Synthesis and characterization of novel polyaniline/metal composites

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SYNTHESIS AND CHARACTERIZATION OF NOVEL POLYANILINE/METAL COMPOSITES

by

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Bachelor of Science
Geneva College, Beaver Falls, PA
1999

A thesis submitted in partial fulfillment of the requirements for the

Master of Science Degree in Chemistry
Department of Chemistry
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Synthesis and Characterization of Novel Polyaniline/Metal Composites

is approved in partial fulfillment of the requirements for the degree of
Master of Science

Examination Committee Chair

Dean of the Graduate College

Graduate College Faculty Representative
ABSTRACT

Synthesis and Characterization of Novel Polyaniline/Metal Composites

by

John Macharia Kinyanjui

Dr. David W. Hatchett, Examination Chair
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University of Nevada, Las Vegas

The chemical synthesis of polyaniline (PANI) is explored using tetrachloroaurate, AuCl₄⁻ and hexachloroplatinate, PtCl₆²⁻. These studies provide a simple method for the direct oxidation of aniline by these metal species and simultaneous formation of bulk quantities of PANI/Au and PANI/Pt composites, respectively. Studies of the PANI/Au composite indicate that the properties of the polymer are consistent with more traditional methods of preparation. The incorporation of metal into the polymer matrix shows an increase in conductance for the doped PANI/Au composite relative to PANI/HBF₄ without Au particles. In the case of the PANI/Pt composite, the polymer is found to exist as an amine salt leading to diminished conductance for the doped PANI/Pt composite relative to PANI/HBF₄ without Pt particles. Most importantly, the data suggests that both metal dispersion and acid doping can be used to adjust the electronic properties of PANI.
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CHAPTER 1

BACKGROUND

1.1 Introduction to Polyaniline

1.1.1 Historical Applications of Polyaniline

Polyaniline (PANI) is an electrically conductive polymer (ECP), which has attracted attention based on its unique electronic properties and applications. Despite being discovered in the late 19th century, the study of the polymer as a novel material for commercial applications began in earnest the late 1980s. PANI has become the material of choice in comparison to other conducting polymers for conductometric applications because of its chemical stability, good conductivity upon doping and its dynamic redox properties. While most preliminary studies have focused on characterization of the complex chemistry of PANI, applications of the material have been the focus of recent studies. For example, PANI is currently used commercially in the passivation of metals to prevent corrosion. This involves dispersing PANI in polar or non-polar solvents to form a primer that can be easily applied to the metal surface. Other applications for PANI include the production of thin transparent antistatic coatings for high-grade electronic components and as a surface finish for printed circuit boards.

1.1.2 Physical and Chemical Characteristics of Polyaniline

The PANI chain structure consists of two main repeating units namely, the imine quinoid (oxidized) and amine benzenoid (reduced) as shown in figure 1.1a below. These
units can be reversibly oxidized or reduced using an applied potential or chemical oxidant/reductant as shown in figure 1.1b.

\[
\begin{align*}
\text{a.} & \quad \begin{array}{c}
\text{Benzenoid (Reduced) Unit} \\
\text{Quinoid (Oxidized) Unit}
\end{array} \\
\text{1-x}
\end{align*}
\]

\[
\begin{align*}
\text{b.} & \quad 
\begin{array}{c}
\text{H} \\
\text{-2e}^- \\
\text{f} (E_{\text{applied}}) \\
\text{f} (\text{Red/Ox}) \\
\text{-2H}^+
\end{array}
\end{align*}
\]

Figure 1.1. Structural units of PANI

The oxidation state of the polymer is determined by the ratio of the quinoid units to benzenoid units with the fully reduced form containing benzenoid units only and the fully oxidized form containing quinoid units only. The main oxidation forms of PANI are leucoemeraldine base (fully reduced), emeraldine base (equal number of benzenoid and quinoid units) and pemigraniline base (fully oxidized). The change in oxidation state is accompanied by a color change with the color of leucoemeraldine base, emeraldine base form and the pemigraniline base being yellow/white, green and purple respectively. Fourier transform infrared (FTIR) spectroscopy is usually employed to estimate the oxidation state (x) of the polymer. By integrating bands attributed to the quinoid and benzenoid units of the polymer and then calculating the ratio between them, one can estimate the oxidation state of the polymer. The oxidation ratio of the polymer, R, can
then be calculated as follows:

\[ R = \frac{1 - x}{x} = \frac{\text{Area}_{\text{benzenoid}}}{\text{Area}_{\text{quinoid}}} \]

where \( \text{Area}_{\text{quinoid}}, \text{Area}_{\text{benzenoid}} \) represents the area of the characteristic quinoid and benzenoid bands, respectively.\(^3\)

The emeraldine base form of the polymer can be further protonated using a protons acid, a process known as “doping” to produce emeraldine salt as shown in figure 1.2. This form of PANI is the most electrically conductive. The conductive properties of the emeraldine salt form of PANI are attributed to its π–bond conjugation, allowing electrons to shuttle freely within the polymer system. The conjugated system is formed as a result of overlapping of carbon p and nitrogen p\(_z\) orbitals and alternating carbon-carbon single and double bonds. The conductivity of other forms of PANI is greatly diminished with the leucoemeraldine (fully reduced) base being electrically insulating.\(^2\)

Hatchett colleagues have examined the effect of doping PANI cast from formic acid with both strong and weak acids using cyclic voltammetry. They have shown that the level of protonation and the final oxidation state of the polymer is dependent on the pK\(_a\) of the protons acid employed.\(^3\) The pK\(_a\) for the \(-\text{NH}_2^+\) and \(-\text{NH}^\equiv\) is 2.5 and 5.5 respectively and therefore a strong acid (pK\(_a\) < 2.5) would be expected to protonate both
the amine and imine groups of the polymer. On the other hand, a weak acid (pKa value between 2.5 and 5.5) would be expected to protonate the \(-N=\) group only. Additionally, the authors propose that weak acids can be employed to adjust the final oxidation state of the polymer due to complex equilibria between amine/imine and the conjugate base of the weak acid.

![Figure 1.2. Structure of the base and salt form of emeraldine PANI](image)

1.1.3 Production Methods of PANI

PANI can be produced either by chemical or electrochemical means. The chemical method is carried through the chemical oxidation of aniline while the electrochemical process involves the anodic oxidation of aniline. Chemically prepared PANI is normally referred to PANI\(^C\) while electrochemically prepared PANI is referred to as PANI\(^E\). The above methods of production are discussed in detail in sections 1.1.3.1 and 1.1.3.2 below.

1.1.3.1 Synthesis of PANI\(^C\)

The most commonly used method for the chemical synthesis of PANI is the chemical oxidation of aniline using ammonium peroxydisulfate \((\text{NH}_4)_2\text{S}_2\text{O}_8\)\(^1\). This is typically carried out in an acidic medium (i.e. hydrochloric, sulfuric, nitric, tetrafluoroboric or...
perchloric acid). The resulting form of the polymer in acid solution is the emeraldine salt.

The advantage of chemical synthesis is that bulk quantities can be produced. Lack of control over the final oxidation state of the resulting polymer material is the main disadvantage of chemical synthesis. The oxidation state of the resulting polymer is solely dependent on the oxidative power of the chemical oxidant used. However, the oxidation state of the polymer can be manipulated externally using reducing or oxidizing solutions.

1.1.3.2 Synthesis of PANI

PANI can be produced electrochemically by the electrooxidation of aniline at an inert electrode using various electrochemical methods. These include galvanostatic, potentiostatic or sweeping methods.\(^1\) Sweeping methods such as cyclic voltammetry are the most common. Thick and uniform films of PANI form, and are then delaminated from the electrode surface. This method involves cycling between -0.25V to 1.0V and stopping at a voltage corresponding to the desired final oxidation state of the polymer. In the presence of a dopant, proton uptake and anion expulsion occurs due to the need to maintain charge neutrality in the system as cathodic potentials are applied. The opposite takes place with anodic potentials.

Genies and colleagues have studied the mechanism for electrochemical PANI formation in acidic solution. They have proposed that formation of the aniline radical cation is the rate-limiting step in an acidic system and therefore important in the formation of short chain units of the polymer (i.e. dimers and tetramers).\(^4\) Figure 1.3 displays the mechanism for the electropolymerization of aniline in acidic solution as proposed by the above authors.
The main disadvantages to the electrochemical methods of PANI production is that only the small-scale production of composites can be feasibly achieved. Furthermore, the extraction of these minute quantities of composite material from the electrode surface for external applications without destroying the material is nearly impossible. However in electrochemical synthesis, the oxidation state of the polymer can be tuned by adjusting the final electrochemical potential providing a more homogeneous material with well-defined properties.\textsuperscript{5} In addition, the material in this form can be processed and cast as free standing films on external devices.\textsuperscript{6}
1.2 Synthesis of PANI/Metal Composites

The incorporation of metal into the polymer matrix of PANI has been a topic of research interest because of innumerable application that can be foreseen for PANI/Metal composites. For example, by uniformly incorporating noble metals into the polymer matrix, discrete reaction sites can be created for selective and sensitive chemical interactions, which leads to a host of potential chemical sensor applications. Furthermore, the incorporation of noble metals has been shown to significantly enhance the electronic properties of the polymer.¹⁷

PANI/metal composites can also be produced both chemically and electrochemically. Chemical production involves the direct oxidation of aniline using corresponding noble metal species to form the polymer. Electrochemical incorporation involves the metal incorporation during PANI oxidation and the corresponding reduction of the metal species to metal as the potential is switched. The electrochemical deposition of metals into PANI has been the traditional method of incorporation. However, the limitations associated with the electrochemical production of the polymer remain that the material must be removed from the electrode to be used in other devices. There is no guarantee that the PANI/metal interaction can withstand such processing. The direct chemical synthesis of these composites using the aniline monomer and a metal anion (e.g. AuCl₄⁻), is preferred over electrochemical synthesis because the metal is incorporated directly into the polymer matrix. This process allows for bulk production of the composites and ease in handling of the resulting product. The two methods of production are discussed in detail in sections 1.2.1 and 1.2.2. Presently, it is unclear whether the metal interacts with the polymer through electrostatic attraction or chemical bonding. However, it has been
proposed that the interaction occurs through the electron rich amino nitrogen.\textsuperscript{17}

1.2.1 Electrochemical Incorporation of Noble Metals

In the electrochemical metal deposition, different methods such as single or double potential chronoamperometry, cyclic voltammetry and constant potential exhaustive electrolysis can be employed.\textsuperscript{1} However, the most common method is cyclic voltammetry, which involves sweeping through a potential range in which the reduction potential of the metal species lies. The electrodeposition of Au,\textsuperscript{7} Pd,\textsuperscript{8} Pt\textsuperscript{9} and Ag\textsuperscript{10} into PANI through electrochemical methods has been carried out successfully and is well documented. The dispersion of some of these metals such as Au has been shown to be within a 3-dimension array of the polyaniline matrix.\textsuperscript{7,17} This is attributed to the fibrillar nature of thick polymer films, which allows easier penetration and reduction of the metal anion.

1.2.2 Chemical Incorporation of Noble Metals

The introduction of noble metals chemically into PANI has been successfully carried out for Au,\textsuperscript{11,12,13,14,15} Pd,\textsuperscript{11,16} Pt\textsuperscript{14} and I\textsuperscript{14} species. This is carried out by reacting the polymer with a solution of the desired metal species. These reactions are typically spontaneous and full or partial reduction of the metal occurs. The depletion of the metal species and the effect on the oxidation state of PANI can then be monitored using spectroscopic methods such as UV/Vis absorption.\textsuperscript{16,17}

Most of the investigations of metal uptake by PANI have focused on the sorption of the metal and not the production of uniform metal clusters distributed on the polymer matrix. The lack of chemical control of the metal-polymer sorption process at the imino nitrogen is the main limitation of the above method, because metal species typically
reduce at the point of contact. Therefore a more novel approach is required to achieve metal dispersion in PANI.\textsuperscript{17}

The uniform dispersion of metals through direct chemical oxidation of the aniline monomer using metal anions has not been greatly investigated as an alternative to the sorption method. The preparation and characterization of PANI/Au, PANI/Pt composites from the chemical oxidation of aniline monomer using $\text{AuCl}_4^-$ and $\text{PtCl}_6^{2-}$, respectively, will be the focus of this thesis project. The resulting composites are characterized and compared to the electrochemically prepared analogs.

1.2.3 Potential Applications for PANI/Metal Composites

The long-term goal for this research project is the development of PANI/Au, PANI/Pt and PANI/Pd chemical sensing, gas storage and catalytic devices. PANI/Au composites can be used as a platform for chemical interactions using functionalized thiol molecules bound to gold particles distributed within the polymer matrix. The alkanethiol molecules can in turn be modified by including different chemical functional groups to provide a range of ion selective sensing devices. For example, Creager and co-workers have developed an amperometric detection system for the hydroxymethylferorrocene analyte using flow injection analysis and the redox properties of an electrode coated with a self-assembled alkanethiol monolayer.\textsuperscript{18} This device represents only one example of how redox properties of analyte systems can be probed in an aqueous environment. This same system can be used to probe more environmentally interesting species such as arsenic, lead and ferric species. In addition, these electrodes are highly sensitive and have a detection limit in the nanomolar range. The dynamic concentration range is between $10^{-4}$ M and $10^{-9}$ M for the analyte.
The typical two-dimensional self-assembled alkanethiol monolayer has a finite sensitivity that is limited based on the overall surface area of the electrode. In comparison, the number of discrete sites available for the oxidation of the analyte molecules is greatly increased in PANI/Au composites due to the increased surface area associated with the dispersed gold particles. The increased surface area afforded with dispersed gold particles will increase the sensitivity of any redox process thus increasing the sensitivity of any device using thiol chemistry.

The use of PANI/Pd for hydrogen storage is based on the unique chemical relationship of the metal with hydrogen gas. The palladium-hydrogen system has been previously investigated and it has been shown that\textsuperscript{19,20} the metal has a high and selective affinity for hydrogen, absorbing stoichiometrically up to nine hydrogen molecules per atom of palladium. More importantly, the hydrogen can be reversibly expelled from the metal. In fact, this selective palladium-hydrogen relationship is employed industrially in the purification of hydrogen gas from such gases as carbon monoxide, carbon dioxide and methane.\textsuperscript{19} To this point, very little work has been carried out in studying the hydrogen storage capabilities of PANI/Pd composites. The ability of the metal to reversibly expel hydrogen gas is critical in the use of polymer/metal materials as a hydrogen fuel source.

The metal can be reused since the metallic properties of the palladium face centered cubic (fcc) lattice remain intact during this physical process. Uniformly incorporated palladium particles in the PANI matrix would enhance absorption and expulsion of hydrogen gas as a result of the high surface provided by the relatively small palladium particles. These composites can then be used to develop hydrogen fuel cells for automobiles and other transit applications. The application of PANI/Pd in hydrogen
storage is limited to a study by Jocowicz and colleagues. In this study, the use of electrochemically prepared PANI/Pd composites as work function hydrogen sensors was examined. The research indicated that the hydrogen sensitivity of palladium containing PANI was greatly affected by the oxidation state of the polymer and the Pd\(^0/Pd\(^{2+}\) ratio in the polymer. This observation indicates that the composition of Pd species in the PANI/Pd composite is extremely important.

The catalytic applications of PANI/Pd and PANI/Pt composites are also envisioned. Both platinum and palladium metal couples have been used as catalysts for a host of organic chemical reactions. For example, palladium is usually employed as a catalyst in heterocyclic chemistry in such reactions as cross-coupling of organohalides with organometallics reagents and C-N, C-P or C-O bond formation reactions of heterocyclic compounds. The dispersion of the metals to act as a catalyst in the PANI matrix ensures maximization of the active surface area of the catalyst. In addition, the electrocatalytic behavior of platinum deposited in PANI has gained a lot of interest lately because of possible application as catalysts in a range of potential mediated electrochemical reactions. The polymer allows potential mediated charge transfer between the polymer matrix, the catalyst and the reacting species in solution. Examples of potential mediated PANI/Pt electrocatalysis for possible fuel cell applications include the electroreduction of oxygen,\(^{23,24}\) electrooxidation of methanol\(^{25,26}\) and hydrogen.\(^{27}\) However, fewer studies have been carried out using PANI/Pd catalysis. One of the few examples of PANI/Pd catalysis is the catalytic effect of PANI containing palladium particles on the hydrogenation of ethylanthraquinone.\(^{28}\) This reaction is an important step in the large-scale production of hydrogen peroxide.
1.3 Problem Definition.

The main goal of this thesis project was to chemically synthesize and characterize PANI/Au and PANI/Pt composites. The synthetic process for these composites is optimized to ensure maximum yield and reproducible composition. We have shown that it is possible to prepare PANI/Au and PANI/Pt composites by spontaneous chemical synthesis using only the aniline monomer with AuCl₄⁻ and PtCl₆²⁻ species respectively. Various methods such as In-situ UV/Vis spectroscopy were employed to ascertain the reaction mechanism for these composites. The mechanism for the formation of the PANI/metal composites gives insight for the optimization of the composite synthesis process in terms of reproducibility and maximin yield. The quality, morphology and metal dispersion of the chemically prepared composites are compared to those of electrochemically prepared composites. One mode of comparison is the oxidation state of the polymer/metal composites. The oxidation state of the polymer and metal influences the properties of the polymer with respect to conductivity and catalytic activity.

Optical and scanning electron microscope (SEM) imaging are used to investigate the metal distribution within the polymer matrix. Additionally, physical properties such as the level of metal dispersion within the polymer can be observed from images obtained by these techniques. Determining the level of dispersion of metal within the polymer matrix is important in examining these composites for the envisioned applications. For example, a uniform distribution of small gold clusters within the polymer is desired in order to maximize the available interaction sites for PANI/Au-thiol sensing applications. Additionally, the size of the metal particles determines the available surface area for chemical interactions (as in the case of PANI/Au) or catalytic interactions (in the case of
PANI/Pt or PANI/Pd). Furthermore, optical imaging offers a visual tool for preliminary confirmation of the metal and a preliminary method for determining metal size within the composite.

1.4 References


CHAPTER 2

EXPERIMENTAL

2.1 Introduction

Various analytical methods are employed in the characterization of PANI/metal composite materials. The chemical composition of composites is determined and correlated through elemental analysis, Fourier transform infrared (FTIR) spectroscopy and X-Ray photoelectron spectroscopy (XPS). Morphological characteristics such as particle size, shape and arrangement of these composites are obtained using imaging techniques including optical imaging, scanning electron microscopy (SEM), transmission electron microscopy (TEM). Additionally, XPS is also used to determine the oxidation state of the metal species in these composites. Electrochemically prepared PANI/Au composite material is characterized and compared to its chemically prepared analog for its composition, polymer quality, conductivity, metal dispersion and metal size.

2.2 Characterization Methodology

2.2.1 Chemicals and Solutions

PANI/Au: Tetrafluoroboric acid, HBF₄ (Aldrich, 44 wt.%, 20,793-4), potassium tetrachloroaurate, KAuCl₄ (Aldrich, 98%, 33,454-5), ammonium peroxydisulfate, (NH₄)₂S₂O₈, Mallinckrodt, 7277-54-0) and aniline, C₆H₅NH₂ (Aldrich, 99.9%, 13,293-4)
were used as received. All solutions were prepared using 18.3 MΩ•cm water obtained from a Barnstead E-pure water filtration system.

PANI/Pt: Tetrafluoroboric acid, HBF₄ (Aldrich, 44 wt.%, 16872-11-0), potassium hexachloroplatinate, K₂PtCl₆ (16921-30-5), ammonium peroxydisulfate, (NH₄)₂S₂O₈, Mallinckrodt, 7277-54-0) and aniline, C₆H₅NH₂ (Aldrich, 99.9%, 13,293-4) were used as received. All solutions were prepared using 18.3 MΩ•cm water obtained from a Barnstead E-pure water filtration system.

2.2.2 Optical Absorption Characterization

The reaction mechanism for electrochemical incorporation of gold into PANI has been studied previously.¹ The reaction mechanism for chemically prepared PANI/Au composite will be presented and compared to the known electrochemical reaction mechanism. *In-situ* UV/Vis spectroscopy is an ideal tool for monitoring the depletion of reacting species and the subsequent formation of the PANI/metal composites through characteristic absorption bands. Distinct spectroscopic bands associated with the monomer, polymer and metal species can be clearly resolved and monitored to show the reaction progress. Characteristic transitions associated with the chemical synthesis of PANI/metal composites can also be monitored with clear chemical transitions allowing for the correlation of depleted and created species in solution. Furthermore, bands associated with PANI provide valuable information concerning the final oxidation state of the polymer based on the electrochromic nature of the polymer.

All UV/Vis spectra were obtained using a StellarNet EPP2000 fiber optic spectrophotometer equipped with a D₂ lamp and tungsten filament source that were coupled into a single fiber bundle. The transmitted light was collected after it passed
through the cuvette by a second fiber and relayed to a photodiode array detector. Figure 2.1 shows a schematic for the spectrophotometer.

![Schematic of the StellarNet EPP2000C Spectrophotometer](image)

The data acquisition times were varied to minimize the volume of data collected and stored. All UV/VIS measurements were performed in a single, teflon capped, quartz cuvette with a path length of 1 cm. The in-situ characterization of reactants and products was performed using an episodic data capture routine.

PANI/Au: The in situ UV/VIS samples were prepared and monitored using 0.20 mL of $2.50 \times 10^{-2} \text{ M} \text{ KAuCl}_4$ and 3.00 mL of 0.02 M aniline in 0.10 M HBF$_4$, respectively. The overall concentration of each species in the cuvette was optimized to ensure optical transparency and the ability to obtain measurable signal throughout the reaction. The
solution conditions employed were used to maintain the magnitude of the signal below two absorbance units at all times. The integration time for the detector was typically 200 ms. The data was collected at regular intervals using an integration time of 28 ms per scan. The episode capture time was initially 0.5 seconds to ensure that changes in solution conditions were monitored at intervals that provided sufficient spectroscopic detail.

PANI/Pt: The *in situ* UV/VIS samples were prepared and monitored using 1.5 mL of $4.14 \times 10^{-2}$ M $\text{K}_2\text{PtCl}_6$ and 1.5 mL of 0.05 M aniline in 0.20 M $\text{HBF}_4$, respectively. The data was collected at regular intervals (15 minutes) using an integration time of 28 ms per scan for an average of 10 scans.

2.2.3 PANI/Metal Bulk Synthesis

PANI/Au: Bulk PANI/Au composite material used for composite characterization was produced by mixing equal volumes of $2.5 \times 10^{-2}$ M $\text{KAuCl}_4$ and 0.22 M aniline both dissolved in 1 M $\text{HBF}_4$, representing a mole ratio of ~10:1 (aniline to $\text{KAuCl}_4$). All material was allowed to settle to the bottom of the reaction vessel for 24 hours prior to filtration. Once the product settled it was collected using vacuum filtration, washed copiously with water, and dried under ambient air conditions. Samples were also dried in a vacuum oven at ~ 70°C prior to characterization to remove any residual water retained after air-drying. The synthetic process was repeated and resulted in an average product weight of $0.0780 \text{ g} \pm 1.25\%$ for the PANI/Au composite. It is important to note that the weight of the product showed no dependence on acid concentration (0 to 2 M $\text{HBF}_4$). $\text{HBF}_4$ was chosen as the dopant acid because it does not degrade the polymer in the same manner as $\text{H}_2\text{SO}_4$ and HCl. Pure PANI samples without gold were obtained using
previously published methods. Elemental analysis was conducted on all samples by Atlantic Micro Labs, P.O. Box 2288, Norcross, GA 30091.

PANI/Pt: Bulk PANI/Pt composite material used for composite characterization was produced by mixing equal volumes of $2.0 \times 10^{-2} \text{ M} \ K_2\text{PtCl}_6$ and 0.22 M aniline both dissolved in varying acid concentrations, representing a mole ratio of $\sim$10:1 (aniline to $K_2\text{PtCl}_6$). All material was allowed to settle to the bottom of the reaction vessel for 48 hours prior to filtration. The materials were thereafter handled in the same manner as described above for the PANI/Au composites. However, in the case of the PANI/Pt composite the weight of the product showed great dependence on acid concentration.

2.2.4 Electrochemistry Experiments

Electrochemistry measurements were carried out using a CH Instrument model CHI660a controlled by electrochemical software provided by the manufacturer. All experiments were carried out in a one-compartment cell. Platinum foil was used as the counter electrode. The potential of the working electrode was always measured against an Ag/AgCl electrode. The polymer synthesis was conducted using 0.5M aniline in 2M $\text{HClO}_4$. The width of the potential window used for each experiment was selected such that the voltammetric peaks corresponding to the proton and the anion doping were fully developed. The potential window was however minimized to ensure polymer degradation was limited.

2.2.5 X-Ray Absorption Spectroscopic Characterization

Despite the visual appearance of metal particles within the polymer matrix, X-ray Photoelectron Spectroscopy (XPS) is employed to verify the oxidation state of the metal species. Furthermore, XPS can be used to estimate the level of doping of the polymer.
This is achieved by integrating the nitrogen edge to resolve positively charged nitrogens resulting from the protonation of the polymer units from the non-charged nitrogens.

XPS data were collected using a Surface Science SSX-100 system with an Al Kα X-ray source (1486.67 eV) for excitation. The system was equipped with a hemispherical electron analyzer with a position sensitive anode. The PANI/Au powder samples were mounted on a double-sided carbon tape placed on a piece of aluminum foil. For this study the carbon 1s peaks were assigned a binding energy of 284.6 eV and used as the energy reference. A chamber pressure of 5 x 10⁻⁹ Torr or lower was maintained for each sample measurement.

2.2.6 Infrared Spectroscopic Characterization

Fourier Transform Infrared (FTIR) spectroscopy is used to compare chemically prepared PANI/metal composites to their electrochemical analogs and the pure polymer. The fingerprint region between 700-1600 cm⁻¹ is usually employed to identify the characteristic peaks of the polymer. The quinoid unit (1590 cm⁻¹), benzenoid unit (1500 cm⁻¹), C-N (1140 cm⁻¹) and out-of-plane C-H peaks (822 cm⁻¹) are examined to determine the similarities or disparities between the PANI/metal composites and pure PANI. The quinoid units represent the higher oxidized form of the polymer while the benzenoid units represent the reduced units.

As discussed in Section 1.1.2, FTIR spectroscopy can also be employed to determine the oxidation state of the polymer. By integrating bands attributed to the quinoid and benzenoid units of the polymer and then calculating the ratio between them, one can obtain the oxidation state of the polymer. The emeraldine base form of the polymer is the most conductive form of the polymer while the other forms are semi conductive to non-
Conductive. Therefore it is important to determine the oxidation state of the polymer prior to the use of the materials in conductive or electrocatalytic applications.

All FTIR measurements were performed using a BIO-RAD FTS-7000 spectrometer using a photoacoustic detector. An average of 100 scans was used to produce each spectrum. All samples were vacuum dried overnight prior to measurement.

2.2.7 Composite Imaging

Optical imaging and scanning electron microscopy (SEM) are used to examine metal dispersion and dimensions in PANI. These techniques provide information concerning the metal particle dimensions as well as visualization of the metal and polymer. This information is required in examining the applicability of composites for the envisioned applications.

The morphology of the polymer and metal particles is also obtained through Transmission Electron Microscopy (TEM) diffraction. The characteristic electron diffraction pattern of the composite materials offers information on the arrangement of particles and the amorphous or crystal nature of the particles making up the composite.

2.2.7.1 Optical Imaging

Optical images of the composites were obtained using an Olympus BX41 optical microscope. The optical dimensions of the microscope image were determined using a 0.1 mm per division standard. For example the 100x objective provides a viewing area of 9625 \( \mu \text{m}^2 \) based on the x and y axis dimensions (\( x = 110 \ \mu\text{m}, \ y = 87.5 \ \mu\text{m} \)). The images were obtained using an Olympus DP-11 2.5 mega-pixel color CCD digital camera in the light transmission mode.
2.2.7.2 Scanning Electron Microscopy

SEM images of PANI/Au composites were obtained using a JEOL 5600 electron microscope equipped with a backscattered electron (BSE) detector. The powder samples were affixed to the sample holder using carbon tape and measurements were performed at an acceleration voltage of 15 kV. Metal shadowing was not required prior to SEM measurement.

2.2.7.3 Transmission Electron Microscopy

Samples were placed on a TEM grid in a dry state and then mounted in a holder. The images were made in the selected area using normal diffraction mode with a HF2000 field emission gun transmission electron microscope poised at 200 kV.

2.2.8 Conductivity Characterization

It is essential to determine conductive properties of PANI/metal composites especially for conductive and electrocatalytic applications. In addition, the incorporation of noble metal particles into the polymer matrix is expected to enhance the conductivity of the polymer. The enhanced conductivity is confirmed by determining and comparing the conductivity of the pure polymer to that of the PANI/metal composite.

A pellet of radius 1.25 cm was pressed from each material using three metric tons of pressure. The contacts were made using a Cascade Microtech C4S-64/50 probe head with Tungsten Carbide electrodes. The four point probe sheet resistance of each pellet was then measured at locations across the surface of the pellet using an HP 34401A Digital Multimeter connected through a Cascade Microtech CPS-05 probe station. Constant pressure for each measurement was maintained for the probed head contacting the substrate. A total of five measurements at different locations, measured twice, are
presented with representative standard deviations and relative standard deviations for the measurements. The resistivity/conductance of the electrochemical samples were estimated using the CHI 660 potentiostat. The conductance was calculated from the linear $V = IR$ response.

2.3 References

CHAPTER 3

PANI/Au COMPOSITE SYNTHESIS AND CHARACTERIZATION

3.1 Introduction

The use of metal clusters embedded in polymer matrices to explore metal-ligand interactions in solution has been not been extensively studied. The PANI/Au system is of particular interest because of the ability to spontaneously form thiol monolayers on gold surfaces. Using PANI/Au/thiol with designed functionality and tailored chemistry at the gold interface is of particular interest. These studies are beyond the scope of this thesis project and will be the focus of further studies. The focus of this chapter is the bulk synthesis of PANI/Au composites using chemical methods.

Previous studies examining the interaction between tetrachloroaurate (AuCl₄⁻) and conductive polymers such as polyaniline¹,²,³ and polypyrrole¹ have focused on the sorption properties of the materials. The spontaneous and sustained reduction to metallic gold from solutions of polyaniline or polypyrrole containing AuCl₄⁻ has also been reported.¹ In some cases the total accumulation of gold in the sorption process has been reported to be as high as five times the original weight of the polymer.² However, lack of chemical control of the gold-polymer sorption process at the imino nitrogen remains a key limitation of such processes. If the goal is to produce uniform metallic clusters embedded in a polymer matrix, then sorption is not adequate. Specifically, the dispersion of the metal in the polymer is limited because the metal anion

25
typically reduces at the point of contact rather than dispersing into the polymer matrix. The polymer can be finely ground to ensure larger unobstructed surface areas for the metal anion to contact. This still does not always ensure the metal is uniformly dispersed. Lack of metal dispersion is not a great concern when the ultimate goal is to simply reduce the gold and recover it from solution. If the goal is a homogeneous mixture of intrinsically conducting polymer with evenly dispersed gold clusters, more novel techniques must be employed.

Electrochemical methods offer precise control of the oxidation-state of the polymer, thus influencing the degree of interaction between the polymer and the metal anion. Diffusion of metallic ions into the polymer matrix occurs as the oxidation state of the polymer is changed restoring charge neutrality in the system. These metallic ions are then reduced into the polymer matrix as the polymer is reduced using the applied potential. This technique is utilized to control the uptake and reduction of AuCl₄⁻ ions forming gold clusters with variable dimensions within the polymer matrix. The quantity of material produced from electrochemical methods is typically quite small which limits the removal and reuse of the material on external devices. There is also no guarantee that the polymer/metal interface produced electrochemically will withstand the processing steps required for use on external devices.

In the course of the electrochemical formation of gold clusters in polyaniline the role of the AuCl₄⁻ anion as an oxidizing agent is examined by Hatchett and colleagues. In this study, p-aminophenol was titrated with AuCl₄⁻ and the reaction product and unreacted starting product were monitored using their characteristic UV/Vis absorption bands. A clear transition between the p-aminophenol and p-iminoquinone was observed based on
spontaneous reduction of the tetrachloroaurate in the solution as demonstrated by a clear isosbestic point in the titration. This study confirmed that the amino groups play a key role in the electron transfer process and reduction of tetrachloroaurate to Au(0). In addition, this study suggested that AuCl₄⁻ could be used as an effective oxidizing agent in the chemical synthesis of polyaniline, providing both the radical cations necessary for polymer formation and metallic gold colloids in the reaction system. In this particular experiment no polymerization occurred because of the para-OH (hydroxyl) substituent.

Although the chemical synthesis of polyaniline using oxidizing agents such as ammonium peroxydisulfate⁴⁻⁶⁻⁷ is well characterized, the synthesis of polyaniline using AuCl₄⁻ is inherently more complex. For example, issues such as the final oxidation state of the metal species, degree of proton doping, degree of incorporation of the metal into the polymer matrix, and chemical composition of the polymer must be addressed. In this chapter, a novel synthetic route for the direct synthesis of PANI/Au composites using AuCl₄⁻ as the oxidizing agent in solutions containing HBF₄ acid is described. The synthetic process is detailed and the chemical characteristics of the system are evaluated and compared to PANI doped with HBF₄. In-Situ UV/Vis studies are used to monitor products and reactants simultaneously and a mechanism is proposed. In addition, optical imaging as well as TEM diffraction are used to probe the metal distribution, size, and crystallinity in the PANI matrix. FTIR and XPS analysis are used to examine the chemical properties of the polymer with and without metal clusters. Finally the sheet conductivity of PANI/HBF₄ and PANI/Au are examined using a four point probe. The production of PANI/Au composite using AuCl₄⁻ suggests that other polyaniline/metal composites can be produced, providing a simple method for producing large quantities of
composites with unique chemical and electrical properties.

3.2 Results and Discussion

3.2.1 PANI/Au Synthesis

The spectra of the reactants, reaction products and the reaction filtrate are presented in Figure 3.1. The reactants, aniline and AuCl₄⁻ are presented in Figures 3.1a and 3.1b, respectively. Both reactants have UV/Vis absorbance bands between 200 – 290 nm, which makes distinguishing changes in the concentration of these species difficult. The aniline and AuCl₄⁻ band are centered at 260 nm and 311.7 nm, respectively. The absorbance band for AuCl₄⁻ can be examined prior to and after completion of the reaction to determine if the consumption of the gold anion is complete. It is difficult to use the band to examine the consumption of AuCl₄⁻ during the reaction because the PANI can have bands that overlap with the reactants. For example, PANI (emeraldine salt) has a π-π* transition between 320 - 360 nm and a polaron-π transition band at approximately 440 nm that can shift depending on solution conditions. 8,9,10 In fact, spectral shifts for the polaron transition are common and indicate oxidative or morphological changes in the polymer. 11,12,13,14

The spectrum of the reaction mixture containing aniline and AuCl₄⁻ in 0.10 M HBF₄ solution is presented in Figure 3.1c (t = 10 s) and 3.1d (t = 70 s), respectively. Two bands associated with the product are observed at 381.3 nm and 727.5 nm. The assignment of the band located at 381.3 nm is difficult because it lies between the π-π* transition of the benzene ring for the polymer and the band associated with the polaron-π transition. The band at 727.5 nm has been assigned previously to the localized polaron-π
Figure 3.1. Bottom to top, UV/Vis spectra of, a. 0.02 M aniline in 0.10 M HBF$_4$, b. 2 mM KAuCl$_4$ in 0.1 M HBF$_4$, c. chemically synthesized PANI/Au colloid in aqueous solution obtained by mixing 0.2 mL of $2.5 \times 10^{-2}$ M KAuCl$_4$ and 3 mL of 0.02 M aniline in 0.1 M HBF$_4$ at time 10 s, d. same conditions as c. data acquired at time 70 s, e. solution after PANI precipitation and filtration.
of the polymer. This band is also known to shift in wavelength as a function of structural and oxidative changes.\textsuperscript{8,9,10} The bands at 381.3 nm and 727.5 nm were used to monitor the formation of PANI (in-situ) during the polymerization process.

The degree of \textit{AuCl}_4^- reduction, formation of polymer and residual oligomeric material in the system is determined using the filtrate from the reaction shown in Figure 3.1e. The benefit of examining the filtrate is that the overlapping bands associated with the polymer are eliminated leaving any unreacted aniline and \textit{AuCl}_4^- behind. Excess aniline is clearly observed in the filtrate spectrum. In addition a small shoulder exists consistent with a small amount of unreacted \textit{AuCl}_4^-.

The amount of gold species remaining is considered to be negligible in order to estimate the weight percent of gold in the PANI. With this assumption it is found that the weight percent of the gold is on the order of 60% \textit{Au} in PANI. This weight percent can be varied as a function of solution concentrations. If desired, the degree of \textit{Au} in PANI can be adjusted using excess aniline and a traditional oxidant to increase the amount of polymer relative to gold.

3.2.2 \textit{In-Situ} UV/Vis Spectroscopy of PANI/Au Composite Synthesis.

The \textit{in-situ} studies were performed using a mixture of 0.20 mL of \textit{2.50 x 10}^{-2} M \textit{KAuCl}_4 and 3.00 mL of \textit{0.02 M aniline} in 0.10 M \textit{HBF}_4. A large excess of aniline was used in comparison to \textit{AuCl}_4^- to facilitate the complete reduction of \textit{AuCl}_4^- in the solution. The mixed absorption bands of both aniline and \textit{AuCl}_4^- are observed between 200 and 290 nm in Figure 3.1a. It is expected that the bands associated with these species would diminish over time, leaving the signature of unreacted aniline if all of the gold species were consumed in the reaction. However, the band for aniline is found to actually increase over the first 70 seconds. Over the same period of time the
characteristic $\pi-\pi^*$ and polaron-$\pi$ bands associated with the polymer emerge as PANI is formed in the solution. Finally a broad band located at 727.5 nm emerges at a slower rate relative to the shorter wavelength band for the polymer as the reaction proceeds. The appearance of absorbance bands associated with reactants at the same time product bands emerge in the spectra is inconsistent with the reaction of aniline and AuCl$_4^-$ . In fact, based on these initial results it is not apparent that the consumption of AuCl$_4^-$ and aniline, and the formation of the polymer in solution are linked. However, the isolated absorbance for AuCl$_4^-$ ($\lambda = 311.7$ nm) over the first 20 seconds displays an initial drop consistent with the consumption of this species from solution (Figure 3.2b). The intensity is based on the reaction of aniline and AuCl$_4^-$ in acidic solution and the formation of colloidal gold, shown below:

\[
3 \text{NH}_3 + \text{KAuCl}_4^- \rightarrow 3 \text{NH}_2^+ + \text{Au}(0) + \text{KCl} + 3\text{HCl}
\]

The gold particles remain suspended in solution causing an increase in the amount of light scattering. This increase causes a shift in the baseline of each spectrum to higher intensity. This trend is observed in Figure 3.2a which shows that the spectra shift to higher absorbance as the concentration of the colloidal gold increases during the reaction. The trend is also repeated for the aniline/AuCl$_4^-$ combination absorbance bands and the bands associated with the formation of PANI.

The bands located at 381.3 and 727.5 nm are key to understanding the synthetic process. There are two clear differences between the band at 381.3 and 727.5 nm. First,
the spectroscopic data shows that the band at 727.5 nm appears after a very short lag time in comparison to the band located at 381.3 nm (~2 seconds). The rate of formation in solution is also quite different. The rate of formation for the species giving rise to the band at 381.3 nm rises rapidly, reaching a maximum at ~10 s. In contrast, after the lag time, the band at 727.5 nm increases at a much slower rate eventually showing a significant change in rate of formation at ~30 s. However, this band continues to rise gradually over the next 40 s in contrast to the band at 381.3 nm. This indicates that the kinetics for formation of the two species is significantly different and likely due to two different chemical species. Wei and co-workers have observed this same trend while monitoring the species present in the reaction mixture during the electrochemical formation of polyaniline.\textsuperscript{15} Based on their linear sweep voltammetry results the authors confirm the initial product formed in the synthesis of polyaniline is the dimer species ($p$-aminodiphenylamine). In fact, the oxidation of the aniline monomer to form dimer intermediates was proposed as the rate-limiting step in the reaction.

The spectro-electrochemical analysis of PANI synthesis by Genies and co-workers showed that the absorbance band for the polymer located below 400 nm is primarily due to the formation of soluble polymer intermediates with little contribution from the large polymer units.\textsuperscript{16} It is proposed that the leveling of this peak with the continued growth of the absorbance band at 727.5 nm is due to the consumption of short chain intermediate structures and formation of the long chain units in solution. In addition, the differences in rate of formation and the lag time between the bands at 381.3 nm and 727.5 nm suggest that the increase in absorbance occurs at the cost of both the short chain oligomeric material (381.3 nm) in the solution and the continued reduction of $\text{AuCl}_4^-$. The band at
Figure 3.2.  

a. *In-situ* UV/Vis spectra of a mixture of 0.20 mL of $2.50 \times 10^{-2}$ M KAuCl$_4$ and 3 mL of 0.02 M aniline both in 0.1 M HBF$_4$. The data shown includes spectra obtained from 0.5 – 5.0 seconds (0.5 second interval), 6 – 10 seconds (1 second interval), 12 – 32 seconds (2 second interval), and 45 – 70 seconds (15 second interval). Arrow indicate progression of band as a function of time. The line passes through the center of the AuCl$_4^-$ band at 311.7 nm. 

b. Plot of UV/Vis absorbance intensity versus time for AuCl$_4^-$ and product (311.7 nm, 381.3 nm and 727.5 nm).
727.5 nm is consistent with formation of the long chain polymeric unit which has been observed previously.\textsuperscript{8,9,10,16,17} Although the UV/Vis spectroscopic data collected over the first 70 seconds is fairly complex, it indicates a colloidal mixture of PANI, short chain intermediates, gold, and the remaining aniline monomer.

Significant changes in the absorbance bands are observed in Figure 3.3a after the first 70 seconds. Although the rate of formation of the short chain intermediates has slowed (381.3 nm) the band and 727.5 nm continues to increase in intensity (Figure 3.3b). This increase can either be attributed light scattering of gold colloids as their concentration increases in solution, or consumption of the short chain intermediates and the formation of long chain structures. It can be surmised from the previous discussion that the reduction of AuCl\textsubscript{4}\textsuperscript{-} will result in formation of short chain dimers, trimers and tetramers with a corresponding increase in the absorbance at 381.3 nm. In contrast, the decrease in intensity of the band at 381.3 nm relative to the increase at 727.5 nm is consistent with increasing chain growth of the polymer at the expense of the smaller chain unit structures in solution. The data indicates that the consumption of the short chain species is critical to formation of long polymer chains. The continued growth of PANI is strongly influenced by the oxidized species and remaining aniline in solution. It is expected that the formation of the longer chain polymer units at the expense of shorter chain units would continue over a period of time until all intermediate species are consumed.

Termination of the synthetic process can be attributed to two related processes. First the continued reduction of AuCl\textsubscript{4} and formation of intermediates ceases when the gold species is consumed. In addition, the reaction of these units to form long PANI chains slows and ceases as the intermediates in solution are also consumed. It is not clear from
Figure 3.3.  

a. The continued reaction of the mixture from Figure 3.2 at times, 70-370 seconds (10 second interval). Arrows indicate progression of band as a function of time.
b. Plot of UV/Vis absorbance intensity versus time for AuCl₆⁻ and product (381.3 nm and 727.5 nm).
the spectroscopic data when AuCl$_4^-$ is completely consumed because of the overlap between the absorbance band of the intermediates and the gold anion. However, it is clear from the spectroscopic data that the consumption of short chain intermediates is not complete prior to 220 s in Figure 3.3b. The band for the intermediate gradually decreases while the band at 727.5 nm continues to increase at a slower rate of increase compared to the period before 220 s. This trend implies that the consumption of AuCl$_4^-$ is complete. Once the reduction of AuCl$_4^-$ ceases, the reaction of intermediate structures to form long chain structures becomes dominant and the solubility of PANI becomes an issue.

Precipitation of the PANI from solution occurs when the solubility limit of PANI is exceeded. In chemical synthesis the precipitation of PANI is solely related to the lack of solubility of PANI in aqueous solvent. For the system presented in this chapter, interaction of the polymer with the gold particles in solution is also an issue. The spontaneous nucleation of PANI onto platinum and gold electrodes is well known and an integral part of the formation of PANI membranes at electrochemical interfaces.$^{17,18,19}$ The UV/Vis spectra displayed in Figure 3.4a clearly show the precipitation of PANI from solution. In this figure, selected spectra are shown for the reaction, which was monitored every 60 seconds from 420 seconds to 7680 seconds. The data clearly shows the decrease in both polymeric bands located at 381.3 and 727.5 nm (Figure 3.4b). However, a rapid loss in signal is observed between 2280 and 2340 seconds due to precipitation of the polymer from solution. This is marked by the appearance of a diminished aniline signal and diminished background signal. The diminished background signal is primarily the result of a decrease in light scattering associated with the loss of gold colloids in solution. This behavior suggests that the polymer and gold are not independent species in
Figure 3.4. a. The continued reaction of the mixture from Figure 3.2 at times, 540 – 2340 seconds (300 second interval), 2340 - 2940 seconds (60 second interval), and 3240 – 7380 seconds (600 second interval). Arrows indicate progression of band as a function of time. b. Plot of UV/Vis absorbance intensity versus time for the product (381.3 nm, 727.5 nm).
the solution. The formation of a polymer/metal composite occurs simultaneously; precipitating from solution once the solubility limit of the material is exceeded. It is interesting to note that not all of the polymeric material has precipitated at the end of this experiment (time = 7680 seconds). However, if the solution is allowed to sit for a few additional hours the signal approaches the baseline leaving the signature band of unreacted aniline in the solution (Figure 3.1e).

3.2.3 Mechanism for the Formation of PANI/Au Composites

The interaction of conducting polymers with AuCl₄⁻ has been examined previously by a number of groups. In each case the polymer was produced separately and then reacted with the gold anion. For example, the chemical synthesis of a polypyrrole/Au has been reported previously by Henry and colleagues. In this reaction, the formation of colloidal polypyrrole was accomplished using ferric chloride as the oxidant prior to the introduction and reduction of AuCl₄⁻. Our system is unique because the colloidal PANI/Au is formed without the aid of any chemical species other than the AuCl₄⁻ anion and aniline.

The chemical synthesis of the PANI using AuCl₄⁻ is similar to the chemical synthesis of PANI using a more common oxidizing agent such as peroxydisulfate. The spectroscopic data indicates that AuCl₄⁻ produces intermediate species in solution that are used as building blocks in the polymerization reaction. Clear differences in the rates of formation between intermediate species and the long chain polymer are also observed. Our spectroscopic data suggests that consumption of the intermediate species is critical in the formation of PANI. Although it is proposed that the mechanism of PANI formation is very similar to that described by Genies, the system presented here is clearly
different. Specifically, in our experiment, nucleation and growth of the polymer onto colloidal metallic surfaces represents a significant deviation from previous mechanisms for the formation of PANI and PANI/metal composites.

3.2.4 PANI/Au Composite Characterization

3.2.4.1 Imaging and Diffraction of PANI/Au Composites

Although the loss of AuCl₄⁻ and the increased baseline in Figure 3.2a is consistent with the reduction of the anion to the zero oxidation state, questions regarding the final oxidation state of the metal species and the relationship between the gold and the polymer remain unanswered. It is well known that the nucleation of aniline radicals and the continued formation of radicals once polymeric units have formed result in the growth of uniform and cohesive films at noble metal surfaces such as Pt and Au electrodes. However, the nucleation of PANI onto gold particles in solution in the absence of potential control has not been studied in detail.

Examination of the reaction product using an optical microscope in the transmission mode reveals that the PANI formed in the solution nucleates onto the gold particles. Gold particles appear as uniformly dispersed dark spots embedded in the polymer matrix with an average diameter of 1 μm. It is impossible to sample and resolve the entire three-dimensional structure using optical objectives in transmitted mode, and some optically dense regions are clearly observed in the image. In addition, the image shows regions where no PANI/Au is observed.

The crystal structure of the gold particles embedded in the PANI matrix was also examined using TEM diffraction. The use of TEM diffraction in Figure 3.5 (bottom) provides information regarding both the polymer and the metallic particles. From the
diffraction pattern two clear conclusions can be drawn. First, the polymer is amorphous producing a characteristic ring pattern in the image. More importantly, the gold particles embedded in the PANI are not amorphous. The diffraction pattern observed is consistent with diffraction by many different crystallographic orientations. From the data it is clear the composite consists of amorphous PANI with embedded poly-crystalline gold particles.

3.2.4.2 FTIR Spectroscopy of PANI/Au Composites

FTIR analysis of the finger print region between 700 - 1600 cm\(^{-1}\) is particularly useful for examining the resonance modes of the benzenoid and quinoid units, and individual bonds (i.e. out-of-plane C-H and C-N) of PANI.\(^{4,19,21}\) The FTIR spectra of pure PANI/HBF\(_4\) and PANI/Au are presented in Figures 3.6a and 3.6b. Clear changes in this region can be observed with respect to the nitrogen heteroatom with the introduction of gold particles. The characteristic bands associated with the benzenoid phenyl ring (~1500 cm\(^{-1}\)) and quinoid phenyl ring (~1590 cm\(^{-1}\)) of the polymer are labeled on the figure. These bands can be used to estimate the oxidation state of the polymer, where the percent oxidized versus reduced units are obtained by integrating the IR bands as discussed previously in Section 1.1.2. of gold particles. The characteristic bands associated with the benzenoid phenyl ring (~1500 cm\(^{-1}\)) and quinoid phenyl ring (~1590 cm\(^{-1}\)) of the polymer are labeled on the figure. These bands can be used to estimate the oxidation state of the polymer, where the percent oxidized versus reduced units are obtained by integrating the IR bands as discussed previously in Section 1.1.2.
Figure 3.5. Top: Optical image (100x) of Au/PANI composite in the reaction solution using transmitted light. Optically dense region of the PANI/Au composite appear as large black areas. Gold particles (black dots) are encapsulated by polymer (light gray material). Clear regions are void spaces (absence of Au(0) or PANI). Bottom: Transmission TEM image obtained from PANI/Au composite.
Figure 3.6. Photoacoustic FTIR spectra of, a. Pure PANI without Au particles and b. PANI/Au composite produced during chemical synthesis using AuCl₄⁻ as the oxidant.

FTIR band assignments and the ratio of the oxidized unit (x) are labeled for clarity.
In the schematic below the oxidized and reduced units in PANI are represented by values $x$ and $1-x$ obtained from the FTIR analysis. Integration of the peaks for PANI/HBF$_4$ and PANI/Au give values of $x = 0.51$ and 0.53 respectively.

$$\frac{1-x}{x} = \frac{Area_{\text{reduced}}}{Area_{\text{oxidized}}} = \frac{Area_{\nu(1500\text{cm}^{-1})}}{Area_{\nu(1600\text{cm}^{-1})}}$$

The equal percentage of oxidized and reduced units in the materials indicates that the materials have similar oxidation states. In fact, the finger print region of the PANI/Au composite is almost identical to that of PANI/HBF$_4$. For example, the characteristic ring bands for aromatic C-C are located at 1597 and 1512 cm$^{-1}$ versus 1593 and 1510 cm$^{-1}$, for the pure polymer and the composite, respectively. In addition, the IR bands for the out of plane C-H are in good agreement with values of 832 cm$^{-1}$ and 829 cm$^{-1}$ for PANI/HBF$_4$ and PANI/Au. The shifts are well within the 4 cm$^{-1}$ resolution used for data acquisition.

A more significant shift for the C-N band is observed when comparing the two materials. The band is located at 1335 cm$^{-1}$ for PANI/HBF$_4$ shifting to lower energy (1323 cm$^{-1}$) for PANI/Au. The 12 cm$^{-1}$ shift to lower energy is significant because it is directly related to differences in chemistry and electron density at the nitrogen group. This difference indicates that the C-N bonds (or amino, imino bonds) within the polymer are influenced by the gold particles. The energy shift indicates that the gold directly
influences the electron density of the C-N bond. The shift is consistent with the donation of electron density from the metal to the imino nitrogen units in the polymer increasing the amount of free charge carriers in the system. The interaction of the gold with nitrogen groups is consistent with the nucleation of PANI onto the gold clusters discussed previously. It is however interesting to note that no large change in the energy for the N-H band is observed (3373 cm\(^{-1}\) and 3369 cm\(^{-1}\)). It is likely that the electron density of the C-N bond is more strongly perturbed than the N-H bond due to the conversion of benzenoid units to quinoid units as electrons are removed from PANI.

3.2.4.3 Elemental Analysis.

The elemental analysis of pure PANI/HBF\(_4\), PANI/Au (with HBF\(_4\)) was conducted to determine the chemical composition of the organic component in each sample. The results of the elemental analysis are shown in Table 3.1. The general repeat unit of PANI can be represented with four aniline units as shown previously with both oxidized and reduced units. The unit formula for this structure is C\(_6\)H\(_4\)\(_5\)N, without proton doping. The formula represents an even number of reduced and oxidized units (x = 0.5). A value of greater than 4.5 for hydrogen can be attributed to the degree of proton doping. In addition, any excess proton in the system requires the uptake of anions to maintain charge neutrality. Anion uptake can be in the form of either Cl from AuCl\(_4\) reduction or, F from HBF\(_4\) dissociation and uptake of BF\(_4\). For example, elemental analysis of PANI/HBF\(_4\) gives a formula unit of C\(_6\)H\(_{5.0}\)NF\(_{0.4}\)S\(_{0.2}\). The degree of anion doping is based on the amount of F present in the elemental analysis. The value obtained for F must be divided by 4 to account for the stoichiometry of BF\(_4\). A value of 0.10 is consistent with the stoichiometry. This number is smaller than expected based on the value of 5.0 obtained.
Table 3.1  

**a. PANI/HBF₄ elemental analysis of the polymer, normalized to nitrogen.**

**b. PANI/Au elemental analysis of the polymer, normalized to nitrogen.**

A.

<table>
<thead>
<tr>
<th>Element</th>
<th>% Composition</th>
<th>Moles</th>
<th>Mole Ratio</th>
<th>Analysis Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>68.05</td>
<td>5.67</td>
<td>6.1</td>
<td>C₆.₁H₅.₀N₁.₀F₀.₄S₀.₂</td>
</tr>
<tr>
<td>H</td>
<td>4.68</td>
<td>4.63</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>13.03</td>
<td>0.93</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>7.28</td>
<td>0.38</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>6.39</td>
<td>0.20</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

B.

<table>
<thead>
<tr>
<th>Element</th>
<th>% Composition</th>
<th>Moles</th>
<th>Mole Ratio</th>
<th>Analysis Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>69.90</td>
<td>5.82</td>
<td>6.3</td>
<td>C₆.₃H₄.₈N₁.₀F₀.₆Cl₀.₁</td>
</tr>
<tr>
<td>H</td>
<td>4.50</td>
<td>4.46</td>
<td>4.8</td>
<td>Percent Au - 58%</td>
</tr>
<tr>
<td>N</td>
<td>13.15</td>
<td>0.94</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>11.04</td>
<td>0.58</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>3.30</td>
<td>0.09</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

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from the elemental analysis for hydrogen and the acid concentration used during the synthesis (1M HBF$_4$). A significant amount of S was found in the elemental analysis of the polymer indicating that peroxydisulfate may play a role in the diminished amount of BF$_4^-$ in the polymer. The elemental composition of the species giving rise to the S signal is unknown. Quantitative analysis of the anion uptake can only be accomplished if the chemical composition of the anion is known. However, an estimate of the contribution can be obtained assuming the charge of the S species. The charge associated with S containing anions is typically -2 (i.e. SO$_4^{2-}$, S$_2$O$_5^{2-}$, and SO$_3^{2-}$). Based on this assumption, the charge associated with the proton doping would then equal the negative charge of the anions present.

In contrast to PANI/HBF$_4$, the elemental analysis of PANI/Au gives a formula unit of C$_{6.1}$H$_{4.8}$NF$_{0.6}$Cl$_{0.1}$. It is clear from the formula that the degree of proton doping is smaller for PANI/Au increasing by only 0.2 units. However, the combined values of 0.15 (0.60/4) for F and 0.10 for Cl indicate that both BF$_4^-$ and AuCl$_4^-$ play a role in the charge neutrality of PANI/Au. In addition, the degree of anion uptake is consistent with the proton doping in the unit formula (0.3 vs. 0.25 for proton and anion, respectively). This could be attributed to decreased protonation due to a blocking effect by the gold particles. In previous electrochemical studies the voltammetric response for proton doping was found to decrease significantly after the introduction of Au due to the blocking of the nitrogen sites. In general the elemental analysis indicates that the composition of PANI/Au is consistent with PANI/HBF$_4$ produced using traditional synthetic methods. The percentage of Au in the composite was estimated to by 58% relative to the organic component using the elemental analysis data.
3.2.4.4 X-Ray Photoelectron Spectroscopy.

X-ray photoelectron spectroscopy was also performed to verify the oxidation state of the metal species and to examine the organic component with respect to the nitrogen moiety and dopant. Figures 3.7.a and 3.7.b show the photoelectron spectra of pure PANI/HBF$_4$ and PANI/ Au, respectively. The presence of metallic gold in the PANI/Au spectrum is marked by the appearance of two Au(0) bands located at 84 eV ($^4f_{7/2}$) and 88 eV ($^4f_{5/2}$). These values are consistent with the previously determined energies for metallic gold embedded in PANI. In comparison, the Au(III) bands for AuCl$_4^-$ are observed at 87 eV($^4f_{7/2}$) and 92 eV($^4f_{5/2}$). The absence of a band at 92 eV indicates that all Au(III) species were reduced. The data also clearly shows that XPS bands associated with metallic Au are absent for the PANI/HBF$_4$ sample.

Analysis of the nitrogen bands in XPS can provide quantitative and qualitative information concerning the speciation of imino, amino, and protonated nitrogen groups in the polymer. Previous studies have shown that the nitrogen peak can be de-convoluted into three different groups including the imino, amino, and protonated nitrogen species using fitting routines. The corresponding energies have been previously determined based on previous studies with binding energies of 398 eV for imino, 400 eV for amino, and > 402 eV for protonated species. The error associated with using multiple Gaussian functions to fit what appears to be a single XPS bands in our data is quite large (>> 5% for each de-convoluted species). It is believed that this approach will limit the accuracy of the quantitative analysis.

From our data, the de-convolution and integration of the nitrogen peak using a multiple peak, Gaussian fitting routine, indicates that PANI/HBF$_4$ consists of $37 \pm 13\%$
Figure 3.7 XPS surveys of a. pure PANI with no gold, and b. PANI/Au composite. The XPS bands are labeled for clarity.
imino groups centered at an energy of 398 eV, 47 ± 16% amino groups centered at an energy of 401 eV, and 16 ± 10% protonated species centered at an energy of 405 eV. Comparative values for PANI/Au are 53 ± 15% for the imino group (398 eV), 25 ± 10% for the amino group (401 eV), and 22 ± 9% for the protonated species (405 eV). The energies associated with the nitrogen species are in agreement with the literature. The percent composition of each species is slightly different based on the calculated values from elemental and FTIR analysis. However, the degree of doping and extent of oxidation is difficult to estimate considering the magnitude of the relative standard deviation. The general lack of agreement of the XPS data when the nitrogen peak is fit to three separate Gaussians is indicative of the error of the technique and calls into question the validity of using this technique for quantitative analysis of a single XPS band. In contrast, when a single Gaussian is used in the analysis, a much lower error associated with the integration is observed. For example, integration of the N^1S band for each sample resulted in a standard deviation of less than 3% for each sample. Based on these results, integration using multiple Gaussian waves is not considered when comparing XPS data to elemental analysis.

Analysis of the dopant is based on the identification of F, S, and Cl in each sample. The identification of F is straightforward with a strong band at 687 eV for both materials. For the elemental analysis data it was found that the PANI/HBF_4 had a smaller percentage of F in comparison to PANI/Au. Comparison of the N and F bands allows the relative percent of dopant versus N in the unit formula to be compared to the XPS data. Each species must be first scaled by the element’s XPS sensitivity factor (F = 1 and N = 0.42), and the stoichiometry of the doping species (four F per dopant anion) must be
considered. Based on these constraints the XPS data confirm the degree of doping by BF$_4^-$ with values of 0.09 and 0.22 for PANI/HBF$_4$ and PANI/Au, respectively. These numbers are consistent with the calculated values of 0.10 and 0.15 obtained from elemental analysis. In addition the low energy S bands centered at 164 eV (S$^2$\textit{p}) and 230 eV (S$^2$\textit{s}) can be identified in Figure 3.7a, which are consistent with doping by the oxidant peroxydisulfate. Without knowledge of the stoichiometry or composition of the sulfur species it is difficult to determine the contribution of this species to the overall doping of PANI/HBF$_4$.

3.2.4.5 Electronic Resistivity/Conductivity

It is well known that the proton doping of PANI strongly affects the conductivity of the polymer. The emeraldine salt is the most conductive state form of the polymer. In this form it contains equal numbers of oxidized and reduced units and the imino groups are protonated with the corresponding counter-ion present to maintain charge neutrality. The doped polymer has increased conductivity relative to the undoped emeraldine form of PANI. It has been shown that the conductivity of PANI increases six-fold as a function of pH decrease from 6 to 0.\textsuperscript{22} Although the polymer is fully conjugated the intrinsic conductivity is limited because there is a lack of free charge carriers in the polymer. Any increase in conductivity of the material can be related to the number of free charge carriers in the proton doped polymer. Based on these trends it would be expected that the conductivity would be greater for the material with the largest degree of doping.

From the elemental analysis data it is found that PANI/HBF$_4$ has a slightly higher degree of proton doping, indicating that the materials should have a higher conductivity.
The four point probe sheet conductivity for a pressed pellet of PANI/HBF$_4$ is $1.1 \times 10^{-4} \pm 12\%$ S/cm. For comparison, the conductivity value obtained for a pellet of PANI/Au using the four point probe is $3.2 \pm 12\%$ S/cm. The $10^4$ increase in conductivity observed for the PANI/Au composite is surprising considering the lower degree of proton doping. The difference in conductivity indicates that increasing the number of charge carriers through proton doping is limited. The degree of free charge carriers is strictly related to the degree of doping in the polymer, based on charge neutrality issues. In comparison, the insertion of metal clusters increases the number of charge carriers through the conduction band of the Au metal in contact with the polymer. This interaction is not diffusion limited because Au is in direct contact with the polymer at all times. The degree of metal incorporation is based on initial solution parameters and nucleation of the polymer on the metal surface rather than the oxidation state of the polymer. Electron density can flow from the metal (valence band) to the polymer increasing the number of free charge carriers in the system and enhancing the overall conductivity of the material.

3.3 References


CHAPTER 4

CHEMICAL AND ELECTROCHEMICAL SYNTHESIS OF PANI/Au COMPOSITES: A COMPARISON.

4.1 Introduction

The synthesis and characterization of PANI using a variety of synthetic methods and analysis techniques is well documented.\textsuperscript{1-4} The complex relationship between oxidation state, proton doping and the conductivity of the polymer has been examined in detail. Previous studies indicate that the proton doping is particularly important in increasing the number of free charge carriers in the polymer, influencing the flow of charge as a function of potential. The electrical conductance $\sigma$, of the polymer is defined by the ratio between the current density $J$, brought about by an applied electric field, $E$.\textsuperscript{5}

$$\sigma = J/E$$

It is clear that as the number of free charge carriers decrease, the current density must also decrease, thus lowering the current density and conductance of the material relative to a constant applied potential. Therefore, increasing the number of free charge carriers in the polymer is critical in enhancing the conductance of the polymer.

In this chapter PANI/Au composite material obtained from the electrochemical uptake and reduction of $\text{AuCl}_4^-$ in a PANI film is compared to the chemically prepared material. The synthetic process for the electrochemically synthesized composite is discussed in this chapter as compared to the chemically prepared composite.
Additionally, the chemical characteristics of each system are compared. Finally, the effect of Au uptake on the chemical and electronic properties of each composite are examined and compared. The results suggest that the complex relationship between the oxidation state of the polymer, the proton doping, and conductance can be directly influenced by the insertion of metallic species into the polymer matrix.

4.2 Results and Discussion

4.2.1 Electrochemical Formation of PANI/Au Composite.

The electrochemical uptake and reduction of AuCl₄⁻ provides an alternative method for producing PANI/Au composite. Electrochemical methods allow the precise control of metal uptake into a PANI film using the applied potential. The product is typically more homogenous because the oxidation state of the polymer can be precisely controlled and adjusted. The amount of product is typically small, often micrograms rather than the milligram to gram quantities afforded by chemical methods. In addition, the material must be removed and processed if one wants to use it on an external device.

The uptake of AuCl₄⁻ occurs as the PANI membrane becomes oxidized. Anion uptake is required to maintain charge neutrality in the system. Reduction of the polymer typically results in the expulsion of the dopant anion as the charge of the polymer becomes more negative. In the case of AuCl₄⁻ the reduction does not result in the expulsion of the anion from the polymer matrix. In fact, the metallic anion is reduced directly into the polymer matrix as the potential is cycled. The general reaction for the reduction of chloroauroate by PANI is given by the following chemical equation:
The electrochemical reduction of chloroaurate results in the conversion of fully reduced benzenoid units into oxidized quinoid units in PANI. It is believed that the electrons are shuttled through the nitrogen heteroatoms in the polymer. Therefore, the gold will likely play an important role in the acid doping of the polymer if the point of contact is the nitrogen sites.

Figure 4.1 shows the cyclic voltammetry (in bold) of a PANI film immersed in a solution containing 1 M HClO₄ with no AuCl₄⁻ and the sequential reduction of gold into the same PANI film in solution containing 1 M HClO₄ and 5 mM KAuCl₄. The characteristic anion and proton uptake/expulsion waves are clearly resolved with half-wave potentials of $E_{1/2} = + 0.756$ V and $+ 0.118$ V vs. SCE, respectively in the absence of chloroaurate. The voltammetric response changes gradually with each additional cycle in the presence of 5 mM KAuCl₄. It is interesting to note that the uptake of ClO₄⁻ and AuCl₄⁻ are indistinguishable in the first scan. However, for scan one the characteristic anion uptake and expulsion for ClO₄⁻ is observed at $E_{1/2} = 0.756$ V vs. SCE with a second voltammetric wave at $+ 0.655$ V vs. SCE. The emergence of a the second voltammetric wave is indicative of the reduction of AuCl₄⁻ to Au(0) in the polymer matrix. The
Figure 4.1. Cyclic voltammogram of a PANI electrode immersed in solution of 1 M HClO₄ with no Au, bottom. Cyclic voltammetric response of the same PANI electrode immersed in a solution containing 5 mM AuCl₄ in 1 M HClO₄, labeled scans 1 thru 6. Scan rate $v = 10$ mV/s and electrode area = 0.015 cm².

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reduction of AuCl\textsubscript{4}\textsuperscript{−} to Au(0) is considered to be irreversible with no observable cathodic current for the re-oxidation of Au(0).

Subtle changes can be observed with respect to the voltammetric waves after each sequential scan. For example the uptake, and expulsion of ClO\textsubscript{4}\textsuperscript{−} shifts to more negative potentials with initial \(E_{1/2}\) values for scan one and six of 0.755 V and 0.735V, respectively. The shift in half-wave potential indicates either a larger thermodynamic driving force is required to expel the anion after the uptake of the gold into the polymer matrix, or the ion must diffuse further into the polymer matrix. If nitrogen sites within the polymer are blocked then the anion will have to diffuse further into the polymer matrix to maintain charge neutrality in the system. The diminished signal of proton uptake and expulsion after the first scan is consistent Blocking of the nitrogen sites.

In contrast to the uptake and expulsion of the anion, the anodic voltammetric waves associated with the reduction of AuCl\textsubscript{4}\textsuperscript{−} to Au(0) shift to positive potential as a function of each scan. The potential shifts from 0.655 V to 0.675V over the six scans. The shift in potential is consistent with a lower thermodynamic driving force for the reduction of AuCl\textsubscript{4}\textsuperscript{−} after the first scan. After the first scan the polymer contains metallic gold particles. Therefore, further gold reduction can occur at two energetically different sites. Gold can either nucleate into the polymer at free nitrogen sites or reduce directly onto gold particles dispersed into the polymer matrix.

It is difficult to tell if each scan results in the reduction of identical quantities of gold into the polymer because the voltammetric wave for ClO\textsubscript{4}\textsuperscript{−} expulsion and AuCl\textsubscript{4}\textsuperscript{−} reduction overlap significantly after the sixth scan. An estimate of the amount of gold reduced for each scan can be obtained by integrating the voltammetric wave for the gold
reduction in scan one. A value of \(~ 0.1\) micrograms of Au is obtained from the integration of the voltammetric wave, with a cumulative total of \(~ 0.6\) micrograms for all six scans. The amount is significant in terms of the weight percent considering that the weight of the polymer on an electrode is likely on the same scale.

The only direct measurement of the influence of gold introduced into PANI comes from the reduced proton uptake and expulsion observed during potential cycling. As shown in Figure 4.1, the reduction of the proton uptake and expulsion was clearly observed after the first scan. The acid concentration is sufficiently high (1 M HClO\(_4\)) so that both the amine and imine nitrogens in the polymer should be protonated during potential cycling. Therefore, any reduction in the proton doping can be attributed to blocking of these sites. The electrochemical doping of a PANI film in 1 M HClO\(_4\), in the absence of AuCl\(_4^−\), is presented in Figure 4.2.a. The characteristic proton and anion doping waves can be observed at \(E_{1/2} = + 0.148\) V and \(E_{1/2} = + 0.759\) V, respectively.

The uptake and reduction of gold in the PANI membrane is shown in Figure 4.2b (second scan shown) for the same electrode used in Figure 4.2a in a solution containing 5 mM AuCl\(_4\) in 1 M HClO\(_4\). The second of two sequential voltammetric scans shows that the reduction of AuCl\(_4^−\) occurs at \(E = \sim + 0.703\) V vs. SCE. The voltammetric response in Figure 4.2b is characterized by diminished proton uptake/expulsion. It is difficult to determine from Figure 4.2b the reduction of anion uptake/expulsion because both ClO\(_4^−\) and AuCl\(_4^−\) are present in the PANI film. In fact, the expulsion of ClO\(_4^−\) and reduction of AuCl\(_4^−\) are not completely resolved in the voltammetric scan. The expulsion of ClO\(_4^−\) appears as a shoulder on the voltammetric wave associated with AuCl\(_4^−\) reduction. Finally, the PANI/Au composite produced in Figure 4.2b is cycled in a 1 M HClO\(_4\).
solution to determine the change in proton and anion uptake and expulsion (Figure 4.2c). The proton and anion doping waves can be observed at $E_{1/2} = +0.149$ V and $E_{1/2} = +0.754$ V. Integrating and comparing the charge from the voltammetric waves in Figure 4.2a and c is a straightforward way of determining whether Au blocks imine and amine sites in PANI. In Figure 4.2a the voltammetric waves for the uptake and expulsion of protons give values of $Q = 8.325 \times 10^{-4}$ C and $Q = 8.766 \times 10^{-4}$ C, respectively. In contrast the values for proton uptake and expulsion in Figure 4.2c are $Q = 4.496 \times 10^{-4}$ C and $Q = 4.959 \times 10^{-4}$ C. The reduction of electrochemically active imine and amine sites is on the order of forty-three percent for proton uptake and forty-six percent for proton expulsion. The same calculations can be performed for anion uptake and expulsion. In this case the results are even more dramatic. The reduction anion uptake and expulsion is on the order of fifty-six and fifty-eight percent. It is possible that the larger reduction in anion uptake/expulsion is an artifact of Au dispersion in PANI. The ability to shuttle electrons (free charge carriers) from the valence band of bulk Au metal to the polymer reduces the need for anion uptake in the polymer. In this scheme the metal acts as a solid-state dopant during potential cycling, shuttling electrons to the polymer as needed to maintain charge neutrality in the system.
Figure 4.2. a. Cyclic voltammogram of a PANI electrode immersed in solution of 1 M HClO$_4$ with no Au. b. Cyclic voltammetric response of the same PANI electrode immersed in a solution containing 5 mM AuCl$_4$ in 1 M HClO$_4$. c. Cyclic voltammetric response of the PANI/Au composite electrode immersed in a solution containing 1 M HClO$_4$. Scan rate $v = 10$ mV/s and electrode area = 0.015 cm$^2$. d. Subtraction of figure c from figure a.
4.2.2 Imaging and Comparison of PANI/Au Composites.

The loss of AuCl₄⁻ signal (λ = 311.7 nm) in Figure 3.2d is consistent with reduction of the anion to the metallic species. XPS was employed to determine that the only Au species in both PANI/Au composites is the fully reduced form Au(0), with no contribution from Au(III). It is well known that the nucleation of aniline radicals and the continued formation of radicals once polymeric units have formed, result in the growth of uniform and cohesive films at noble metal surfaces such as Pt and Au electrodes. However, the nucleation of PANI onto gold particles in solution in the absence of potential control has not been studied in detail. In addition electrochemical methods allow the nucleation and dispersion of Au to be controlled. The metal particles for each composite are formed under very different circumstances suggesting that the distribution and size may be significantly different also. Differences in the distribution and size of the Au particles in chemically and electrochemically produced composite materials were probed using scanning electron microscopy.

The uptake and reduction of AuCl₄⁻ to Au(0) in an electrochemically grown PANI membrane is examined in Figure 4.3a and b. Both of the SEM images are at the same magnification for comparison. Pores with various dimensions characterize the film morphology at the membrane surface. The porous nature of the film at the surface is deceiving because the film is not uniformly dense. The initial formation of a compact layer is typical with a more open structures forming as the film thickness increases. The same electrode was subjected to 5 voltammetric scans in 5 mM AuCl₄⁻ in 1 M HClO₄, Figure 4.2b. Gold particles on the surface and within the pores are visible in the SEM image. The Au particles are affixed to the polymer membrane. In addition, there
are regions where individual gold particles are resolved. However, other regions show aggregates of gold particles that are not spatially resolved from neighbors. These regions are located on the outer surface of PANI. The images indicate that gold nucleation occurs at two different sites. The anion can reduce in the PANI matrix or at sites where the gold anion has been previously reduced.

A comparison of chemically and electrochemically formed PANI/Au composite is presented in Figure 4.4. The electrochemically reduced gold particles can be seen in the PANI membrane in Figure 4.4a. The morphological voids described previously are visible with individual gold particles and aggregates present throughout the PANI membrane. The particles seem to be well dispersed on the surface and within individual pores. Gold particles have nucleated to both the surface of the polymer and strands within the voids. The particle diameter for the electrochemically formed PANI/Au composite is on the order of ~ 150 to 300 nm. In contrast, the electrochemically formed PANI/Au composite is characterized by much larger gold particles on the order of ~ 1 µm.

The large discrepancy in particle size for each composite can be related to the synthetic method employed. In the case of electrochemical assembly, AuCl₄⁻ diffuses into the polymer and disperses into the PANI matrix based on the charge of the polymer and the driving force for charge neutrality. Nitrogen groups in the polymer act as a point of contact and the groups are evenly distributed in the PANI matrix. Therefore, nucleation of the gold at these sites disperses the particles evenly within PANI. In addition, aggregation can only occur as each successive cycle is performed and Au is reduced in the vicinity of existing gold particles. However, if nitrogen sites are blocked
Figure 4.3  

a. SEM image of PANI electrode prior to uptake and reduction of $\text{AuCl}_4^-$.

b. SEM image of PANI/Au composite after uptake and reduction of $\text{AuCl}_4^-$. 

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Figure 4.4. SEM image of PANI electrode after uptake and reduction of $\text{AuCl}_4^-$. b. SEM image of chemically prepared PANI/Au composite. Both images appear at the same magnification for direct comparison of particles size.
the attractive forces between the anion and the nitrogen are minimized, reducing aggregation. In contrast, the aggregation of Au occurs rapidly in solution during the chemical synthesis because the particles are free to diffuse and interact with other particles prior to polymer formation and nucleation. Once a critical mass of gold is obtained PANI nucleates onto the metal surface thus encapsulating the particles. Once the polymer nucleates to the gold surface, aggregation is eliminated, and the solubility limit is exceeded for the composite. Precipitation occurs rapidly after this point in the synthesis. The particle size in the chemically produced composite is based on the aggregate size and the critical mass of Au required for the nucleation of PANI.

4.2.3 FTIR Spectroscopy of PANI/Au Composites.

FTIR analysis of the fingerprint region between 700 - 1600 \text{ cm}^{-1} \text{ is particularly useful for examining the resonance modes of the benzenoid and quinoid units, and individual bonds (i.e. out of plane C-H and C-N) of PANI.}^{28,33,49,9,10} \text{ The FTIR spectra of chemically and electrochemically formed PANI/Au are presented in Figures 4.5a and 4.5b. The characteristic bands associated with the benzenoid phenyl ring (~1500 \text{ cm}^{-1}) and quinoid phenyl ring (~1590 \text{ cm}^{-1}) of the polymer are labeled on the figure. These bands can be used to estimate the oxidation state of the polymer as discussed in Section 1.1.2, where the percent of oxidized versus reduced units is obtained by integrating the IR bands. Integration of the peaks for PANI/Au gives a value of } x = 0.53 \text{ indicating the chemically formed composite contains proportional amounts of the quinoid and benzenoid moieties (Figure 4.5a). This is consistent with the reaction mechanism in which the aniline radical is formed during gold reduction. In contrast the integration of the peaks for the electrochemical formed PANI/Au composites yields a value of } x = 0.70 \text{.}
(Figure 4.5b). A relatively large portion of the polymer units exist in the oxidized form after the electrochemical reduction of \( \text{AuCl}_4^- \). The increased number of oxidized units is consistent with the withdrawal of electron density from the amine sites in the polymer, forming the imine moiety.

Examining the fingerprint region indicates the chemically formed PANI/Au composite is nearly identical to that of the emeraldine salt form of PANI where there is an equal number of oxidized and reduced groups \( (x = 0.5) \). For example, the characteristic ring bands for aromatic C-C are located at 1597 and 1512 cm\(^{-1}\) versus 1593 and 1510 cm\(^{-1}\), for the emeraldine salt and the composite, respectively. In addition, the IR bands for the out-of-plane C-H are in good agreement with values of 832 cm\(^{-1}\) and 829 cm\(^{-1}\). The shifts are well within the 4 cm\(^{-1}\) resolution used for data acquisition. A more significant shift for the C-N band is observed when comparing the two materials. The band is located at 1335 cm\(^{-1}\) for the emeraldine salt shifting to lower energy \( (1323 \text{ cm}^{-1}) \) for PANI/Au. The 12 cm\(^{-1}\) shift to lower energy is significant because it is directly related to differences in chemistry and electron density at the nitrogen group. The difference indicates that the C-N bonds (or amino, imino bonds) within the polymer are influenced by the gold particles. The energy shift indicates that the Au directly influences the electron density of the C-N bond. The interaction of the Au with nitrogen groups is consistent with the nucleation of PANI onto the gold clusters discussed previously. Comparison of the electrochemically formed PANI/Au with the chemically formed PANI/Au is used to highlight the effect the gold particle has on the polymer for each composite. The chemically prepared composite showed very little change in comparison to the emeraldine salt form of PANI. In addition, the number of oxidized
Figure 4.5. Photoacoustic FTIR spectra of, a. Chemically prepared PANI/Au composite and b. Electrochemically prepared PANI/Au composite. FTIR band assignments and the ratio of the oxidized unit (x) are labeled.
and reduced units is nearly identical for the two materials. This is not the case for the electrochemically formed PANI/Au composite. The bands observed at 1593 cm⁻¹ and 1323 cm⁻¹ shift to higher energy, 1619 cm⁻¹ and 1338 cm⁻¹ for the electrochemically produced PANI/Au composite. These bands are influenced by the withdrawal of electron density and a shift to higher energy as a function of increasing quinoid units. In contrast, the benzenoid bands for the two materials are 1510 cm⁻¹ and 1514 cm⁻¹ indicating that the insertion of gold into the PANI matrix has little effect on the benzenoid units in the polymer. Finally, significant differences in the band shapes and intensities are observed for the composite materials. The IR bands for the electrochemically formed PANI/Au, between 1350 and 700 cm⁻¹, are significantly higher in intensity than the chemically prepared composite. It has been suggested that this enhancement is caused by a surface enhancement based on the gold particles. The size of the gold particle is obviously important because no enhancement in the chemically produced composite is seen.

4.2.4 Conductance of PANI/Au Composites.

It has been reported that the conductivity of PANI increases six-fold as a function of pH decrease from 6 to 0. Although the polymer is fully conjugated the intrinsic conductivity is limited because there is a lack of free charge carriers in the polymer. Any change in conductivity of the material is strongly related to the number of free charge carriers in the proton doped polymer. In addition, the oxidation state of the polymer plays a significant role. In addition it has been shown that the most conductive state of PANI is obtained when there is equal numbers of oxidized and reduced units (x = 0.50). Withdrawal of electron density from the polymer and the formation of excess quinoid groups can have a significant influence on the polymers ability to shuttle charge. Based
on these trends it is expected that the conductivity would be greater for the material having equal numbers of oxidized and reduced units and highest level of acid doping.

The four point probe sheet conductance for a pressed pellet of the emeraldine salt (x = 0.50) obtained using ammonium peroxydisulfate as an oxidant in the presence of 1 M HBF₄ is \(1.4 \times 10^{-4}\) S/cm. For comparison the conductance value obtained for a pellet of chemically formed PANI/Au made from \(2.5 \times 10^{-2}\) M KAuCl₄ and 1 M HBF₄ is 3.2 S/cm. A significantly lower value of \(3.5 \times 10^{-7}\) S/cm is obtained for the electrochemically formed composite on gold coated mica. The differences between the chemically produced materials is indicative of the hopping distance for the electrons on the polymer chain as well as the change in carrier sites since the materials were at nearly the same oxidation state. The results indicate that the flow of electrons when gold is present is enhanced for the chemically produced PANI/Au composite. The smaller value for the conductance obtained for the electrochemically formed composite is likely due to the degree of oxidation which results from the reduction of the gold species. The degree of proton doping is reduced due to the withdrawal of electron density thus, reducing the conductance of the material. It is impossible to know which factor, oxidation of the polymer or reduced proton doping, influences the conductance more. However, the cumulative effect is that the presence of gold does not overcome the conductance barrier of this doping level and oxidation state.

4.3 References


CHAPTER 5

PANI/Pt COMPOSITE SYNTHESIS AND CHARACTERIZATION

5.1 Introduction

The unique chemical and electronic properties of conductive polymers have contributed to the continued research of the materials. Detailed studies of conductive polymers such as polyaniline (PANI) and polypyrrole (Ppy) have centered on the influence of the method of preparation, doping, influence of chemical constituents and morphology on the physical and chemical properties of the materials. As mentioned previously in Chapter 1, acid doping and the oxidation state of PANI have been shown to dramatically affect the conductivity of the polymer. PANI is unique among conductive polymers in that it can undergo both proton and anion doping as a function of applied potential and changing oxidation state. The uptake and expulsion of ionic species from PANI membranes is based on the need to maintain charge neutrality in the polymer membrane. The incorporation of acid has an added bonus by providing the necessary free charge carriers required for the enhanced conductivity of the previously undoped polymer. Using solid-state dopants (metal clusters) is a somewhat new approach to providing free charge carriers within the polymer membrane. This method relies on the influence of the metal on the chemical and physical properties of PANI.

As stated in Chapter 1, chemical synthesis allows larger quantities of the composite to be produced and used, ex-situ, without a large degree of processing as compared to
electrochemical synthesis. It was shown in Chapter 3 that chemical synthesis methods can be employed to produce gram quantities of PANI/Au composites with enhanced conductivity. In that study, polymer initialization and growth is achieved using AuCl₄⁻ as the chemical oxidant, producing gold particles embedded in the polymer matrix. The result is a PANI/Au composite with enhanced conductivity (~10⁴ relative to PANI without Au).

In this chapter the direct synthesis of PANI/Pt composite using PtCl₆²⁻ as the oxidizing agent in solutions containing acid, HBF₄ is described. The synthetic process is detailed and the chemical characteristics of system are evaluated and compared to PANI doped with HBF₄. In-situ UV/Vis studies are used to monitor products and reactants simultaneously and the polymer initialization reaction for the composite synthesis is proposed. In addition, SEM imaging and XPS are used to probe the Pt metal for such information as size and the oxidation state in the material. FTIR studies are used to examine the chemical properties of the polymer with and without metal clusters. Finally the sheet conductance of PANI/HBF₄ and PANI/Pt are investigated using a four point resistance/conductance probe. The synthesis of PANI/Pt composite using PtCl₆²⁻ suggests that the anion can be used to initiate the formation of PANI/metal composite. The composite can be produced with unique chemical properties that are directly influenced by the incorporation of the Pt particles into the PANI matrix.

5.2 Results and Discussion

5.2.1 PANI/Pt Synthesis.

The spectra of the reactants, reaction products, and the reaction filtrate are presented in Figure 5.1. The reactants, aniline and PtCl₆²⁻ are presented in Figures 5.1a and 5.1b,
respectively. Both reactants have UV/Vis absorbance bands between 200 - 440 nm, which makes distinguishing the changes in the concentration of these species difficult. Aniline has a single band at 254 nm while the PtCl₆²⁻ has small shoulder bands at 244.5 nm and 270.0 nm respectively. One absorbance band for PtCl₆²⁻ is resolved relative to aniline at 454.0 nm. This band for PtCl₆²⁻ can be examined prior to and after completion of the reaction to determine if consumption of the anion is complete. It is difficult to examine this band in-situ to determine the concentration of PtCl₆²⁻ during the reaction because there is significant overlap with absorbance bands associated with PANI formation in solution. For example, PANI has a well known π-π* transition between 320 - 360 nm and a polaron-π transition at approximately 440 nm, which shift in wavelength depending on solution conditions.¹⁷-¹⁹ Spectral shifts of the polaron-π transition are common and indicate oxidative or morphological changes in the polymer.²⁰-²³

The spectrum of the reaction mixture containing 1.5 mL of 0.05 M aniline and 1.5 mL of 4.14 x 10⁻³ M K₂PtCl₆ in 0.20 M HBF₄ solution is presented in Figure 5.1c (t = 15 min) and 5.1d (t = 30 hours), respectively. The emergence of the polymeric bands associated with the product can be observed as an increase in intensity of the absorbance band located at 381 nm. In addition, a broad, weak absorbance band at 689 nm emerges slowly over the time period of the synthesis (~30 hours). The assignment of the band located at 381 nm is difficult because it lies between the π-π* transition of the benzene ring for the polymer and the band associated with the polaron-π transition. In addition, the convolution of the absorbance from the product and reactants makes it difficult to make an assignment for the band. However, the band at 689 nm has been assigned previously to the localized polaron-π transition of the polymer.³²-³⁴ The degree of overlap

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Figure 5.1. Bottom to top, UV/Vis spectra of, a. 0.05 M aniline in 0.20 M HBF₄, b. 4.14 \times 10^{-3} \text{ M} \text{ K}_2\text{PtCl}_6, c. 4.14 \times 10^{-3} \text{ M} \text{ K}_2\text{PtCl}_6, d. chemically synthesized PANI/Pt colloid in aqueous solution obtained by mixing 1.5 mL of 4.14 \times 10^{-3} \text{ M} \text{ K}_2\text{PtCl}_6 and 1.5 mL of 0.05 M aniline in 0.20 M HBF₄ at time 30 hr, e. solution after PANI precipitation and filtration.
between the absorbance bands of the products and reactants minimizes the ability to evaluate concentrations of individual species \((in-situ)\) during the polymerization process.

For the reasons discussed in the previous paragraph, the degree of \(\text{PtCl}_6^{2-}\) reduction, formation of polymer and residual oligomeric material in the system was determined using the filtrate from the reaction shown in Figure 5.1e. The benefit of examining the filtrate is that the overlapping bands associated with the polymer are eliminated. In Figure 5.1e, the absence of the band at 454 nm marks the complete reduction of \(\text{PtCl}_6^{2-}\). However, a second band centered at 380 nm is also present in the filtrate. It is likely that this band is a byproduct of the reduction of \(\text{PtCl}_6^{2-}\) to \(\text{PtCl}_4^{2-}\) rather than the complete reduction to Pt metal in solution. A band centered at 382 nm is present in UV/Vis spectrum of \(\text{PtCl}_4^{2-}\) as shown in Figure 5.1c. The reduction of \(\text{PtCl}_6^{2-}\) to \(\text{PtCl}_4^{2-}\) and subsequent reduction of \(\text{PtCl}_4^{2-}\) to metallic platinum are shown in the reactions below:

\[
\begin{align*}
\text{PtCl}_6^{2-} + 2e^- & \rightleftharpoons \text{PtCl}_4^{2-} + 2\text{Cl}^- \quad E = 0.440 \text{ V vs SCE} \\
\text{PtCl}_4^{2-} + 2e^- & \rightleftharpoons \text{Pt}(0) + 4\text{Cl}^- \quad E = 0.514 \text{ V vs SCE}
\end{align*}
\]

Additionally, the formation of short chain polymeric species can not be ruled out as contributing to the band centered at 295 nm.

5.2.2 In-Situ UV/Vis Spectroscopy of PANI/Pt Composite Synthesis.

The chemical reaction of a mixture of 1.5 mL of \(4.14 \times 10^{-3} \text{ M K}_2\text{PtCl}_6\) and 1.5 mL of \(0.05 \text{ M aniline}\) in \(0.20 \text{ M HBF}_4\) was monitored for 48 hours, \(in-situ\), using UV/Vis spectroscopy. A mole ratio of \(~1:12\) (\(\text{K}_2\text{PtCl}_6\) to aniline was used to facilitate the complete reaction of \(\text{PtCl}_6^{2-}\) in the solution. The mixed absorption bands of both aniline and \(\text{PtCl}_6^{2-}\) are observed between 200 nm and 290 nm in Figure 5.2a. Analysis of the
UV/Vis spectra over the course of the reaction is extremely difficult due to the overlap of product and reactant absorbance. However, there are clearly emerging species in solution consistent with the formation of the polymer. The emergence of the characteristic π-π* and polaron-π bands associated with the polymer appear as increasing absorbance at 381.3 nm and 689 nm, respectively. In addition, a clear shift in baseline absorbance is observed indicative of light scattering effects due to Pt colloids in solution. Based on these initial results it is apparent that the reaction of PtCl₆²⁻, aniline and the formation of the polymer and Pt colloids in solution are linked.

Taking the difference between the first spectrum (time = 1 hour) and each subsequent spectrum is helpful in the de-convolution of the absorbance bands. The results of this treatment are presented in Figure 5.2b. Each spectrum in the episodic data capture represents a single 1-hour interval over the 48-hour experiment. The emergence of polymeric bands are now clearly visible with the characteristic π-π* (381.3 nm) and polaron-π (689 nm) bands associated with the polymer increasing in absorbance intensity over time. In addition, the large excess of aniline appears as a flat line that shifts to higher intensity over time after the subtraction. The shift is again consistent with the reduction of PtCl₆²⁻ to Pt colloids in solution. It is difficult to determine the relative increase in absorbance due to the formation of products in solution and the relative increase due to light scattering by Pt colloids. Therefore, no quantitative measurements are performed during the transient portion of the experiment while concentrations of solution species are changing. A more noticeable difference in the absorbance bands between 300 and 400 nm can be observed in Figure 5.2b. There are at least two distinct absorbance waves that emerge over the course of the experiment. The first band (347.6
Figure 5.2. a. In-Situ UV/Vis spectra of a mixture of 1.5 ml of $4.14 \times 10^{-3}$ M K$_2$PtCl$_6$ and 1.5 ml of 0.05 M aniline in 0.20 M HBF$_4$. The data shown includes spectra obtained from 0.25 - 48 hours (1 hour interval) b. Subtracted spectra for the reaction mixture in (a). Inset: Plot of reaction time versus absorbance: (i) band at 347.6 nm (ii) band at 381.3 nm (iii) band at 690.0 nm
nm) emerges and dominates the absorbance over the first 17 hours as seen in Figure 5.2b and inset (i). This band flattens after 17 hours and a second band at 381.3 nm emerges and becomes dominant. Assignment of the band at 347.6 nm is straightforward with the \( \pi-\pi^* \) transition for PANI typically between 320 - 360 nm. The assignment of the band located at 381.3 nm is difficult because it lies between the \( \pi-\pi^* \) transition of the benzene ring for the polymer and the band associated with the polaron-\( \pi \) transition.

The spectro-electrochemical analysis of PANI synthesis by Genies and co-workers showed that the absorbance bands for the polymer located below 400 nm are primarily due to the formation of soluble polymer intermediates.\textsuperscript{24} However, some of the contribution from the absorbance below 400 nm was also attributed to long chain polymeric species. Wei and co-workers have observed this same trend while monitoring species present in the reaction mixture during the electrochemical formation of polyaniline.\textsuperscript{25} Based on their linear sweep voltammetry results, the authors confirm the initial product formed in the synthesis of polyaniline is the dimer species (p-aminodiphenylamine). Over time these building blocks were used to form longer polymeric units in solution. The emergence of a band at 381.3 nm in Figure 5.2b after 17 hours is consistent with the formation of short chain intermediate structures followed by the formation of long chain polymeric units in solution.

The bands located at 381.3 and 689 nm are key to understanding the synthetic process. The band at 689 nm is consistent with the formation of the long chain polymeric units. Once the reduction of the PtCl\(_6^2^-\) ceases, the reaction of intermediate structures to form long chain structures becomes dominant and the solubility of PANI becomes an issue. In our system the interaction of the polymer with the Pt particles in solution is the
The spontaneous nucleation of PANI onto platinum and gold electrodes is well known and an integral part of the formation of PANI membranes at electrochemical interfaces. However, there is also the possibility that the PtCl$_6^{2-}$ is not fully reacted before the long chain polymer is formed. There is no way to rule out the reduction of PtCl$_6^{2-}$ after the long chain polymer is formed. After approximately 48 hours the product appears as a precipitate at the bottom of the reaction vessel and is filtered from the reactant solution. The degree of interaction between the polymer and Pt not clear at the end of the reaction. Questions regarding the oxidation-state of the polymer and metal remain unanswered. In addition, with exception to the reaction filtrate in Figure 5.1e the degree of metal incorporation and speciation in the polymer is unknown.

5.2.3 Mechanism for the Formation of PANI/Pt Composites

The interaction of conducting polymers with metal anions has been examined previously by a number of groups. In most cases the polymer was produced separately and then reacted with the metallic anion. For example, the chemical synthesis of a polypyrrole/Au has been reported previously. In the reported reaction the formation of colloidal polypyrrole was accomplished using ferric chloride as the oxidant prior to the introduction and reduction of the metal anion. Our system is unique because the colloidal PANI/Pt is formed without the aid of any chemical species other than the PtCl$_6^{2-}$ anion and aniline. The chemical synthesis of the PANI using PtCl$_6^{2-}$ is similar to the chemical synthesis of PANI using a more common oxidizing agent such as peroxydisulfate. The polymer initiation reaction and subsequent reaction mechanism can be presented based on the UV/Vis data as follows:
It is believed that the PtCl\textsubscript{6}\textsuperscript{2-} is initially converted to PtCl\textsubscript{4}\textsuperscript{2-} during the oxidation of the aniline monomer to the radical cation shown above. The PtCl\textsubscript{4}\textsuperscript{2-} is converted to Pt(0) by short-chain oligomeric species (i.e. dimers, tetramers etc). Previous studies in our laboratory have shown that no reaction occurs between K\textsubscript{2}PtCl\textsubscript{4} and the aniline monomer over period of one month. The reduction reactions and potentials for the PtCl\textsubscript{6}\textsuperscript{2-} and the PtCl\textsubscript{4}\textsuperscript{2-} species have been presented earlier. However, based on the electrochemical potentials, the thermodynamic barrier associated with the oxidation of the short chain oligomers is lower as compared to the oxidation of the monomer, therefore making the reduction of PtCl\textsubscript{4}\textsuperscript{2-} to metallic platinum possible.\textsuperscript{25} The reduction reactions and potentials corresponding to aniline and \textit{p}-aminodiphenylamine dimer are presented as follows:

The trend of the UV/Vis band centered at 347.6 nm associated with the formation of the short chain units of the polymer as shown in Figure 5.2b inset (i) further supports the
proposed mechanism. While the band centered at 689 nm (Figure 5.2b inset (ii)) attributed to the formation of long chain polymeric units continues to grow, the band at 347.6 nm flattens after 17 hours. It is believed that this marks the end of the formation of short chain polymer intermediates through the reduction of PtCl$_6^{2-}$ to PtCl$_4^{2-}$. The band at 689 nm continues to grow as the reduction of PtCl$_4^{2-}$ to metallic platinum by intermediates continues.

Spectroscopic data indicates that PtCl$_6^{2-}$ produces intermediate species in solution that are used as building blocks in the polymerization reaction. Clear differences are also observed in the rates of formation between intermediate species and the long chain polymer. Our spectroscopic data suggests that consumption of the intermediate species is critical in the formation of PANI. Although it is believed that the mechanism of PANI formation is very similar to that described by Genies, our system is clearly different. Specifically, nucleation and growth of the polymer onto colloidal Pt surfaces represents a significant deviation from previous mechanisms for the formation of PANI and PANI/metal composites.

5.2.4 PANI/Au Composite Characterization

5.2.4.1 FTIR Spectroscopy of PANI/Au Composites.
The IR spectroscopy of PANI/Pt and PANI/HBF$_4$ was examined to determine how the insertion of the metal influences the chemical properties of the polymer. FTIR analysis of the fingerprint region between 700 - 1600 cm$^{-1}$ is particularly useful for examining the resonance modes of the benzenoid and quinoid units, and individual bonds (i.e., out of plane C-H and C-N) of PANI. The FTIR spectra of pure PANI/HBF$_4$ and PANI/Pt are presented in Figure 5.3a and 5.3b, respectively. The characteristic ring bands for aromatic...
C-C stretching are located at 1597 and 1512 cm\(^{-1}\) versus 1590 and 1493 cm\(^{-1}\) for the pure polymer and the composite, respectively. In addition, the IR bands for the out-of-plane C-H can be compared with values of 832 cm\(^{-1}\) and 825 cm\(^{-1}\), for PANI/HBF\(_4\) and PANI/Pt. The shifts to lower energy between 7 and 19 cm\(^{-1}\) are indicative of higher electron density in the polymer and exceed the 4 cm\(^{-1}\) resolution used for data acquisition. Clear changes in this region can be observed with respect to the nitrogen heteroatom with the introduction of platinum particles in the finger print region. The characteristic bands associated with the benzenoid phenyl ring (\(~1500\) cm\(^{-1}\)) and quinoid phenyl ring (\(~1590\) cm\(^{-1}\)) of the polymer are labeled on the figure. As discussed in Chapter 1, these bands can be used to estimate the oxidation state of the polymer, where the percent oxidized units, versus reduced units, \(1-x\), are obtained by integrating the IR bands as shown in the schematic below. For emeraldine salt, the integrated peaks have shown that the benzenoid and quinoid units are approximately equal (i.e., \(x \approx 0.5\)). Integration of the peaks for PANI/HBF\(_4\) and PANI/Pt give values of \(x = 0.51\) and 0.40, respectively.

\[
\begin{align*}
\text{where,} & & \frac{1-x}{x} = \frac{\text{Area}_{\text{reduced}}}{\text{Area}_{\text{oxidized}}} = \frac{\text{Area}_{\nu (1500 \text{ cm}^{-1})}}{\text{Area}_{\nu (1500 \text{ cm}^{-1})}} \\
\text{This value indicates that the polymer created using PtCl}_6^{2-} \text{ as an oxidizing agent is more reduced in comparison to the emeraldine salt form of PANI. This value also suggests that reduction of PtCl}_6^{2-} \text{ and PtCl}_6^{2-} \text{ ceases or is complete prior to the formation of the long}
\end{align*}
\]
Figure 5.3. Photoacoustic FTIR spectra of, a. Pure PANI without Pt particles and b. PANI/Pt composite produced during chemical synthesis using PtCl$_6^{2-}$ as the oxidant. FTIR band assignments and the ratio of the oxidized unit (x) are labeled for clarity.
polymer chains in solution. One would expect a greater percentage of quinoid units in
the polymer if a significant portion of Pt species were reduced post polymer formation
due to the withdrawal of electron density from the polymer. This was observed in the
electrochemical reduction of AuCl₄⁻ by PANI in Chapter 4.

The C-N moiety plays an important role in the analysis of the composite. A more
significant shift in energy is observed for the C-N stretch when comparing the composite
to PANI/HBF₄. The characteristic band is located at 1334 cm⁻¹ for PANI/HBF₄ shifting
to 1316 cm⁻¹ for PANI/Pt. The 18 cm⁻¹ shift to lower energy represents a significant
change because it is directly related to differences in chemistry and electron density at the
nitrogen group. The energy difference indicates that the C-N bonds have decreasing
resonance (i.e. double bonded structure) between the ring and nitrogen after the insertion
of the Pt metal into the polymer matrix. In addition the relative intensity of the C-N bond
is significantly diminished in the case of the PANI/Pt composite while the relative
intensities of other bands remain fairly constant. The diminished signal is consistent with
segregation of the electron density of the lone pair electrons (lower resonance) at the
nitrogen due to strong interactions between the heteroatom and the metal. The
diminished out of plane C-H stretch in Figure 5.3b also supports the change in electronic
structure of the PANI/Pt composite. The increased segregation of electron density within
the polymer reduces ring resonance thus significantly reducing the IR intensity of
secondary bonds such as C-H and N-H the most.³¹,³²

Segregation of charge within a polymer is consistent with polymeric salts and the
nitrogen heteroatom is the key chemical constituent in the process. Spectroscopic
evidence for the formation of amine and imine salt is obtained from the N-H and C-H
bands. The spectroscopic region between 2600 and 3600 cm\(^{-1}\) is used to provide information regarding the chemical functionality of the C-H and N-H groups within the polymer. For example, if a portion of the polymer is fully reduced, the characteristic weak N-H stretch of a secondary amine would be expected to be seen between 3300 – 3500 cm\(^{-1}\). The assignment of the N-H stretch of PANI/HBF\(_4\) is straightforward with an IR band at 3373 cm\(^{-1}\) (Figure 5.3a). A similar band assignment of 3347 cm\(^{-1}\) for the N-H stretch in the PANI/Pt can be made (Figure 5.3b). However, this signal represents only a small fraction of the total signal for nitrogen groups within the polymer for PANI/Pt. A broad band that overlaps with the aromatic C-H bands can be observed in the spectrum of the composite.

Secondary amine salts typically have a broad absorbance band between 2700 – 3200 cm\(^{-1}\) that overlaps with the aromatic C-H stretch. In addition they exhibit multiple combination bands between 2000 and 1700 cm\(^{-1}\). For PANI/Pt, a broad band exists between the values of 2700 – 3200 cm\(^{-1}\), which is in direct agreement with the literature. It is also obvious that the aromatic C-H stretching appears as single bands on top of the broad band (3253 cm\(^{-1}\), 3194 cm\(^{-1}\), and 3124 cm\(^{-1}\)). Four combination bands between 1700 – 2200 cm\(^{-1}\) are also observed for the PANI/Pt composite, with the most intense band at 1953 cm\(^{-1}\). One could argue that these bands simply represent the ring overtones typically observed for substituted aromatic rings. If this were the case, the bands for the pure polymer in the absence of Pt would be seen because they share the same polymeric structure (i.e., para substitution). These bands are not seen prior to the introduction of Pt indicating that substitution is key to the overtone bands.
5.2.4.2 Elemental Analysis.

The elemental analysis of pure PANI/HBF$_4$, PANI/Pt (with HBF$_4$) was conducted to determine the chemical composition of the organic components in each sample. In addition, the Pt content was determined for the PANI/Pt sample. The unit formula for the emeraldine salt (x = 0.5) form of PANI is C$_6$H$_{4.5}$N, without assuming a contribution to the hydrogen from proton doping. Therefore, values greater than 4.5 for hydrogen can be attributed to a higher degree of proton doping, or a more reduced polymer (i.e, x < 0.5). In addition, any excess proton in the system requires the uptake of anions to maintain charge neutrality in the system. Anion uptake can be in the form of Cl$^-$ from the reduction of PtCl$_6^{2-}$ to PtCl$_4^{2-}$ or PtCl$_4^{2-}$ to Pt(0) and F from BF$_4^-$ uptake. Elemental analysis does not rule out the incorporation of either PtCl$_6^{2-}$ or PtCl$_4^{2-}$ at this point. XPS analysis discussed later indicates that the contribution of PtCl$_6^{2-}$ and PtCl$_4^{2-}$ is insignificant in the doping of the PANI/Pt composite. The percentage of Pt in the composite was estimated to be 38% relative to the organic component using the elemental analysis data. This is based on a value the total weight percentage of elements C, H, N, Cl, and F in the sample (62% of the total).

Table 5.1a and b show only the organic component (scaled to 100%) from the elemental analysis of the chemically oxidized PANI/HBF$_4$ and PANI/Pt respectively. It should be noted that the fluorine is in the anionic form BF$_4^-$. Therefore the value for F$^-$ must be scaled by a factor of 0.25 to correspond to the contribution from BF$_4^-$. The amount of anion in the polymer can be related to the degree of proton doping for PANI/HBF$_4$. A value of 0.4 for F$^-$ gives a value of 0.1 for BF$_4^-$, which is smaller than the contribution of hydrogen from the proton doping of the polymer (0.5). However, a

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significant amount of sulfur was found in the PANI/HBF$_4$. This species is incorporated into the polymer when peroxydisulfate ($S_2O_8^{2-}$) is used as the oxidant to initiate polymerization. Unfortunately the chemical composition of the incorporated anion containing sulfur is not known in the polymer. Quantitative analysis of the anion uptake can only be accomplished if the chemical composition and oxidation state of all the anions is known. The complications associated with anion identification preclude an exact interpretation of the elemental analysis data for PANI/HBF$_4$. Given the uncertainty, the degree of anionic doping is estimated to be in the range of 0.2 - 0.3. The final ratio analysis yields the following $C_{6.1}H_{5.0}N_{1.0}F_{0.4}S_{0.2}$ unit formula.

The elemental analysis for PANI/Pt is significantly different than the results obtained for PANI/HBF$_4$. Elemental analysis of the composite gives a formula unit cell of $C_{6.1}H_{6.2}N_{1.0}F_{0.04}Cl_{0.9}$. A significantly higher amount of hydrogen is present in the polymer composite compared to the pure material ($H_{6.2} - H_{4.5} = H_{1.7}$). The increase in hydrogen can be linked to a more reduced polymer ($x < 0.5$), which was confirmed by FTIR analysis. It can also be indicative of a higher degree of proton doping. The amount of $F^-$ in the form of $BF_4^-$ is significantly diminished in the composite (0.01) compared to PANI/HBF$_4$ (0.1). The primary dopant for the PANI/Pt composite is the chloride ion, $Cl^-$ (0.9). The combination increased hydrogen and chloride ion in the material indicates that the polymer contains a significant degree of protonated nitrogen in addition to an increased percentage of benzenoid units. The increase in chloride as a dopant is a direct result of increased protonation of the nitrogen within the polymer. These groups interact strongly with $Cl^-$ through the formation of nitrogen/chloride salt groups. The elemental analysis and FTIR data both indicate that the PANI/Pt composite has functional groups
consistent with the formation of an amine/chloride salt.

5.2.4.3 X-Ray Photoelectron Spectroscopy.

Figures 5.4a and b shows the photoelectron spectra of PANI/HBF₄ and PANI/Pt, respectively. The presence of metallic Pt in the PANI/Pt spectrum is marked by the appearance of two Pt (0) peaks located at 71.2 and 74.5 eV which can be assigned to Pt⁴f. These values are consistent with the previously determined energies for metallic Pt. In comparison, the energy for the Pt(II) ⁴f₇/₂ XPS bands is observed at 73.9 eV. Similarly the ⁴f XPS bands for Pt(IV) are observed at 74.5 and 77.8 eV. However, the ⁴f XPS bands always appear as doublets. The lack of XPS intensity at 77.8 eV indicates that the XPS intensity observed at 74.5 eV is strictly due to metallic Pt in the polymer.

The absence of a the peaks for Pt(II) indicates that this species does not contribute greatly to the anion doping of the PANI/Pt composite. As expected, the data also clearly shows that PANI/HBF₄ does not have any XPS bands peaks associated with ionic or metallic Pt.

Analysis of the nitrogen peaks in XPS can provide both quantitative and qualitative information concerning the speciation of imino, amino, and protonated nitrogen groups in the polymer. Previous studies have shown that the nitrogen peak can be de-convoluted into three different groups including the imino, amino, and protonated nitrogen species using fitting routines. The corresponding energies have been determined based on previous studies with binding energies of 398 eV for imino, 400 eV for amino, and > 402 eV for protonated species. However, the error associated with using multiple Gaussian functions to fit what appears to be a single XPS peaks is large (> 10% for each de-
Table 5.1  

a. PANI/HBF₄ elemental analysis of the polymer, normalized to nitrogen.

b. PANI/Pt elemental analysis of the polymer, normalized to nitrogen.

A.

<table>
<thead>
<tr>
<th>Element</th>
<th>% Composition</th>
<th>Moles</th>
<th>Mole Ratio</th>
<th>Analysis Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>68.05</td>
<td>5.67</td>
<td>6.1</td>
<td>C₆₋₁H₅₋₀N₁₋₀F₀₋₄S₀₋₂</td>
</tr>
<tr>
<td>H</td>
<td>4.68</td>
<td>4.63</td>
<td>5.0</td>
<td></td>
</tr>
<tr>
<td>N</td>
<td>13.03</td>
<td>0.93</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>7.28</td>
<td>0.38</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>S</td>
<td>6.39</td>
<td>0.20</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.00</td>
<td>0.00</td>
<td>0.0</td>
<td></td>
</tr>
</tbody>
</table>

B.

<table>
<thead>
<tr>
<th>Element</th>
<th>% Composition</th>
<th>Moles</th>
<th>Mole Ratio</th>
<th>Analysis Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>58.43</td>
<td>4.87</td>
<td>6.09</td>
<td>C₆₋₁H₅₋₂N₁₋₀F₀₋₄Cl₀₋₉</td>
</tr>
<tr>
<td>H</td>
<td>4.97</td>
<td>4.93</td>
<td>6.21</td>
<td>Percent Pt - 38%</td>
</tr>
<tr>
<td>N</td>
<td>11.23</td>
<td>0.80</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>0.65</td>
<td>0.034</td>
<td>0.043</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>24.72</td>
<td>0.70</td>
<td>0.875</td>
<td></td>
</tr>
</tbody>
</table>
convoluted species). The error severely limits the accuracy of any quantitative analysis. Comparison to previous analysis in the literature was not possible because adequate error analysis was not provided in these references. Therefore, the de-convolution was not performed on the PANI/Pt data. The ratio of nitrogen compared to dopant is considered using single Gaussian integration only.

Analysis of the dopant is based on the identification of F, Cl in each sample. The identification of F is straightforward with a strong band at 687 eV for both materials. For the elemental analysis data it was found that the PANI/HBF₄ had a significantly larger percentage of F in comparison to PANI/Pt. This agrees with the elemental analysis of both compounds. Comparison of the N and F peaks allows the relative percent of dopant versus N in the unit formula to be compared to the XPS data for PANI/HBF₄. Each species must be first scaled by the element's XPS sensitivity factor (F = 1 and N = 0.42), and the stoichiometry of the doping species (four F per dopant anion) must be considered. Based on these constraints the XPS data confirm the degree of doping by BF₄⁻ with values of 0.09 for PANI/HBF₄. This number is consistent with the calculated value of 0.10 from elemental analysis. In addition the low energy sulfur peaks centered at 164 eV (S²⁺) and 230 eV (S²⁻) can be identified in Figure 5.4a, which are consistent with doping by the oxidant peroxydisulfate. Without knowledge of the stoichiometry or composition of the sulfur species it is difficult to determine the contribution of this species to the overall doping of PANI/HBF₄.

The same treatment can be used to examine the F content in the PANI/Pt composite. However, the low intensity of the data precludes analysis using Gaussian fitting due to the low signal to noise ratio. Comparison of elemental analysis and XPS data for F was
Figure 5.4. XPS surveys of, a. pure PANI with no platinum. and b. PANI/Pt composite.

The XPS bands are labeled for clarity.
not attempted. Chloride analysis was performed due to the large content of the species determined from the elemental analysis. Two bands are present at 198 and 273 eV for chloride corresponding to the $^2$s and $^2$p orbitals, respectively. The $^2$s band is used with a corresponding sensitivity factor of 0.4 to estimate the doping due to chloride. Single Gaussian integration of the nitrogen and chloride XPS bands indicates that there is approximately 1.2 chlorides per nitrogen in the polymer. This value is higher than the value obtained from elemental analysis (0.90). Although the value is slightly higher, it is consistent with the proposed formation of an amine/chloride salt.

### 5.2.4.4 Scanning Electron Microscopy of PANI/Pt Composites.

Although the loss of $\text{PtCl}_6^{2-}$, the formation of $\text{PtCl}_4^{2-}$, and the increased baseline in Figure 5.2b is consistent with the two-part reduction of the anion to the metallic species, questions regarding the final oxidation state of the metal species and the relationship between the Pt and the polymer remain unanswered. It is well known that the nucleation of aniline radicals and the continued formation of radicals once polymeric units have formed result in the growth of uniform and cohesive films at noble metal surfaces such as Pt and Au electrodes. However, the nucleation of PANI onto platinum particles in solution in the absence of potential control has not been studied in detail. Interaction of solution formed metal species and the polymer can be probed using SEM imaging.

The SEM analysis of the PANI/Pt composite is shown in Figure 5.5. It must be stated that SEM is a surface technique that precludes the dispersion analysis of the polymer. However, incorporation of Pt within the polymer matrix is consistent with known nucleation properties of the polymer on Pt metal. The surface analysis of the composite provides the first visualization of the Pt particles with the polymer and the polymer. The
Pt particles appear on the surface as \( \sim 1\mu \text{m} \) spheres on the PANI surface in top image in Figure 5.5. The polymer appears a small ribbons of material inter-dispersed with the Pt particles. Some of the particles appear to be embedded in the polymer while other seem to be affixed to the surface.

A higher magnification SEM image of the same surface is presented in the bottom image in Figure 5.5 which shows the details of a group of Pt particles on PANI. The Pt particles on the surface have sufficiently strong interactions with the polymer and remain affixed to the polymer after significant washing to remove residual salt and acid from the polymer. In addition the composite is crushed into small particles for SEM analysis. If the Pt were not bound to the polymer either electrostatically or through the sharing of electron density it would be expected that the particles would be dislodged or washed from the composite during these treatments. The XPS data and the SEM data support the formation of PANI with dispersed Pt particles with a relatively constant diameter of \( \sim 1\mu \text{m} \).

5.2.4.5 Electronic Resistivity/Conductivity.

From the elemental analysis data it was found that PANI/HBF\(_4\) has a slightly higher degree of proton doping. It has been reported that the conductivity of PANI increases six-fold as a function of pH decrease from 6 to 0.\(^3\)\(^7\) Although the polymer is fully conjugated the intrinsic conductivity is limited because there is a lack of free charge carriers in the polymer. Any increase in conductivity of the material can be related to the number of free charge carriers in the proton doped polymer. However, the formation of an amine/chloride salt and the segregation of charge within an ionic polymer should decrease the amount of free charge carriers in the PANI/Pt composite.
Figure 5.5 Top: SEM image of PANI/Pt composite at x1000 magnification. Bottom: SEM image of PANI/Pt composite at x4300 magnification.
The four point probe sheet conductance for a pressed pellet of PANI/HBF$_4$ is $1.1 \times 10^{-4} \pm 12\%$ S/cm. For comparison the conductance value obtained for a pellet of PANI/Pt using the four point probe is $3.6 \times 10^{-7} \pm 10\%$ S/cm. The $\sim 10^3$ fold decrease in conductance indicates that Pt particle inclusion decreases the total number free of charge carriers. The degree of free charge carriers is strongly related to the degree of doping in the polymer based on charge neutrality issues. The degree of metal incorporation is based on initial solution parameters and nucleation of the polymer on the metal surface rather than the final oxidation state of the polymer. Although a relatively larger component of the fully reduced ring structure is observed in the PANI/Pt composite in comparison to PANI/HBF$_4$, the electron density associated with the organic component is fixed after the insertion of Pt into the polymer. The sequestering of the electron density within the PANI/Pt results in decreased conductance for the material.

5.3 References


20. Han, C-C., Hong, S-P. Macromolecules 2001, 34, 4937.


CHAPTER 6

CONCLUSIONS

The goal for this thesis project was to chemically synthesize PANI/Au and PANI/Pt composites and compare them to their electrochemical analogs. The chemical synthesis and characterization has been achieved for both composites. A comparison was only carried out for the electrochemical and chemical PANI/Au composites. The results of these studies have been provided in this document.

It has been shown that AuCl₄⁻ is a suitable oxidizing agent for the direct chemical polymerization of aniline. The formation of the PANI/Au composite proceeds spontaneously until all of the AuCl₄⁻ and radical aniline species in solution are consumed. Precipitation of the composite occurs as the polymer chain length increases and the solubility limit of the colloidal suspension is exceeded. Optical images clearly show polymer encapsulated gold particles that are uniformly distributed throughout the material. In addition, optical and TEM images indicate the particle diameter is relatively constant (~1 µm). The uniformity in gold particle distribution and dimension in the images suggest that solution parameters such as concentration of oxidizing/reducing species as well as the mole ratio of each component can be used to control particle size.

The results suggest that the gold encapsulated by the PANI influences the electronic properties of the polymer. Electrochemically produced PANI/Au composites utilize the oxidation state of the polymer in the uptake and reduction of AuCl₄⁻ to Au(0) in the
polymer. The subsequent uptake and expulsion of protons and anions is severely diminished indicating nitrogen sites are blocked by the Au particles. In addition, the uptake and reduction of AuCl\(_4^-\) increases the number of oxidized units in the polymer in comparison to the electrochemically formed composite.

The differences in oxidation states for the PANI/Au composite produced chemically or electrochemically are minimized with respect to the electronic properties of the materials. For each synthetic method the results suggest that the gold incorporation by PANI influences the electronic properties of the polymer regardless of the method of preparation. The conductance of each material is enhanced by a factor of \(\sim 10^4\) in comparison to PANI without gold. The data indicate that Au dispersion in PANI supplements proton doping as a primary means of increasing the free charge carriers and conductance of the polymer.

PtCl\(_6^{2-}\) has also been shown to be a suitable oxidizing agent for the direct chemical polymerization of aniline. The formation of the PANI/Pt composite proceeds as PtCl\(_6^{2-}\) is reduced to form PtCl\(_2^{2-}\). The continued reaction of PtCl\(_4^{2-}\) with the aniline monomer is not energetically favorable. Reduction of aniline ceases once the PtCl\(_6^{2-}\) is consumed. Reaction of PtCl\(_4^{2-}\) with oligomeric, short chain units, is energetically favorable and continues the reaction and formation of longer chain units in solution. Precipitation of the composite occurs as the polymer chain length increases and the solubility limit of the colloidal suspension is exceeded. SEM and XPS data indicate that the polymer contains Pt(0) particles with constant diameter (~1 \(\mu\)m). The uniformity of Pt particles in the images suggests that solution parameters such as concentration of oxidizing/reducing species as well as the mole ratio of each component is important. The results suggest that
Pt encapsulated by PANI influences the electronic properties of the polymer. The conductance of the material is diminished by a factor of ~1000 in comparison to PANI without Pt. The data indicate that Pt dispersion in PANI decreases the resonance of the ring structures in the polymer decreasing the free charge carriers available to the polymer backbone.

The chemical synthetic method outlined in this thesis provides a new technique for producing gram quantities of polymer/metal composite materials with uniform high metal dispersion and high chemical reproducibility.
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