubes were assembled into a 2D thin film and electrochemical behavior studied by cyclic voltammetry. The extent of defect formation was studied using Raman spectroscopy. The study shows that acid treatment introduces defects in the nanotubes that facilitate faster electron transfer and more electrochemically active sites. The intent of this work was to show that the density and defects on the carbon nanotube network could be tailored for electrochemical applications by combining the acid treatment and laminar flow deposition (LFD) method. We have also

studied the effect of density and defect on Platinum nanoparticle deposition on these networks, specifically for catalysis applications.

Keywords: Laminar flow deposition, acid treatment, cyclic voltammetry, electron transfer rate

INTRODUCTION

Carbon nanotubes (CNT) have unique properties which make them ideal for applications in many different areas such as catalysis, transistors, and sensors[1, 2]. The high aspect ratio and all atoms being surface atoms has made this material a focus of researchers in the area of electrochemical energy applications[3,4]. CNTs have been shown to possess ideal properties as catalyst support for platinum nanoparticles to be used in fuel cells[5-7].The first step in making the CNTs as catalyst support is to fabricate them into electrodes. Most of the studies aimed at harnessing the electrochemical properties of CNTs employed random 2D networks, bundles, thin films or paste electrodes[3, 5, 8, 9]. CNT networks have been made using chemical templating methods by utilizing the affinity between CNT and amino groups[10, 11]. In this method, glass or silicon substrate modified with specific amines are immersed in CNT solution. The CNTs are then adsorbed on to the substrates and thus help in making CNT networks. A better control to the amount of CNT adsorbed has been established by the unique Laminar flow deposition method (LFD) used in our group[12]. This method utilizes nitrogen stream to control the time and rate of deposition. The electrochemical properties of the 2D networks and also the Pt nanoparticles that are supported on the CNTs depends on the

density / number of carbon nanotubes present in each network. Hence we investigated the utility of this method in fabricating CNT network for electrochemical applications.

When CNT supports are used, the metal deposition takes place preferably at the defect sites. Hence by controlling the defect formation, the deposition of Pt can be tailored. In this paper, we focus on the defect formation on CNTs using mild acid treatment. The electrochemical behavior of acid treated CNTs had been studied previously in comparison to that of graphite[13]. Electrode kinetics is faster at the edge plane of graphite than the basal plane. Various functional groups such as quinoid, carboxyl and carboxylate are produced on the glassy carbon as well as on the CNTs by acid treatment. These functional groups act as axial ligands for metal deposition[14, 15]. The pretreatment also opens the ends of the tubes by oxidizing the tips. Thus the acid treated CNTs have two different regions; the largely un-reactive walls of the nanotubes that are comparable to the basal planes of graphite and the highly reactive ends that are comparable to the edge planes of graphite [16]. Both the regions have distinct electrochemical properties due to the difference in chemical bonding; the defect sites at the ends of SWNTs provide electrochemically active sites for redox reactions.

CNT SOLUTION PREPARATION AND PURIFICATION

Solution of acid treated CNT was prepared, (1mg/ml) using aqueous solution of 1% (w/v) sodium dodecyl sulfate (SDS J.T.Baker). This solution was sonicated at 6W for 1hour (probe sonication, Model 500, Fisher). Sonications helped in debundling of the CNTs. CNTs

have a tendency to form bundles in aqueous solution because of the hydrophobic walls. As-prepared CNTs consist of impurities from metal catalysts (that are used to grow CNTs from carbon source) and amorphous carbon. These impurities were removed by centrifugation process. Multiple centrifugation cycles (usually 3 cycles) were done at 18000 G for 30-45 minutes /cycle (Beckman, GS-15R). After each centrifugation, the supernatant was collected and centrifuged again. The impurities settled at the bottom were discarded. After the sonication and centrifugation completed, the CNT solution concentration was determined by UV-VIS spectroscopy. The concentration of the solution was a significant parameter in controlling the density of CNT network.

FORMATION OF 2D NETWORK

2D networks of SWNT were formed by laminar flow deposition method (LFD). Aminopropyl silane coated glass slides were used as substrate. Each deposition cycle in LFD comprises of wetting the silane coated glass slide with 100µL of SWNT suspension followed by drying using Nitrogen flow at 40-60 psi. The nitrogen flow helps in drying of the aqueous layer via laminar flow. The nitrogen flow was directed using a handheld air gun (Silvent) at an angle of 30°.The SWNTs were aligned in the direction of nitrogen flow. For the present studies, random network was formed by blowing nitrogen in different directions. The deposit was then washed with nanopure water in order to remove the residual surfactant (SDS). 2D

CNT electrode was fabricated as shown in the Figure 4.3. Ag paint was used as metal contact. Area of the electrode was defined by using clear nail polish.

ACID TREATMENT

Acid treatment was done to functionalize the carbon nanotubes. First 0.1g of as prepared SWNT (from Carbolex Inc.) was taken and mixed with 60 ml of 3M nitric acid in a round bottomed flask. The SWNTs were then refluxed in the acid at ~70ºC for 16 hours. After 16 hours the mixture was then filtered and washed with nanopure water until the PH changed to 7. Cellulose membrane was used for filtering purpose. The acid treated SWNT was then dried at 70C for 2-4 hours. Acid treated CNT was then dispersed in SDS (1mg/ml of CNT in 0.1% SDS) to make CNT solution. This solution was also purified by sonication and centrifugation as in the previous section.2D network of acid treated cnts was also made as described in the previous section.

CHARACTERIZATION TOOLS

The concentration of solution was determined by UV-VIS spectroscopy. AFM imaging (AFM, Molecular Imaging, PicoPlus). AFM was used to determine the purity of solution and density of network. Conductivity studies of the CNT network was performed in probe station (Keithley, 4200SCS). Electrochemical studies were conducted using Autolab potentiostat. The defect level of CNTs was determined by Raman spectroscopy.

RESULTS AND DISCUSSION

SOLUTION PURITY, CONCENTRATION AND DENSITY CONTROL

Two different solutions with initial concentration of 1mg/ml and 0.5mg/ml were made. The solution purity and final concentration were evaluated before making the networks. The AFM image (in Figure 4.1) shows that impurities were removed by consecutive centrifugation cycles. The as-prepared CNT solution had amorphous carbon impurities which are large in size and could be easily observed in the images. After each centrifugation cycles, the larger impurities settled at the bottom of centrifugation tube. Therefore, after 3 centrifugation cycles we obtained clean CNT solution suitable for our electrochemical studies. Removal of impurities is significant because we are interested in studying the electrochemical behavior of CNTs. The metal catalyst impurities has been shown to interfere with the electrochemical properties of CNTs to a larger extent[17].

The solution concentration, time for which the solution is in contact with the amine terminated surface, no. of deposition cycles are the three parameters that determine the density of the CNT network. In our investigation, we fixed the deposition time to be constant (2-3 seconds for each deposition cycle). The solution concentration varies from the initial concentration, after sonication and centrifugation were done. The concentration was determined by UV-VIS spectroscopy and comparing with the calibration plot that we got in our group[18]. Figure 4.2 shows the UV-VIS spectra of 0.05mg/ml solution after the purification cycles. The final concentration was determined to be 0.06mg/ml. The density of

CNTs had been determined earlier by counting the no. of tubes per unit area[18]. The density increased linearly with the solution concentration and no. of deposition cycles. However the coverage increased linearly up to ~ 25 cycles after which the CNT layers started forming on top of already formed layer. In other words, the amine terminated glass surface is completely covered with CNTs after 25 cycles. , after this the CNTs are adsorbed onto the already deposited CNTs due to Vanderwaal's interactions. This is evident from the AFM image of 25 deposits shown in figure. After the surface saturation around 25 cycles, thickness of the CNT films start increasing. The vanderwaal's interaction works well for the CNTs because of the long contact angles with the already adsorbed CNT. The schematic in figure 4.4 shows the pattern of growth of CNT layers.

DENSITY EFFECT ON THE ELECTROCHEMICAL PROPERTIES OF CNT NETWORK

The effect of density of the carbon nanotubes on the electrochemical behavior of the CNT network was studied**.** Samples with different number of depositions, for e.g. 30, 60, 90 deposits were made. Cyclic voltammetry in Fe^{2+}/Fe^{3+} solution was done to study the electrode behavior. Figure 4.5 shows the comparison of macro and microelectrode behavior in Fe solution. Figure 4.6 shows the CV of three different density samples. The scan rate used was 10mv/sec. The voltammetric curves show increase in current with increase in the CNT density. We did not observe any diffusion limited plateau in the scan range used, for the 30 and 60 deposit samples (made with solution 0.5mg/ml). In the low density networks, the

distance between the individual CNTs are farther apart so there is no overlapping of the diffusion layer. Hence the mass transport is predominantly due to radial diffusion. Mass transport is very effective and thus larger than the electron transfer rate.

When the density of the CNTs increased, the electrode started to show macro electrode behavior; hence the linear diffusion became predominant. Therefore we started to observe the diffusion limited peaks for Fe oxidation and reduction for the sample with 90 deposits (made with solution initial concentration 1.00mg/ml). Figure 4.7 shows increased scan range for the 90 deposit network. The diffusion limited peaks are clearly seen in this voltammogram. This effect of the density of CNTs was also extended to Pt deposition. Figure 4.8 shows the Pt deposition on two different densities of CNT network.

Pt deposition was $0.11 \times 10^{-6} g/cm^2$ on the 30 deposit sample and it was $0.1 \times 10^{-5} g/cm^2$ on the 60 deposit sample under the same deposition conditions. As we can see in the 60 deposit sample, the initial deposition charge is higher and after 50 seconds, it follows steady state behavior due to the overlapping of already nanoparticles. Figure L show the 60 deposit network before and after Pt deposition. Hence by controlling the density of the network, we could manipulate the electrode behavior of CNT network for Pt nanoparticle support. Figure 4.9 shows the AFM image of CNT network before and after Pt deposition.

ACID TREATMENT AND DEFECT ENGINEERING

RAMAN SPECTROSCOPY

Acid treatment helps in the removal of amorphous carbon and metal catalyst impurities as well as shortening of the tubes. As expected, the acid treatment also introduced defects in the CNTs. The structural changes were illustrated by the change in G and D band intensity and peak area in the Raman spectra. Figure 4.10 shows the Raman spectra of as prepared and acid treated CNTs. The acid treated sample shows more disorder compared to that of the as prepared CNTs.The G band was around 1590cm^{-1}. The D band for the as prepared CNT was selected around 1296cm^{-1} and for the 2, 6h acid treated CNT, it was ~1330cm^{-1}. The G/D ratio for the as prepared CNT was 17.7 where as for the 2 and 6 hours acid treated samples, it was 1.5 and 1.4 respectively. This ratio shows that the acid treatment indeed introduced defect sites in the CNTs. By varying the time needed for acid treatment, the extent of defect formation could be controlled.

CYCLIC VOLTAMMETRY STUDIES OF ACID TREATED CARBON NANOTUBES

Electrochemical characterization was done by cyclic voltammetry in blank and Pt solution. Figure 4.11 shows the CV of as prepared CNT in blank solution which is 50mM perchloric acid. Figure 4.12 compares the CVs of as prepared and acid treated CNTs in blank solution between -1.0V and 1.5V at a scan rate of 10mV/s. The magnitude of current is much higher for the acid treated CNT compared to the as prepared CNTs. It depends on the

concentration of surface functional groups such as –COOH groups. The oxygen functionalities act as electron transfer sites. At the same time, they increase the hydrophilicity of the CNTs. When the hydrophilicity is enhanced, the electrolyte solution can have better contact with the CNTs and access to the internal pore structure thereby increasing the effective surface area. It is evident from the CVs that acid treated CNT has higher double layer charging. Hence the surface functional groups introduced by nitric acid treatment increased the electron transfer rate as well as the effective surface area of the CNTs.

The effect of pretreatment on metal nanoparticle deposition was studied by taking the example of Platinum. Figure 4.13 shows the CV of 2D electrode of as prepared CNT in potassium tetrachloroplatinate solution. Perchloric acid was used as the supporting electrolyte. The figure 4.13 shows CV in Pt solution overlaid on top of blank solution. The voltammetric curve shows no diffusion limited peak in the scanned range which is indicative of the fact that the redox process is not limited by mass transport. Pt deposition starts to take place around 0.5V. Figure 4.14 shows the CV in blank and Pt solution of the acid treated CNT network. The current for Pt deposition is also much higher in acid treated CNT compared to that of as prepared CNT. The CV of APCNT looks like a flat line when compared to that of the acid treated CNT (Figure 4.15).

Due to acid treatment, there are 2 outcomes: a) the creation of functional groups on the surface of CNTs. These functional groups make the CNTs more hydrophilic and hence the accessible surface area of the electrode increases. Also these groups act as metal

nanoparticle anchoring sites. The Pt nanoparticle deposition takes place on these sites thus these defect sites are the sites of fast electron transport. b) The second effect of acid treatment is the shortening of the CNTs. Hence when same concentration of the CNT solution is used to make the electrodes, the acid treated CNTs have shorter tubes. We know the ends of CNTs are electrochemically active than the sidewalls of the CNTs

Platinum deposition was done at constant potential for 10 minutes in the as prepared and the acid treated CNTs. The density of the CNT network was precisely controlled using the LFD method. Substrates with 40 deposition cycles were used for this experiment. As the defect sites are preferable sites for metal deposition, the amount of Pt deposited on the acid treated CNT was higher than that on the as prepared CNTs. Figure 4.16 shows the Pt deposition on as prepared and acid treated CNTs.

CONCLUSION

In the first part of the paper, we have shown the effect of CNT density on the electrochemical behavior of the network. We were able to show the evolution of macro electrode behavior with increase in density of the network. The laminar flow deposition provides a novel way to fabricate CNT network electrodes with varying utility either as macro or microelectrode. Further work to quantify the density with each deposition cycle for higher number of depositions using absorbance measurements has been proposed. In the second part of the paper, we have shown that the defects act as electron transport site on the

CNT network. The mild acid treatment using 3M nitric acid introduces defects on the CNTs. These defects can be controlled by the time of acid treatment, acid used and also the reflux conditions. The Raman spectra showed the extent of defect formation under different acid treatment time. The acid treated CNTs show higher electrochemical activity compared to that of the as prepared CNTs. From the Pt deposition it is evident that the metal nanoparticle deposition takes place preferably on the defect sites. Treatment with stronger acid (concentrated nitric acid) and with nitric acid: sulfuric acid mixture and Raman spectroscopy to be done to determine the ideal conditions for acid treatment. Hence by combining the LFD method and acid treatments, we show the possibility of engineering CNT networks with designed properties as catalyst support.

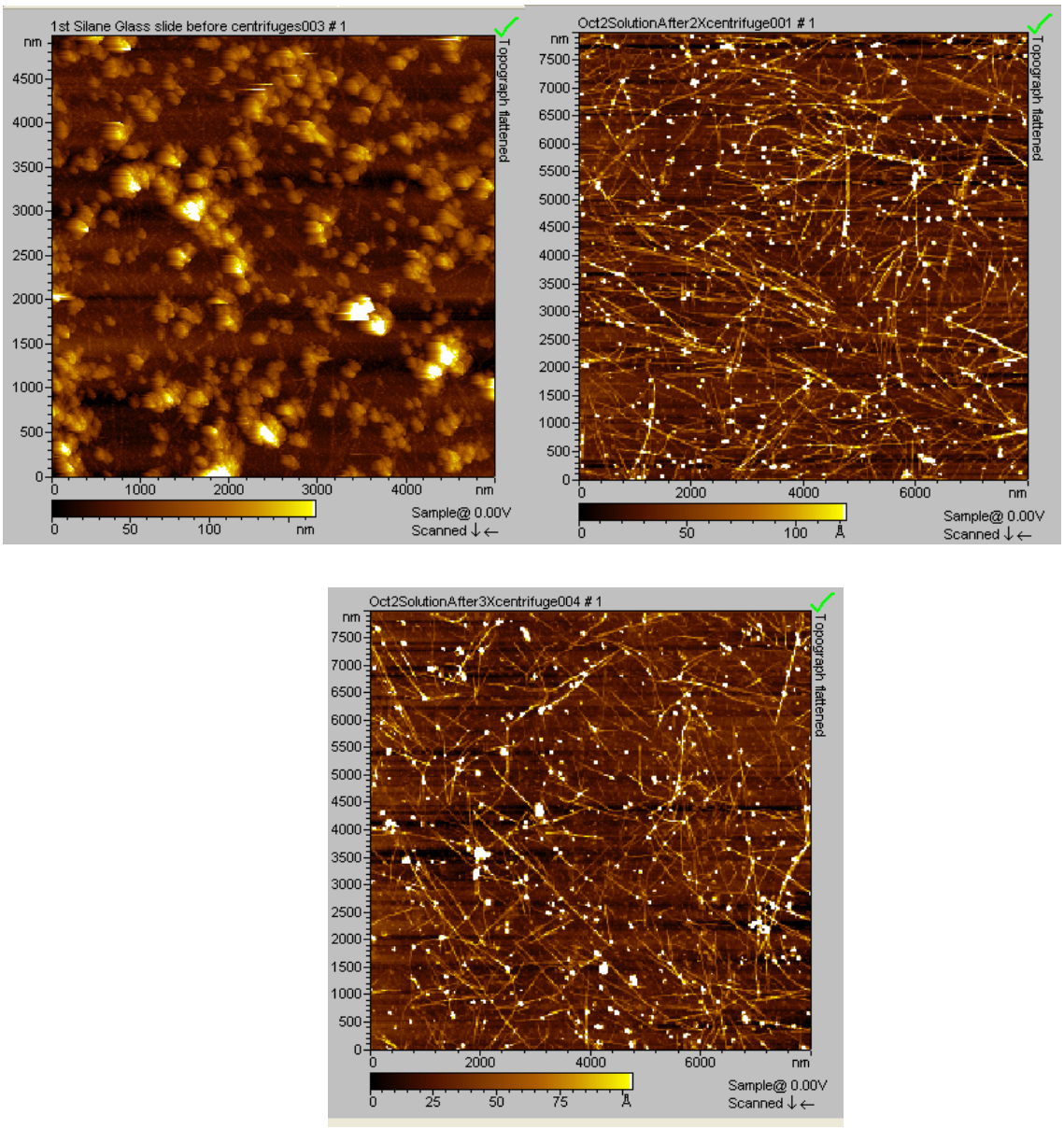


Figure 4.1 AFM image of CNT before purification, after purification (after 2nd and 3rd centrifugation cycles)

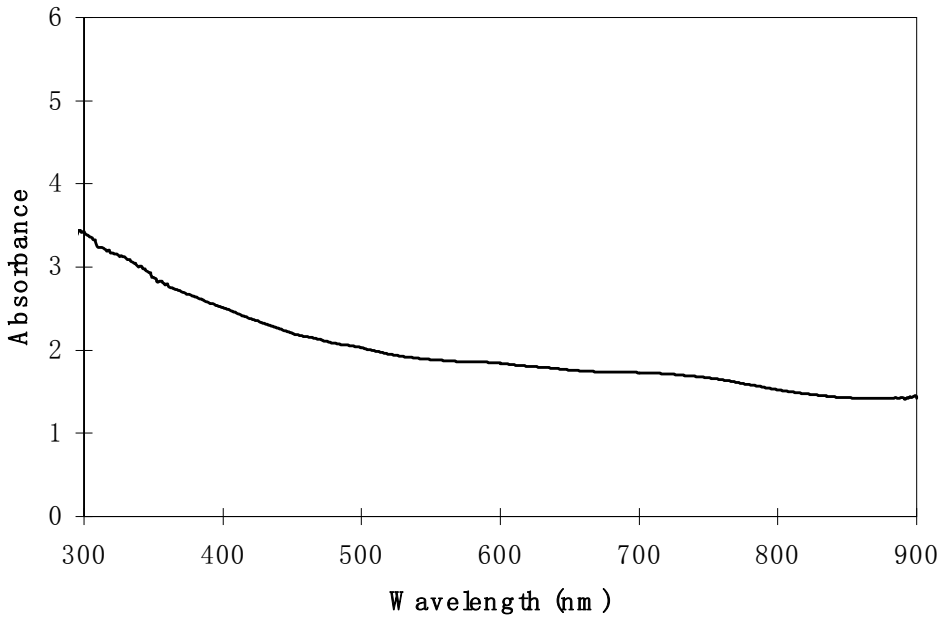
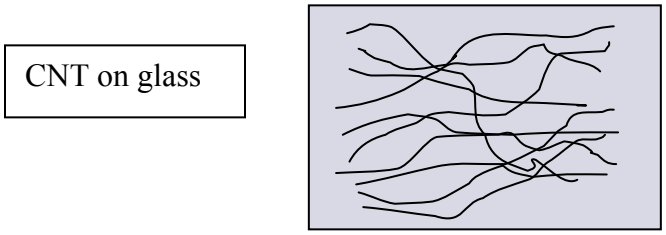
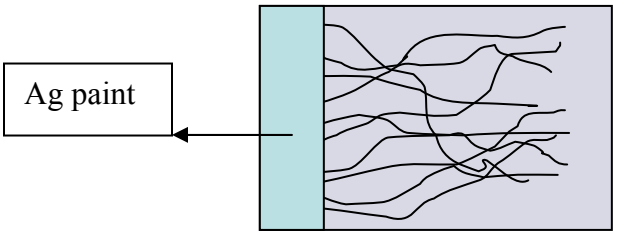


Figure 4.2 UV-VIS Spectra of CNT solution with initial concentration 0.5mg/ml after Sonication and 3 Centrifugation cycles

a)



b)



c)

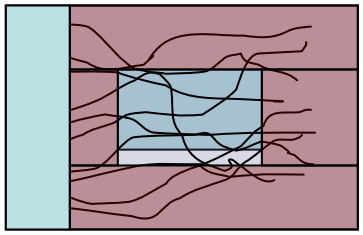


Figure 4.3 Fabrication of 2D network a) CNT deposited on silane coated glass substrate b) Silver paint for electrical contact c) defining electrode area using nail polish

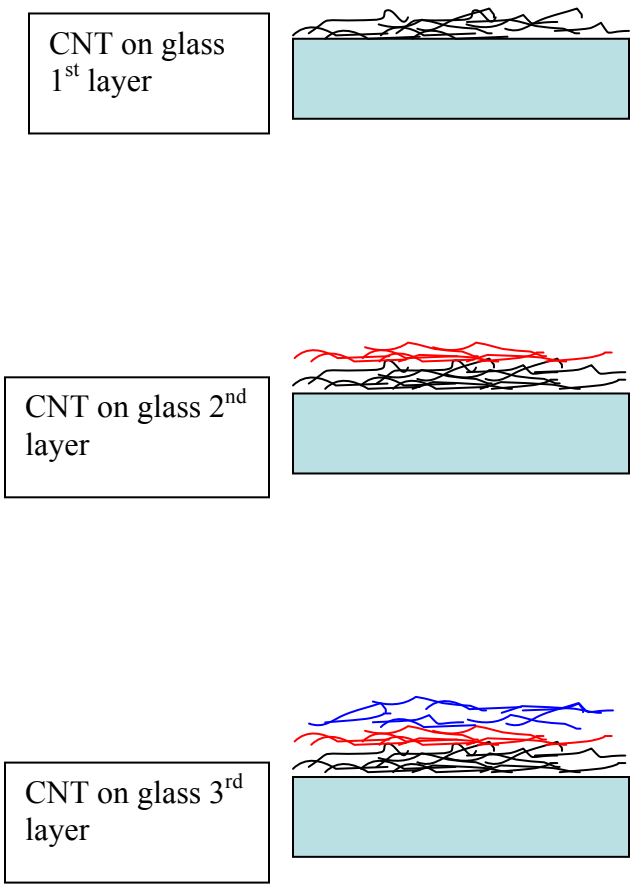


Figure 4.4 Pattern of growth of CNTs on the silane coated glass substrate. Black, red and blue indicates different layers of CNT formed on the surface

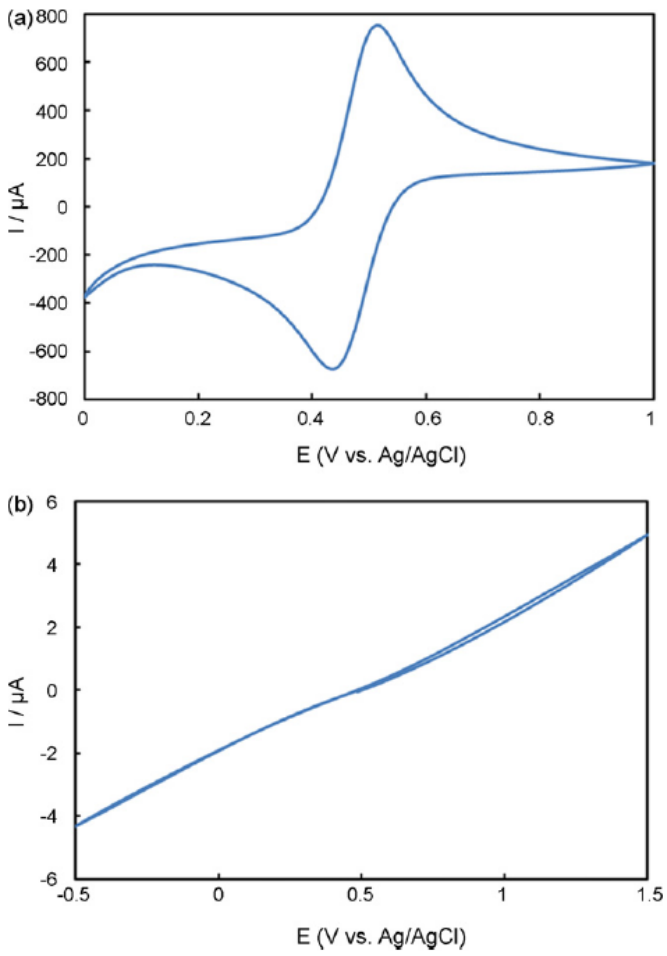


Figure 4.5 Comparison of cyclic voltammetric behavior of macro electrode (Au thin film) and micro electrode (CNT, 25 deposits)

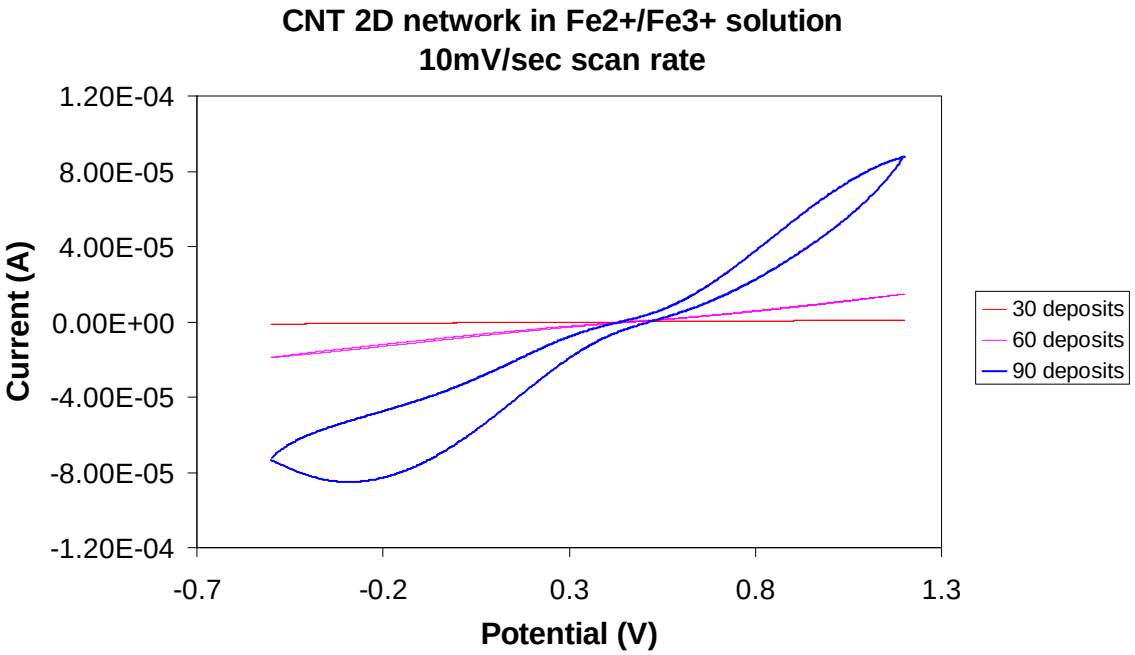


Figure 4.6 Comparison of CVs of CNT networks (of 3 different densities) in Fe^{2+} / Fe^{3+} solution

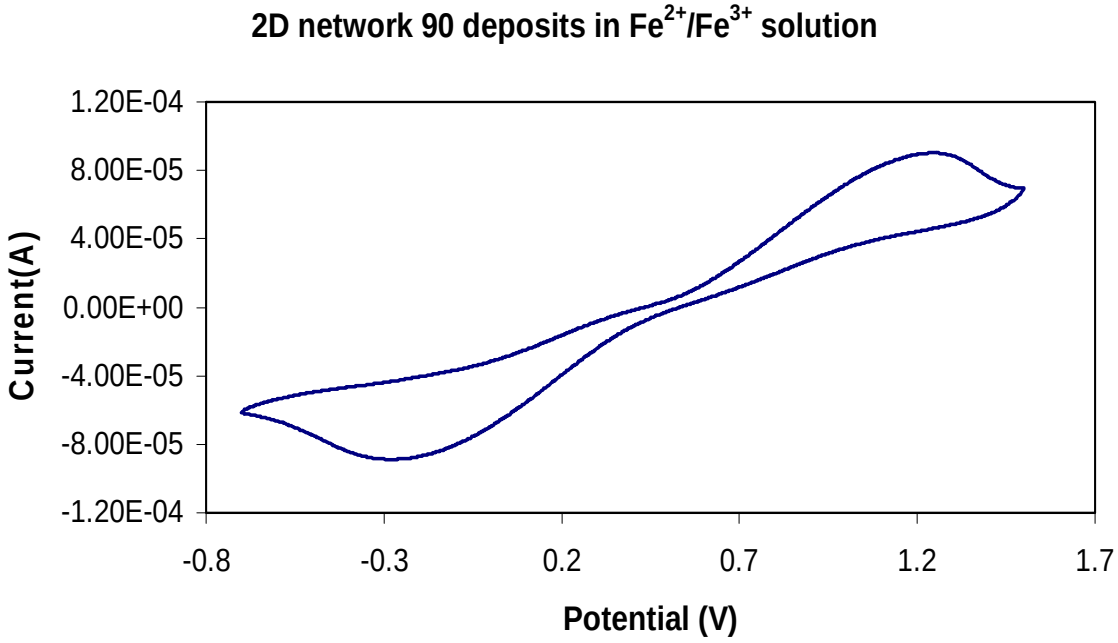


Figure 4.7 CV of 90 deposit CNT network in Fe solution. The increased scan range shows clearly the diffusion limited peaks.

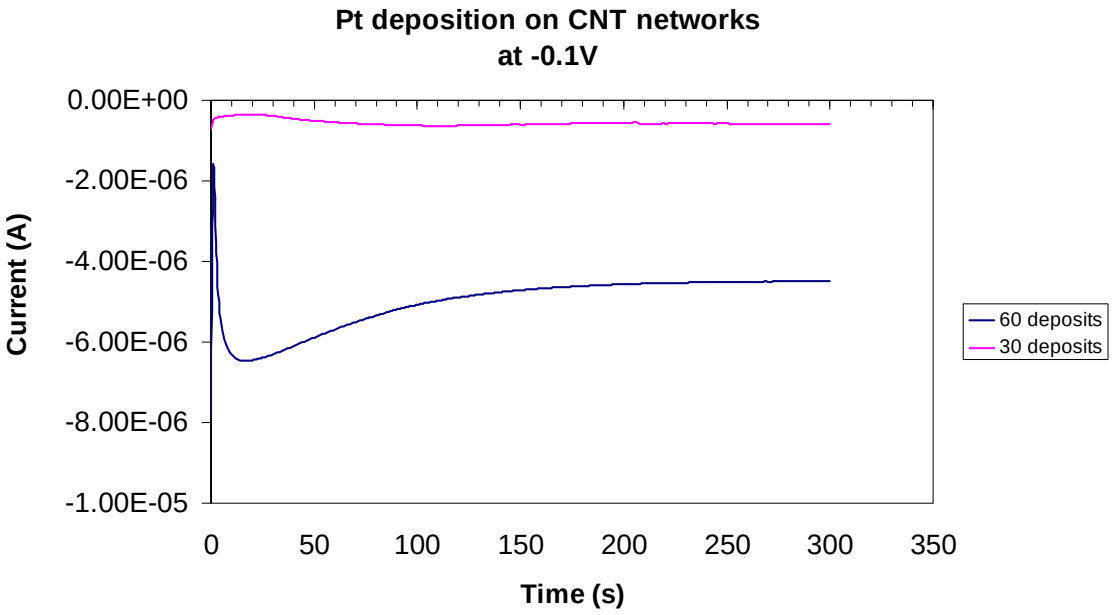
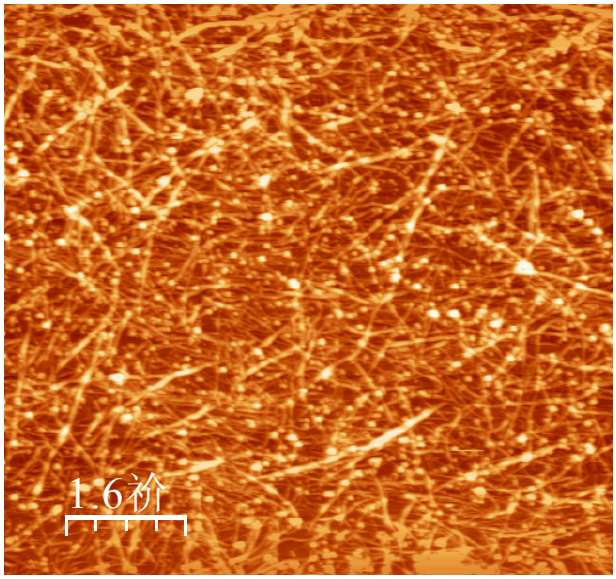


Figure 4.8 Current-time traces of Pt deposition on CNT networks

a)



b)

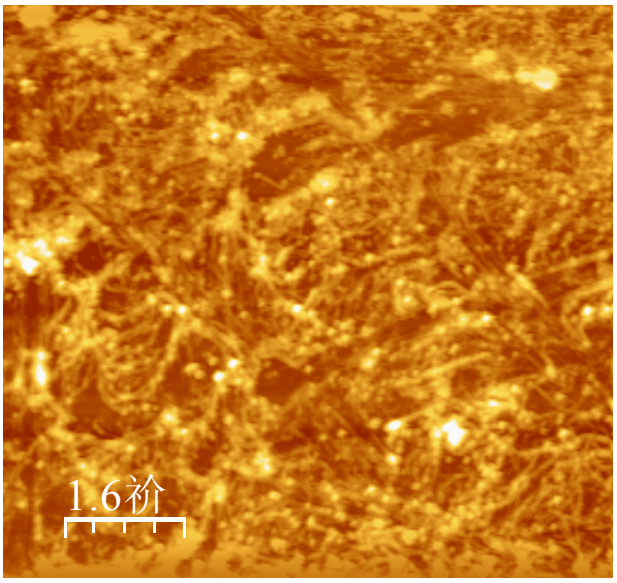


Figure 4.9 CNT netwotk before (a) and after (b) Pt deposition (40 deposit network)

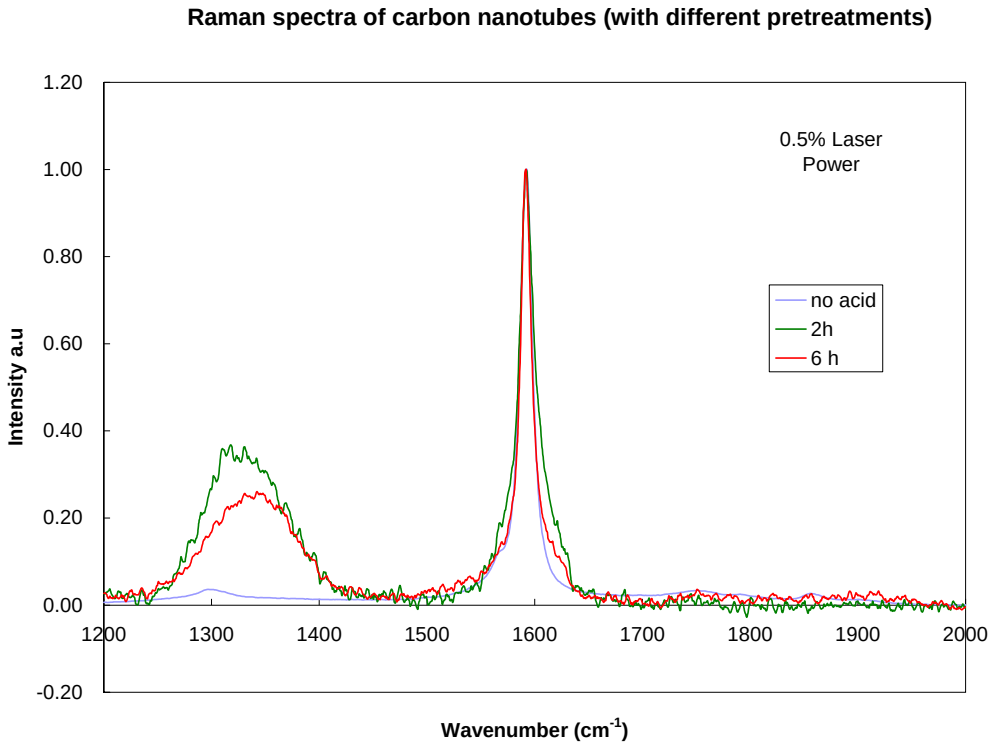


Figure 4.10 Raman Spectra of as prepared and acid treated CNTs

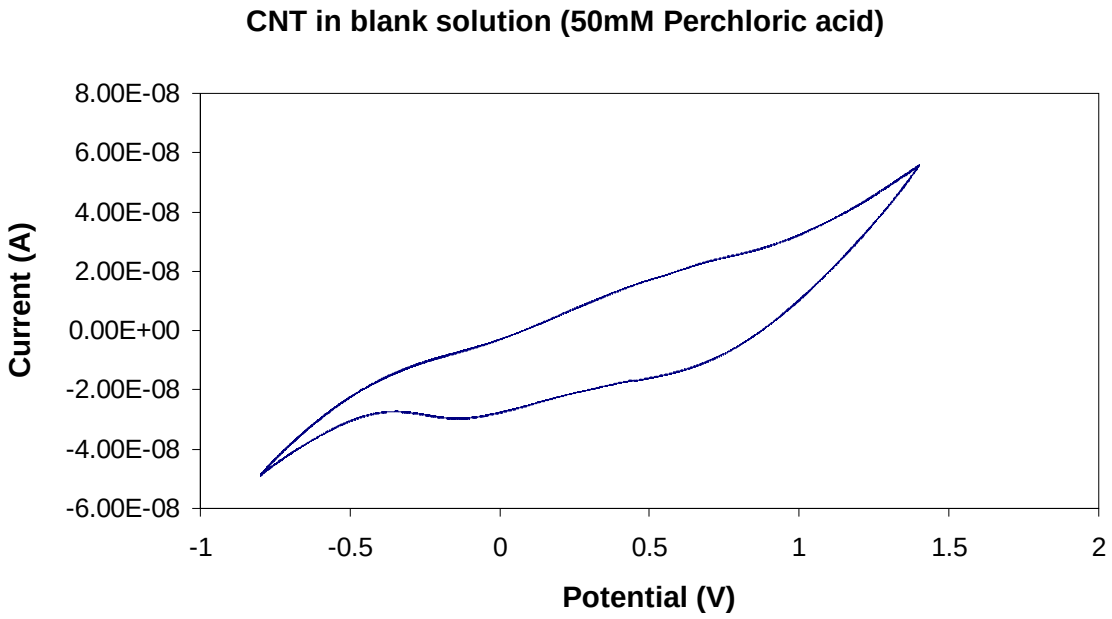


Figure 4.11 CV of as prepared CNT in blank solution

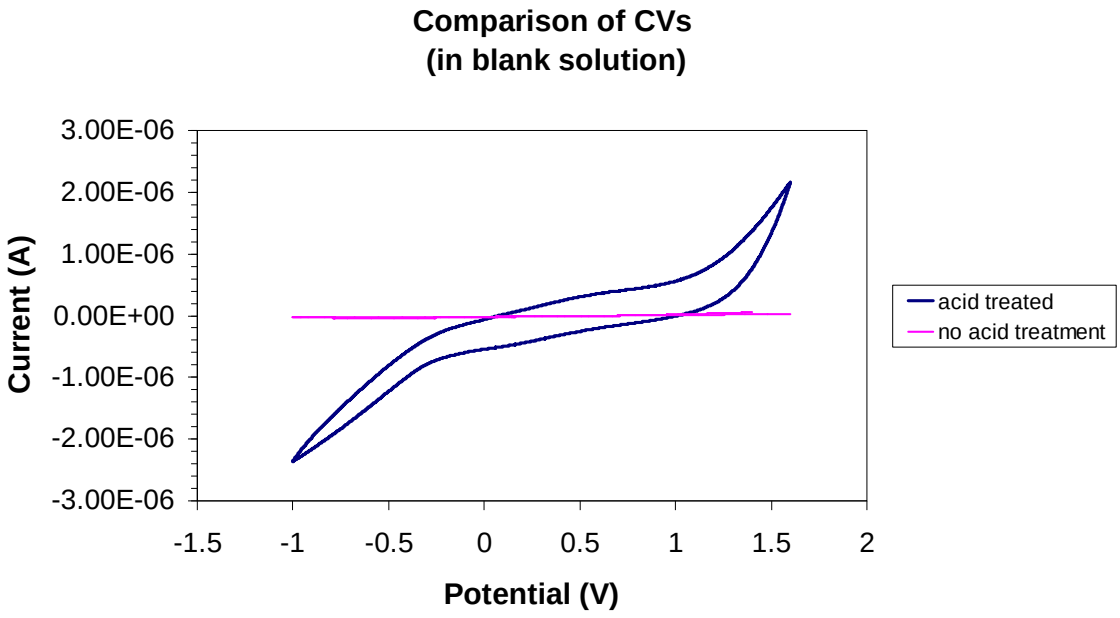


Figure 4.12 CV of as prepared and acid treated CNT in blank solution

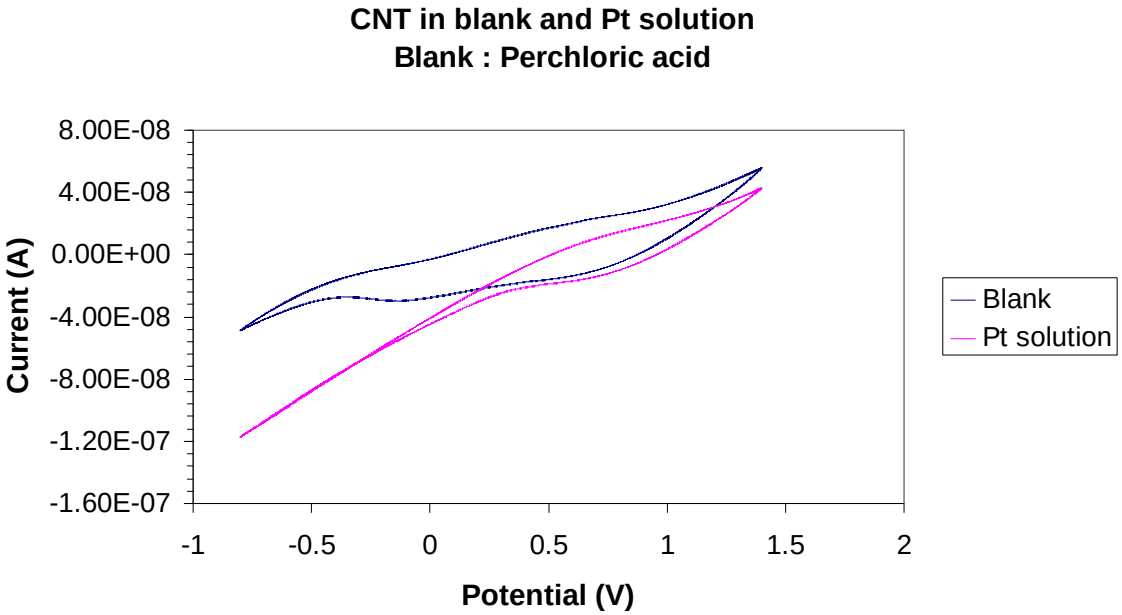


Figure 4.13 CV of 2D electrode of as prepared CNT in potassium tetrachloroplatinate solution and blank solution

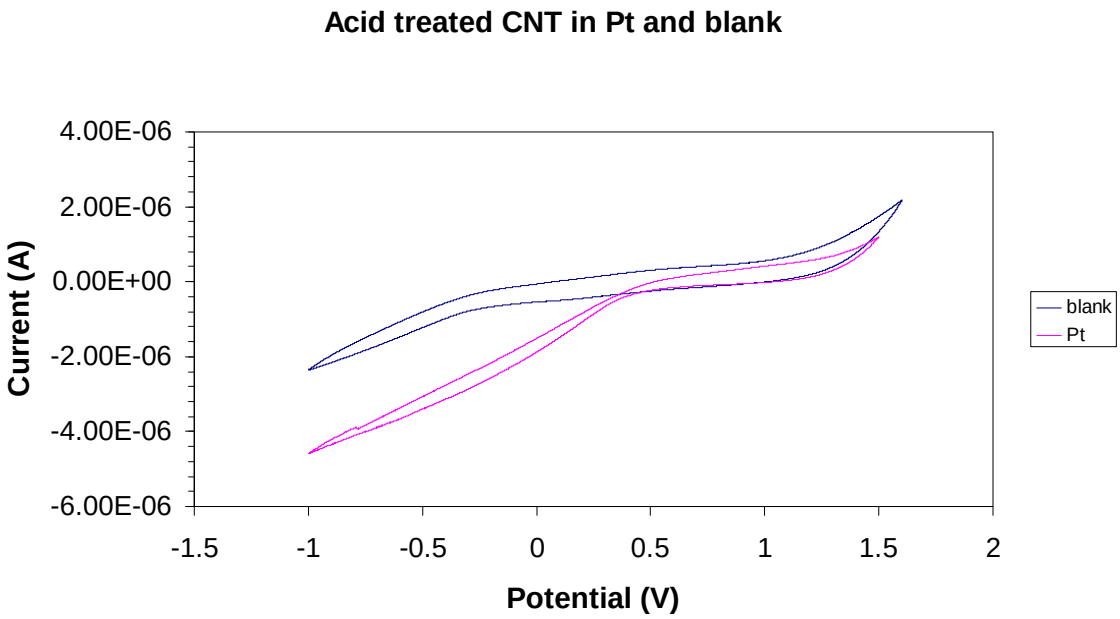


Figure 4.14 CV of 2D electrode of acid treated CNT in potassium tetrachloroplatinate solution and blank solution

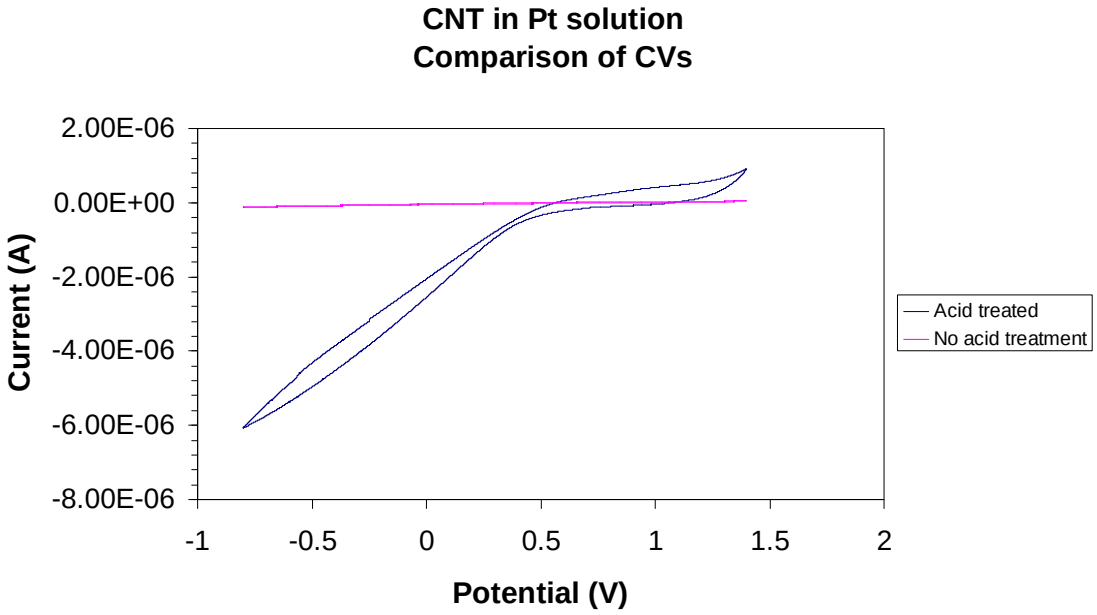


Figure 4.15 CV of as prepared and acid treated CNT in Pt solution

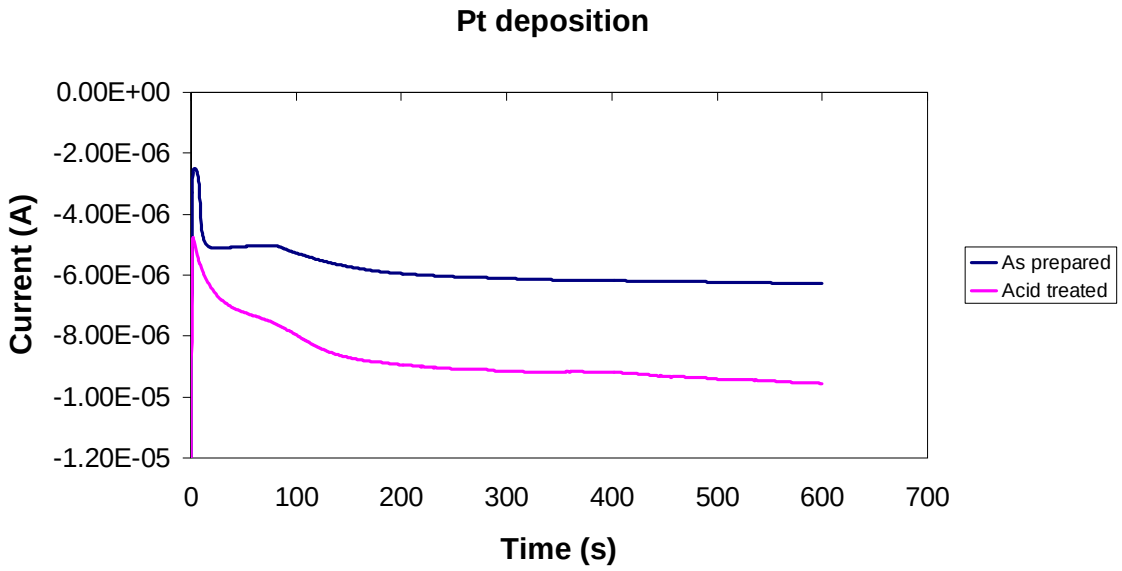


Figure 4.16 Pt deposition on as prepared and acid treated CNT.

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CHAPTER 5

CONCLUSION AND FUTURE WORK

In this dissertation we demonstrated the deliberate tailoring of Pt thin films and CNT network as catalyst support for Pt nanoparticles. The size and shape effects of nanoscale devices are evident in the area of catalysis. By our work, we have shown control at the atomic level using electrodeposition techniques.

In the chapter 3, the formation of Pt thin by electrochemical ALD using surface limited redox replacement was demonstrated. From our experimental studies, we prove that atomic level control is achieved in the Pt thin film growth. The OCP change monitored during the exchange process showed that the final potential reached after 3 minutes was high enough to strip any residual copper. EPMA analysis showed no copper was present in the resultant film. From EQCM studies, we knew that the exchange efficiency was almost 100%. The charge calculations and cyclic voltammetry showed that the Pt film growth is not ideal layer by layer in the initial cycles when copper was used as sacrificial element. Electrochemical annealing using Iodine was attempted; however exchange efficiency was greatly reduced. In Redox replacement reaction, difference in potential between Cu and Pt deposition acts as the driving force. We proposed to use Pb as sacrificial layer and thus the

driving force will be more (difference in potential between Pb and Pt). This in turn will help the Pt atoms move faster and overcome the barrier for interlayer diffusion, resulting in layer by layer growth in all the replacement cycles. Presently this is being studied in the research group and initial results are promising.

In the second part of the dissertation, formation of 2D networks of carbon nanotubes had been investigated in detail. Carbon nanotube networks showed promise as catalyst support for fuel cell applications. The properties of catalyst support affect the catalyst performance to a greater extent. In the chapter 3, the structural and electrochemical properties, methods or purification of carbon nanotubes were reviewed. The unique properties of CNT that make them ideal catalyst support were discussed showing examples in literature. Understanding the fundamental electrochemical properties of the CNTs is critical to harness them for fuel cell catalysis.

In the chapter 4, a novel method to control the density of carbon nanotubes for electrochemical applications was demonstrated. The effect of CNT density on the Electrochemical behavior of CNT network was shown in the first part of the chapter. We were able to show the evolution of macro electrode behavior with increase in density of the network. CNT network electrodes behaving as either microelectrodes or microelectrodes were devised by the novel method – Laminar flow deposition proposed by our group. AFM images showed increasing CNT density with increase in number of deposition cycles. Pt nanoparticle deposition was done on CNT networks of different densities. As the network

with higher CNT density had more surface active sites, more Pt deposition was seen on these networks compared to that of the low density networks. Quantification of surface coverage by absorbance studies has been proposed as part of future work. In the second part, we demonstrated the effect of acid treatment on the electrochemical behavior of CNTs. Defect sites were created on the CNTs by mild acid treatment with 3M nitric acid. The defect sites act as electron transfer sites for electrochemical reaction. Raman spectroscopy was used to get information about the extent of defect formation. It was shown that the acid used, time of acid treatment and reflux conditions determine the defect formation. Acid treated CNTs showed higher electrochemical activity. Owing to the presence of defect sites, Pt deposition was more on the acid treated CNTs. Hence we showed that using the LFD method and acid treatment, we could control the density and distribution of Pt nanoparticles. Further work to quantify the defect formation under different acid treatment conditions is underway.