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The Fabrication of Photocatalytic and SERS Active Noble Metal-Loaded TiO2 Nanoparticles

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University of California, Irvine

“The Fabrication of Photocatalytic and SERS Active Noble Metal-Loaded TiO$_2$ Nanoparticles”

DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

Paolo Reyes

Dissertation Committee:
Professor John C. Hemminger, Chair
Professor Reginald M. Penner
Professor Wilson Ho

2016
DEDICATION

To

My family and friends

for their kindness and support

on my journey

We are not going in circles, we are going upwards.
The path is a spiral; we have already climbed many steps.

Herman Hesse

“Siddhartha”

As long as I'm learning something,
I figure I'm OK - it's a decent day.

Hunter S. Thompson
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ACKNOWLEDGEMENTS

My thesis work would not have been accomplished without the support and guidance of the people I have met. I would like to thank Dr. John Hemminger for his guidance and knowledge as an advisor. He has provided the funding and equipment needed to complete my projects. Dr. James Taing trained me on the evaporator instrument and UV lamp operation. Cyril Mccormick troubleshooted all electrical problems associated with the evaporator and UV lamp instruments. Dr. Matt Law provided his glove box for gold precursor weighing. Jayde introduced the idea of plasma cleaning the HOPG surface to increase the population of TiO$_2$ nanoparticles.

Dr. Jiang-Guo Zheng and Dr. Matthew Sullivan trained and supervised me on the SEM and TEM instruments. Dr. Qiyin Ling and Mike Makowski trained me on the Kratos XPS system and sample preparation. Mike, Dr. Kathryn Leftwich, and Dr. Yu Liu provided further XPS data. Dr. Dmitry Fishman trained me on the UV-Vis and Raman microscope instruments and helped calculate the enhancement factor associated with Raman intensity measurements. He has also endured through my experiments involving thiophenol. Dr. Reginald Penner provided the potentiostat for Cu electroplating and Xiaowei Li performed the experiments.

Eric Wong, Mya Li, Raul O’Campo, Jerry Guo, Julie Hsu, and Dr. Gianmarc Grazioli for helping me survive year 1 theoretical courses. Dr. Allie Thomas, Dr. Safa Khan, Dr. Guofong Sun, Dr. Randima Galhenage, Anthony Babore, Joel Langford, Jared Bruce, and members of the Law and Penner group have all contributed to my progression and accomplishments of my graduate career. I cannot thank you all enough and shall cherish my experiences for years to come.
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Photocatalytic and SERS Active Noble Metal-Loaded TiO₂ Nanoparticles

By

Paolo Reyes

Doctor of Philosophy in Chemistry

University of California, Irvine 2016

Prof. John C. Hemminger, Chair

Fabricated noble metal-loaded TiO₂ nanoparticles situated on highly oriented pyrolytic graphite have been studied for photocatalytic enhancement and surface enhanced Raman spectroscopy properties. Plasma treating the HOPG surface results in an increase of TiO₂ nanoparticle population. This increases the number of noble metal nucleation sites as well as increasing the likelihood for organic molecules to chemisorb on metal surfaces for molecular detection. High resolution characterization can be made to observe changes in surface morphologies of specific nanoparticles before and after experimentation.

Platinum nanoparticles deposited onto TiO₂ substrates were analyzed for photocatalytic efficiency by Methylene Blue (MB) photodegradation. Various Pt morphologies on TiO₂ were fabricated to determine photodegradation in relation to Pt surface area coverage. Pt morphologies ranged from individual Pt nanoparticles, partially encapsulated TiO₂ particles, and completely encapsulated Pt-TiO₂ (Noted as Small, Medium, and Encapsulate). Individual Pt nanoparticles (Small) on TiO₂ were found to be the most efficient in photodegradation with the highest rate constant compared to low surface area coverage (k/SA).
Ag-TiO$_2$ nanoparticles were fabricated in order to observe surface enhanced raman phenomena (SERS) with adsorbed thiophenol molecules. These particles were fabricated by coating the substrate in Ag precursor salt and irradiating the surface with UV light. Raman microscopy was used to determine signal intensity of adsorbed thiophenol. Signal enhancement was quantified by an enhancement factor (EF) calculation of $\sim10^5$ in magnitude.

Bi-metallic loaded TiO$_2$ nanoparticles were fabricated via sequential photodeposition. Initial attempts at fabricating distinct Pt and Au nanoparticles on TiO$_2$ were made, however other methods need to be considered as Pt/Au-TiO$_2$ were encapsulated by opposing metal material. Ag-Pt-TiO$_2$ nanoparticles were fabricated by utilizing the Ag substrate coating method after Pt nanoparticles were photodeposited. Scanning electron microscopy reveals Ag nanoparticles forming alongside Pt nanoparticles adsorbed onto TiO$_2$. SERS studies were performed on these particles to determine Ag antenna capabilities for enhancing nearby molecules adsorbed on Pt. Cyclohexene was used as a probe molecule that binds exclusively to Pt surfaces and dehydrogenates into benzene near room temperatures. Benzene signal was observed on Ag-Pt-TiO$_2$ surfaces and an EF of $\sim10^4$ was observed.
INTRODUCTION

Titanium dioxide (TiO$_2$) is one of the most versatile metal oxides with a myriad of applications ranging from pigmentation, self-cleaning paints, water splitting, waste removal, semiconductors, and hydrogen production.$^{[1]}$ As a result of its widespread importance, the surface chemistry of TiO$_2$ has been widely studied. While most of the fundamental studies have utilized either macroscopic TiO$_2$ single crystals or thin films, it is expected that TiO$_2$ nanoparticles will exhibit important differences in their electronic structure (e.g., surface gap states and bandgap narrowing) as compared to bulk TiO$_2$. Indeed, the effect of TiO$_2$ particle size on their photocatalytic activity has been reported by Xu, et al.$^{[2]}$ Activation of TiO$_2$ nanoparticles through UV-light exposure can photo-generate electrons and electron holes to induce reduction and oxidation chemistry leading to complex reactions, making it an effective photocatalyst.$^{[3]}$

In addition, deposition of noble metals TiO$_2$ have been reported to result in a more effective photocatalyst due to strong metal support interactions.$^{[4]}$ These transition metal TiO$_2$ catalysts have applications in water splitting, and chemical degradation.$^{[5]}$ We have devised a nanoparticle loading system for metal-loading observations as well as testing photocatalytic and Raman enhancement properties. Our previous research has shown that the photodeposition of metal nanoparticles on TiO$_2$ substrates is possible with selective deposition and particle size control.$^{[6]}$ Some particle deposition methods require exploring different techniques as differences in noble metal species lead to morphological differences after photodeposition. As a result, techniques ranging from coating TiO$_2$ nanoparticles to step-potential electrodeposition have been explored and will be described in detail.
One application of metal-TiO$_2$ (M-TiO$_2$) nanoparticles is the degradation and removal of hazardous chemicals in the environment through non-harmful methods. Methylene blue (MB) is a dye molecule commonly used in textile industries to colorize jeans. Removal of the dye is difficult as it is resilient to environmental factors, however there are several methods involving the removal of methylene blue dye from solution.$^{[7-9]}$ Utilizing the photocatalytic properties of Pt-TiO$_2$ nanoparticles for dye removal is a desirable option due to its photodegradation ability through UV activation.$^{[10]}$

While M-TiO$_2$ research is extensive, the nature of co-deposited noble metals onto TiO$_2$ has yet to be fully studied however, as the techniques for forming a bi-metallic loaded system often restrict the morphologies of adsorbed metals, often involving choosing metals that are distinct in lattice fringes for TEM analysis.$^{[11]}$ Fabrication techniques of Au-Pt-TiO$_2$ nanoparticles have been explored in order to form distinct individual Au and Pt nanoparticles nucleating on TiO$_2$ substrates. This morphology is ideal as distinct metal nanoparticles may provide their own photocatalytic enhancements in tandem and may significantly improve TiO$_2$ performance.

The co-deposition of Ag metals loaded onto the surface of M-TiO$_2$ may enhance Raman signal intensity known as Surface Enhanced Raman Scattering (SERS).$^{[12, 13]}$ One of the most prominent applications with Raman active nanomaterials is molecular detection and mapping.$^{[14]}$ However, the nature of materials being utilized for Raman chemical detection is still being investigated. The morphology and type of metal nanoparticles being deposited on TiO$_2$ can potentially affect the nature of SERS; therefore the fabrication of a fundamental system where different types of metal nanoparticles are loaded onto the surface of TiO$_2$ nanoparticles is ideal in order to determine the parameters for enhancement. Our system of adsorbed TiO$_2$ nanoparticles
can provide observations for SERS phenomena due to the large surface area for metal adsorption and nucleation. Therefore, we have explored the prospect of fabricating Ag-Pt-TiO$_2$ nanoparticles for organic molecule detection and observations for enhanced Raman intensity. These particles may work in conjunction with Ag acting as an antenna for the detection of molecules adsorbed exclusively on nearby Pt nanoparticles, which are known to be relatively inert to the influence of Raman irradiation.$^{[15]}$
CHAPTER 1: FABRICATION OF TiO$_2$ NANOPARTICLES

1.1 Introduction

The study of titanium dioxide (TiO$_2$) is an ever-expanding field of research with a myriad of new research articles detailing properties associated with the metal oxide. Research progress on TiO$_2$ has currently not waned at all as we are still in the midst of discovering physical properties and applications for this ubiquitous material. Currently, the majority of the world has adapted the metal oxide for paints and pigment applications for clean surfaces.$^{[16]}$ Despite its efficiency in keeping surfaces clean, the inherent photo-active properties of TiO$_2$ allow for more environmentally friendly photocatalytic applications, such as water splitting, waste removal, semiconductors, and hydrogen production.$^{[17, 18]}$ As a result, articles and books have been produced solely on TiO$_2$ with utmost focus on the utilization of photocatalytic ability.$^{[5, 18]}$

Of course, the reason why so many articles and research groups focusing on TiO$_2$ photo-activity exist is because of the many factors that influence the metal oxide and its performance in photo-activity. What makes titanium dioxide so interesting is that it is a naturally-occurring photocatalyst with a relative band gap of 3-3.2 eV, depending on the crystal structure of rutile or anatase. Meaning oxidation and reduction chemical reactions occur at the surface of TiO$_2$ due to photo-generated holes and electrons respectively.$^{[18]}$ The majority of fundamental studies have been performed on bulk, single-crystal TiO$_2$; however there is much to be gained on experiments performed on nanometer scaled titanium dioxides regarding catalytic activity. At the nano-scale, TiO$_2$ band gap properties differ from bulk morphology as a result of quantum effects in relation to particle size. Thus, nano-scaled structures have to be closely observed in order to understand
any significant excitation changes or energy requirements for photo-activity.\textsuperscript{[19]} A model TiO\textsubscript{2} system where morphological changes can be observed before and after experimentation is ideal. Results from this model allow us to relate photocatalytic effects among TiO\textsubscript{2} and metal dopant morphology.

Observing at the nano-scale can be quite difficult, especially when trying to pinpoint exact physical morphological changes over time. With the majority of experiments being performed on suspended TiO\textsubscript{2} particles or thin films, the need to identify noble metal nucleation sites and encapsulation has risen for more precise observations. My research approaches TiO\textsubscript{2} on a fundamental level to observe nano-scaled photo-activity properties in terms of energy band gap changes, influencing the band gap via metal co-doping mechanisms, reduction/oxidation reactions occurring on TiO\textsubscript{2} nanoparticle surfaces, and observing signal enhancement from possible surface plasmon resonance (SPR) activity via morphological and surface modification.

Typically, TiO\textsubscript{2} at the nanoscale absorbs light in the ultra-violet range without any surface modification. When absorption occurs, electrons are excited from the valence (VB) to the conduction band (CB) and leave behind a photo-generated electron hole (h\textsuperscript{+}) in the CB. The requirement for this charge excitation is for TiO\textsubscript{2} to be exposed to wavelengths shorter than 400 nm.\textsuperscript{[20]} These excited electrons and holes are able to instigate redox reactions with any chemicals adsorbed on the surface of the particle. For example, photo-generated electron holes are able to oxidize water into hydroxyl radicals which participate in many pollutant removal reactions such as the degradation of methylene blue.\textsuperscript{[7, 21, 22]} Excited electrons can also participate in reactions to allow metals to adsorb or “dope” onto the surface with varying morphology. Deposited metals may alter the electronic state properties of TiO\textsubscript{2} due to the size, coverage, nucleation site, and nature of the metal.\textsuperscript{[11]}
Noble metal particles doped on the surfaces of titanium dioxide can greatly affect its photocatalytic abilities. Metals such as Pt, Au, and Ag provide many alterations toward TiO$_2$ behavior, effectively enabling it to behave as a heterogenous catalyst at the metal/semiconductor interface. Platinum is able to promote charge-transfer separation by accumulating excited electrons transferred from the conduction band and keeping the formed electron holes at the TiO$_2$ phase.$^{[23]}$ Platinum is also able to shift the band edges of TiO$_2$, which promotes electron charge transfer processes.$^{[24]}$ Au was also found to be an excellent promoter of charge separation, but is greatly dependent on Au particle size instead of coverage. Au also introduces visible light activity to TiO$_2$, meaning longer wavelengths are able to activate the semiconductor.$^{[25,26]}$ Ag not only promotes charge separation, but is also more efficient in photoreduction experiments, such as the photoreduction of nitrate to ammonia as Ag displays the best H$^+$ reduction capability.$^{[27]}$

Experiments on the deposition of noble metal particles onto TiO$_2$ are usually focused on a single metal. The nature of co-deposited noble metals onto TiO$_2$ has yet to be fully studied however, as the presence of two or more metal species adsorbed on the surface could potentially affect the photocatalytic properties of a Metal-TiO$_2$ catalyst. Therefore the photocatalytic mechanisms of these particles need to be studied extensively in order to gain insight for potential application use in a larger scale. One area of interest is how plasmons on the surface interfaces of co-deposited metal/TiO$_2$ supports behave when activated via visible or ultraviolet light. Au-TiO$_2$ catalysts deposited with Pt nanoparticles have been shown to photo-induce hydrogen formation in the visible light due to SPR of Au and Pt sites acting as effective H$_2$ reduction sites.$^{[28]}$

Plasmon effects that are exhibited by Au or Ag nanoparticles have been of particular interest as they are often utilized to enhance spectroscopic signaling, more specifically signal enhanced Raman spectroscopy (SERS). Co-deposition of Ag or Au metals loaded onto the
surface of TiO$_2$ surface can help produce metal structures to help improve Raman signal, however the size and distribution of these nanoparticles have to be controlled for enhancement efficiency. Therefore the parameters of co-depositing noble metal nanoparticles onto TiO$_2$ surfaces have to be determined as some noble particles such as Pt may alter the loading of Au particles onto Pt-TiO$_2$ from the enhanced charge separation. Typically, these nanostructures have to be within a few nm of each other in order to produce ideal localized plasmon resonance.$^{[29]}$ Once the ideal size and distribution for noble metal particle deposition is complete, SERS experiments can be performed with various probe molecules in order to determine enhancement factor. These SERS tests will be performed with various M-M/TiO$_2$ co-catalysts to determine which metals produce significant signal enhancement.

In order to help study co-deposition metal affects, we have anchored linear TiO$_2$ particles on step edges and defect sites of highly oriented pyrolytic graphite (HOPG) through thermal evaporation as a unique support for noble metals. Stable rows of spherical and rod-shaped TiO$_2$ nanoparticles allow us to observe physical change of specific particulates after every deposition experiment. From here we can use a variety of imaging and characterization technique that range from scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS) to determine nanoparticle morphology, and composition.
1.2 Stable TiO₂ Nanoparticles Situated on Highly Oriented Pyrolytic Graphite

Our titanium dioxide arrays are unique as they provide a way to characterize any changes made toward the TiO₂ surface after metal deposition. Mainly, we are able to take scanning electron microscope (SEM) images of particular TiO₂ nanoparticles before and after noble metal photodeposition. Observing specific nanoparticles allow us to observe metal nanoparticle deposition properties and to identify new metal nanoparticles that are sequentially deposited onto TiO₂. These particles have been observed to be stable at temperatures around 800°C, high vacuum pressure, and in aqueous solutions. In order to achieve isolated particles, TiO₂ particles are evaporated, via physical vapor deposition (PVD), onto the step edges of HOPG in high vacuum (~10⁻⁷ torr) in an evaporator (Edwards 306A Coating System).

HOPG samples are prepared by cleaving top layers off the surface by the scotch tape method to reveal step edges along the surface. The fabrication steps are detailed in Figure 1.1. The freshly cleaved HOPG sample is then loaded onto molybdenum sample holders held together by copper rods which are connected to a current applicator. The exposed face of HOPG is tilted in a perpendicular angle relative to the line of particle flight from a titanium shot. Current is also applied to the Cu rod holders which then carry the applied current to the Mo holders to heat the substrate to a desired temperature of above 800°C (~820°C). The temperature was measured by placing a thermocouple in between the heated HOPG and a Macor ceramic spacer. Titanium shots (99.995% (metals basis)) are resistively heated which cause titanium molecules to evaporate from the surface of the slug. Evaporated titanium particles are adsorbed onto the surface of heated HOPG (Grade ZYB, Momentive Performance). Due to the heated
HOPG surface, adsorbed Ti atoms will mobilize to seek out a preferential defect site for nucleation. These preferential defect sites happen to be the step edges found on the HOPG surface. Resulting particles are affected by the amount TiO$_2$ being deposited as well as the temperature of heat applied to HOPG.

Figure 1.1: TiO$_2$ nanoparticle fabrication process involving HOPG cleaving, substrate annealing, and TiO$_2$ evaporation/formation.

The amount of titanium oxide depositing on the surface of HOPG is measured through a quartz crystal microbalance (QCM). A measured thickness of 1.2 nm TiO$_2$ deposited on the surface is observed to be the most ideal amount in order for the formation of nanoparticles and rods. Heating the HOPG substrate up to 800°C has been found to be the most ideal temperature to form nanoparticles and rods exclusively on the step edges via thermal energy as seen at Figure 1.2. Lower temperatures have resulted in different morphological phases such as film or interconnected islands of TiO$_2$ which are not exclusive to the step edges. This may be due to less
thermal energy being applied to TiO$_2$ adatoms, reducing their mobility to move toward the step edges as the most stable area to coalesce and form particles and rods.$^{[30]}$ After a deposition the substrate is left to anneal at 800°C for 3 hours to desorb any contaminants/residual water in high vacuum. Samples were then immediately placed in a dessicator to prevent oxidation or into a photocatalytic cell for metal photodeposition.

**Figure 1.2**: TiO$_2$ particles of different morphology depending on the annealing temperature of the HOPG substrate. A and B: Zoomed in images of TiO$_2$ islands on HOPG heated to 400°C. C and D: Zoomed in images of TiO$_2$ arrays formed on HOPG heated to 800°C.$^{[6]}$
1.3 Characterization of TiO$_2$ Nanoparticles

TiO$_2$ nanoparticles were subjected to a variety of characterization techniques. TiO$_2$ nanoparticles were observed with SEM imaging and measured using ImageJ. Linearly arrayed TiO$_2$ nanoparticles were measured to have a pseudodiameter of 18 nm on average for the rounder particles as seen in Figure 1.3. The rods were measured to have a pseudodiameter of 23 nm on average. Highly dispersed TiO$_2$ nanoparticles were observed to be more round compared to the linear arrayed particles, therefore they were observed to have a pseudodiameter of 10.9 nm on average (Figure 1.4).

![Figure 1.3: Pseudodiameter distribution of linear TiO$_2$ nanoparticles.](image-url)
Composition of nanoparticles was analyzed with an energy dispersive X-ray detector (EDS) attachment to the SEM. In Figure 1.5, titanium and oxygen signals were observed at 4.6 and 0.5 keV respectively. Transmission electron microscopy (FEI/Philips TEM) is used to determine the crystal phase of TiO$_2$. Top layers of samples were cleaved off with Scotch tape in order for TEM analysis. From Figure 1.6 lattice fringes can be observed on TiO$_2$ nanoparticles. These lattice fringes can be measured through FFT analysis in ImageJ to reveal the phase. TiO$_2$ nanoparticles were observed to have a lattice space measurement of 3.2 Å coinciding with the rutile phase, the most common natural form, of TiO$_2$.\[31\] There was no observation of anatase or brookite phases in our samples. This may be due to the nature of TiO$_2$ evaporation and coalescence from HOPG substrate heating.
Figure 1.5: EDS spectra of TiO$_2$. Ti and O signals are confirmed through the 4.6 and 0.5 keV signal respectively.
**Figure 1.6:** Transmission electron microscope image of a TiO$_2$ nanoparticle with observable lattice fringe spacings.
1.4 Formation of Highly Dispersed TiO$_2$ Nanoparticles

Figure 1.7: Fabrication steps of highly dispersed TiO$_2$ nanoparticles situated on HOPG. Samples are cleaved and plasma cleaned in order to create more sites for TiO$_2$ nucleation.

The morphology of linear TiO$_2$ nanoparticle arrays allows us to observe morphological differences with metal dopants on the surface. However, the volume of TiO$_2$ nanoparticles is sparse. Photocatalytic efficiency and Raman scattering experiments require a higher population of nanoparticles in order to observe signal, therefore we have developed a method in order to fabricate highly dispersed TiO$_2$ nanoparticles on the surface of HOPG. Figure 1.7 details the extra fabrication steps on HOPG in order to create defect sites. The HOPG samples were prepared by cleaving the surface using Scotch tape and immediately placed into the SEM (FEI Magelllan) chamber under high vacuum. The SEM chamber is fitted with an in-situ plasma cleaner that is used to clean and create defect sites on the surface of HOPG. The defect pits
provide favorable TiO$_2$ adatom nucleation into nanoparticles.$^{32}$ After plasma cleaning the surface with air inside the chamber the samples were immediately placed in the evaporator chamber for TiO$_2$ deposition. As seen in Figure 1.8, SEM images confirm the formation of highly dispersed TiO$_2$ nanoparticles. EDS analysis confirms the Ti and O signal. TEM analysis confirms the rutile phase of TiO$_2$. The highly dispersed particles are more round compared to the rods that are formed alongside the step-edge defect sites. The increased population of TiO$_2$ allows an increase in the number of active sites for metal deposition. In regards to molecular detection with SERS active Ag nanoparticles the higher number allows for more probe molecules to be adsorbed onto the surface therefore increasing the likelihood of detection.
**Figure 1.8**: Differences in TiO$_2$ morphology due to plasma cleaning the surface of HOPG prior to TiO$_2$ deposition.
1.5 Exploring TiO$_2$ Morphologies

While TiO$_2$ nanoparticles are investigated for their unique properties, other types of TiO$_2$ morphologies are of great interest to surface science studies. The bridge between nanoscale and bulk material properties is limited as intrinsic property changes between the two scales are usually significant. However, by performing experiments on larger TiO$_2$ morphologies at the nano and microscale we can begin to understand surface related reactions that may translate into bulk properties while retaining a high resolution analysis on distinct surfaces.$^{[33, 34]}$ We have fabricated various TiO$_2$ morphologies in order to study water desorption as a function of metal oxide surface area coverage. By situating TiO$_2$ onto HOPG, we are able to characterize different TiO$_2$ morphologies more effectively.

Linear TiO$_2$ nanoparticles, linear dendritic TiO$_2$ structures, dendritic island TiO$_2$ structures, and a TiO$_2$ thin film have been fabricated for this study. Altering the HOPG substrate temperature during TiO$_2$ physical vapor deposition results in significantly different TiO$_2$ structures. Substrate heating at 800 °C yields linear TiO$_2$ nanoparticles (Figure 1.9A). Heating the HOPG to 300 and 200 °C yields linear dendritic and dendritic island TiO$_2$ structures respectively (Figure 1.9B and 1.9C). At 200 °C a thin film of TiO$_2$ is fabricated (Figure 1.9D).

All morphologies have been deposited with the same deposition thickness of 1.2 nm as measured by a quartz crystal microbalance. Samples were then annealed at their respective temperatures of 2 hours in order to allow Ti material formation and remove foreign molecules on the surface. By reducing the applied current and temperature to the substrate we are able to control the morphology of TiO$_2$. We assume that the substrate temperature affects the mobility of Ti adatoms nucleating on surface defect sites on HOPG.
SEM analysis confirms the formation of linear TiO$_2$ nanoparticles, dendritic structures, and TiO$_2$ film. Linear TiO$_2$ nanoparticles were observed to be consistent with previous fabrication attempts. Dendritic structures were confirmed to form on the surface of HOPG. The linear dendritic TiO$_2$ structures were observed to have a common linear thread as a base for “branches” of TiO$_2$ material. This is consistent with previous studies with linear dendritic structure formation.$^{[35]}$ We hypothesize that the increased substrate temperature allows Ti adatoms to be mobile enough to prefer nucleation on step edge defect sites yielding a linear morphology. Dendritic islands have been observed by lowering the temperature to 300 °C. The islands contain longer TiO$_2$ branches stemming from a central point of TiO$_2$ nucleation. We assume that Ti adatoms prefer to nucleate with other mobile adatoms resulting in a formation of a morphological structure resembling more of a 3D nanoparticle. For the film, we have observed nano-scale cracks on the surface of the film, meaning that the film is not completely uniform on the surface. TEM analysis of linear TiO$_2$ nanoparticles has confirmed the rutile phase of TiO$_2$. However, we could not observe lattice fringes on the other TiO$_2$ morphologies and assume they are amorphous. EDS analysis of all TiO$_2$ morphologies confirm the Ti and O signal and associated keV values previously mentioned.
Figure 1.9: SEM imaging of Linear TiO$_2$ nanoparticles (A), Linear Dendritic TiO$_2$ structures (B), Dendritic TiO$_2$ Island structures (C), and TiO$_2$ film (D).
Water desorption studies have been performed by Anthony Babore through temperature programmed desorption spectroscopic analysis. Each sample has been annealed to 800 °C in order to reduce TiO₂ surfaces prior to water deposition. The observations and analysis of water desorption is currently being prepared for publication.

1.6 Conclusion

TiO₂ nanoparticles have been fabricated onto the defect sites of highly oriented pyrolytic graphite via physical vapor deposition in an evaporator chamber. The particles are in the rutile phase form after annealing. Two types of layouts have been developed in the form of linearly arrayed and highly dispersed nanoparticles. Linearly arrayed nanoparticles are ideal in observing noble metal morphologies after deposition. Highly dispersed nanoparticles allow a higher volume of metal nanoparticles to form in order to observe significant trends in photocatalytic performance and contain a higher number of active sites for metal deposition/nucleation. The evaporator instrument allows various TiO₂ morphologies to be fabricated. Linear TiO₂ nanoparticles, to linear dendritic TiO₂, dendritic islands, and TiO₂ film have been fabricated to study water desorption trends via TPD.
CHAPTER 2: METHYLENE BLUE PHOTODEGRADATION BY Pt LOADED TiO\textsubscript{2} NANOPARTICLES

2.1 Introduction

While most of the fundamental studies have utilized either macroscopic TiO\textsubscript{2} single crystals or thin films, it is expected that TiO\textsubscript{2} nanoparticles will exhibit important differences in their electronic structure (e.g., surface gap states and bandgap narrowing) as compared to bulk TiO\textsubscript{2}.\textsuperscript{[5]} Typically, TiO\textsubscript{2} at the nanoscale absorbs light in the ultra-violet range. When absorption occurs, electrons are excited from the valence (VB) to the conduction band (CB) and leave behind a photogenerated electron hole (h\textsuperscript{+}) in the CB. The requirement for this charge excitation is for TiO\textsubscript{2} to be exposed to wavelengths shorter than 400 nm in order to overcome the 3.0 eV bandgap.\textsuperscript{[20]} These excited electrons and holes are able to instigate reactions with any molecules adsorbed on the surface of the particle seen in Figure 2.1. Rutile TiO\textsubscript{2} consists of oxygen vacancy sites which are ideal for metal ion – TiO\textsubscript{2} lattice bonding.\textsuperscript{[36]} These reactions are usually initiated by the created electron – hole pair undergoing charge transfer to pre-adsorbed species on the surface of TiO\textsubscript{2}.\textsuperscript{[37]} However, the electron – hole pairs typically recombine if they do not find recipients for charge transfer.

Adsorbed molecules undergo reduction and oxidation reactions through photogenerated electrons and holes (\(e^-\) and \(h^+\) respectively) and eventually degrade into byproducts. This charge transfer mechanism also enables metals from a perursor solution to adsorb onto the surface active sites. Metal nucleation typically begins at the TiO\textsubscript{2} lattice where foreign metal atoms may reside in lattice vacancies, known as “doping.” The substitution of a metal atom into the TiO\textsubscript{2} lattice allows metal particle nucleation and eventual nanoparticle formation depending on the
parameters of precursor concentration and excitation source energy. Ciacchi et al details various routes of platinum nucleation starting from the reduction of K₂PtCl₄. Pt⁰ and Pt⁽¹⁾–Pt⁽¹⁾ complexes form after the precursor salt has been reduced by free electrons on the TiO₂ surface. These complexes form the building blocks and sites for Pt nucleation into eventual Pt nanoparticle formation. Depending on the metal precursor, various types of metals may alter the electronic state properties of TiO₂ due to the size, coverage, nucleation site, and nature of the metal.

![Figure 2.1](image.png)

**Figure 2.1:** Schematic of free electron and hole generation in TiO₂ nanoparticles by absorption of UV light.
Indeed, the effect of TiO$_2$ particle size on their photocatalytic activity has been reported by Xu, et.al.$^{[2]}$ In addition, deposition of metals such as Ag, Au, and Pt, on TiO$_2$ has been reported to result in a more effective photocatalyst due to strong metal support interactions, which result in visible light absorption. These transition metal TiO$_2$ catalysts have applications in water splitting, and chemical degradation.$^{[25, 26, 39, 40]}$ Previous research has shown that the photo-deposition of metal nanoparticles on TiO$_2$ nanoparticle substrates is possible with selective deposition and particle size control. The morphology of Pt nanoparticles on TiO$_2$ may determine how well pollutants can be oxidized or reduced over time by UV exposure.$^{[2]}$

One application of metal-TiO$_2$ nanoparticles is the degradation and removal of hazardous chemicals that pollute the environment. Methylene blue (MB) is an ubiquitous thiazine dye molecule commonly used in textile industries to colorize jeans. These textile factories are often near water sources and can lead to the dye seeping into natural habitats. Removal of the dye is difficult as it is resilient to environmental factors such as microbial degradation and pH.$^{[41]}$ There are several methods involving the removal of methylene blue dye from solution, yet the greenest option is mostly preferred. Utilizing the photocatalytic properties of TiO$_2$ nanoparticles for dye removal is a desirable option due to its ability to photodegrade methylene blue into less harmful products.$^{[8, 9]}$

In this study we present the fabrication and observation of photocatalytic activity of linearly arrayed Pt- TiO$_2$ nanoparticles toward photodegradation of the common dye molecule methylene blue via UV-light irradiation. In particular, we determine the effect of Pt nanoparticle loading and morphology has on the photocatalytic activity of TiO$_2$ nanoparticles. Methylene blue photodegradation is closely monitored via UV spectrometry in relation to Pt-TiO$_2$ morphology.
2.2 Fabrication of Pt-TiO$_2$ Nanoparticles

Pt-TiO$_2$ nanoparticles were fabricated via photodeposition from a metal precursor salt solution in the presence of TiO$_2$ nanoparticles. Linear TiO$_2$ nanoparticles were fabricated through the physical vapor deposition method described in chapter 1. After fabrication the TiO$_2$ substrates were placed in a photoelectrochemical cell containing an aqueous solution of 1µM K$_2$PtCl$_4$ (Sigma Aldrich) seen in Figure 2.2. Specifications of the photoelectrochemical cell can be seen in Appendix B. K$_2$PtCl$_4$ serves as the precursor solution for Pt nanoparticle formation on the TiO$_2$ substrate. The salt solution was degassed with Ar (AirGas) for 20 minutes in order to displace and remove oxygen in order to prevent vacant electron-hole recombination. TiO$_2$ bandgap UV radiation (365 nm, 200 W Hg lamp) irradiated the salt solution and the TiO$_2$ nanoparticles that coated the HOPG substrate, resulting in the deposition of Pt on the TiO$_2$. Continued UV illumination resulted in additional Pt deposition on the TiO$_2$ substrate. Pt nanoparticles were observed to encapsulate the TiO$_2$ nanoparticles after 60 minutes of UV exposure. This growth of material was a result of longer UV exposure time, allowing more Pt material to deposit on TiO$_2$. Following the Pt photodeposition, the samples were washed gently with HPLC grade deionized water and air dried in a desiccator (Fischer Price) for 24 hours before SEM (FEI Magellan), EDS (FEI Magellan), and XPS (Kratos) analysis. Particle size analysis was performed after SEM imaging with ImageJ.
In this article “Small” samples refer to TiO$_2$ loaded with an average Pt nanoparticle pseudodiameter of 4.7 nm (Figure 2.4A). “Medium” samples refer to TiO$_2$ particles loaded with an average Pt nanoparticle pseudodiameter of 7.3 nm and large Pt aggregates (~25nm in diameter) that partially coated the surface of TiO$_2$ nanoparticles (Figure 2.4B). “Encapsulated” samples refer to titania completely enveloped by excess material, resulting in a combination of aggregates and no exposed areas of TiO$_2$ (Figure 2.4C). FFT analysis of the Pt nanoparticle lattice fringes in TEM images (Figure 2.4D) reveals a d-spacing length of 2.3 Å, confirming the (111) plane of platinum (Figure 2.4E).$^{[42]}$ EDS analysis confirms the presence of Pt species on TiO$_2$ with the 2.05 keV peak (Figure 2.2). XPS analyses reveal a peak at 71.0 and 72.4 eV corresponding to binding energy of Pt4f metal and PtO respectively. Annealing the sample to 800 °C resulted in a significantly lower signal of PtO, meaning the majority of Pt nanoparticles have been properly converted into Pt metal.
Figure 2.2: SEM of Pt nanoparticles photodeposited onto TiO$_2$ supports and resulting EDS spectra confirming Pt species on TiO$_2$. 
2.3 Photocatalytic Degradation of Methylene Blue

In order to determine the photocatalytic efficiency of Pt-TiO$_2$ nanoparticles, we exposed Small, Medium, and Encapsulated Pt-TiO$_2$ nanoparticles to dilute aqueous solutions of methylene blue. Methylene blue degradation from photocatalysis has been shown to follow a pseudo-first order reaction order and undergoes a complex degradation pathway as seen in Figure 2.3.[43,44] Methylene blue was diluted to 1µM with HPLC-grade deionized water. Pt-TiO$_2$ samples on HOPG were placed in a fluorimeter cuvette cell (International Crystal Laboratories) filled with diluted MB solution. Cells were sealed with a Teflon stopper wrapped in Para-film. Cuvettes with methylene blue were exposed to TiO$_2$ bandgap radiation (UV light through a monochromator selected at 365 nm) for 15 min. intervals. The UV spectrum (Cary 50 Photospectrometer) of the methylene blue solution was taken after every 15 minutes of UV exposure until 120 minutes. The methylene blue UV-Vis spectrum consists of two significant peaks 668 ($\lambda_{\text{max}}$) and 609 nm (Figure 2.5). MB degradation was followed using the 668 nm absorption peak. The resulting MB by-products do not exhibit a significant peak at 668 nm.
Figure 2.3: Example of methylene blue molecule photodegradation pathway.
Figure 2.4: Platinum decorated TiO$_2$ nanoparticles with varying metal load and sizes. Small Pt (A) Medium Pt (B) and Encapsulated Pt (C). The TEM image (D) of TiO$_2$ depicts lattice fringes of Small Pt nanoparticles on TiO$_2$ with accompanying D-spacing of Pt metal (F).

Control experiments (Figure 2.6A) show that TiO$_2$ nanoparticles and UV light are necessary components for photodegradation to occur. In particular, the following controls were run: Bare MB with no UV and TiO$_2$ nanoparticles (MB Dark), MB with bare HOPG and UV (MB HOPG + UV), MB with TiO$_2$ nanoparticles with no UV (MB TiO$_2$ + Dark), MB with TiO$_2$ nanoparticles with UV (MB TiO$_2$ + UV), and MB with UV and no TiO$_2$ nanoparticles (MB + UV). Even with the low concentration of TiO$_2$ nanoparticles present in these experiments some photodegradation of MB is observed for the TiO$_2$ nanoparticle sample. The amount of methylene blue degraded is observed to be dependent on the length of UV irradiation time activating the TiO$_2$ nanoparticles. Without a photocatalytic material (i.e. bare HOPG sample) the concentration of MB remains constant.
Figure 2.5: UV/Vis spectrum of 1 µM methylene blue. $\lambda_{\text{max}}$ at 668 nm is used to follow the degradation of the methylene blue.
Figure 2.6: (A): Control experiments measuring methylene blue concentration change de-graded over UV exposure time. T = 25 °C. (B): MB concentration change versus time when TiO$_2$ is doped with varying Pt nanoparticle size and morphology.
2.4 Results and Discussion

We have observed photocatalytic activity with TiO$_2$ from the photodegradation of methylene blue and performed the same experiment with Pt-TiO$_2$ particles in order to compare photocatalytic efficiency and observe any dependence on Pt loading amounts. Figure 2.6B shows the concentration of MB as a function of UV irradiation time. Various amounts of Pt nanoparticles were loaded onto TiO$_2$ and tested for activity under similar conditions. Loading amounts were categorized by particle coverage of TiO$_2$ substrates as described previously. “Small Pt Load” had individual discernible Pt nanoparticles deposited on TiO$_2$. “Medium” samples consisted of a majority of TiO$_2$ surfaces occupied by Pt nanoparticles and partial encapsulation. “Encapsulated” samples were Pt-TiO$_2$ samples that had completely enveloped TiO$_2$ nanoparticles in platinum material.

The varying loading amounts, however, exhibited photodegradation behavior that was inconsistent in dependence with Pt loading amounts. Medium Pt-TiO$_2$ particles did not exhibit enhanced photocatalytic behavior over bare TiO$_2$ particles. The total amount of MB degraded was similar to bare TiO$_2$. MB photodegradation by Small Pt nanoparticles was similar to encapsulated Pt-TiO$_2$ degradation trend. We have found that extending the irradiation time to 210 minutes shows that photodegradation rate is continuous and evidence of surface poisoning by the degradation of products of MB has not been observed.
Table 2.1: Nanoparticle surface coverage (SA), total concentration degraded, MB molecules removed per surface area, and apparent rate constant (k) normalized by SA.

<table>
<thead>
<tr>
<th></th>
<th>Surface Area (cm²)</th>
<th>Total MB Removed (µM)</th>
<th>MB molecules/cm²</th>
<th>k/SA x 10² (min⁻¹ cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare TiO₂</td>
<td>0.035 (TiO₂)</td>
<td>0.13</td>
<td>4.20x10¹⁵</td>
<td>2.87</td>
</tr>
<tr>
<td>Encapsulated Pt</td>
<td>0.063 (Pt and TiO₂)</td>
<td>0.15</td>
<td>5.70x10¹⁵</td>
<td>1.75</td>
</tr>
<tr>
<td>Medium Pt</td>
<td>0.052 (Pt and TiO₂)</td>
<td>0.13</td>
<td>5.90x10¹⁵</td>
<td>1.79</td>
</tr>
<tr>
<td>Small Pt</td>
<td>0.035 (Pt and TiO₂)</td>
<td>0.21</td>
<td>1.40x10¹⁶</td>
<td>4.57</td>
</tr>
</tbody>
</table>

In order to better understand and compare photo-degradation rates one must scale the rate data appropriately. Active surface areas (SA) were compared with scaled rate constants (k) in order to better understand MB photodegradation with each sample (Table 2.1). Here we describe the active surfaces area as to where MB molecules are actively photodegraded. The Bare TiO₂ sample only took into account exposed TiO₂ nanoparticles surface areas. For Pt-TiO₂ samples, the exposed TiO₂ and Pt surface areas, with no differentiation between exposed Pt and TiO₂ surfaces, were considered sites for MB photodegradation. These active surface areas were determined and quantified from SEM images of each sample viewed from a 90° angle of the exposed HOPG surface. The number of MB molecules degraded was calculated in relation to the SA of each sample. The reaction rate (k) pertaining to each particle type was calculated in order to better understand efficiency of degradation for each sample. Reaction rates were determined from plotted degradation trends to reveal a pseudo-first order reaction. In order to make a fair comparison, scaled reaction rate constants are normalized to quantified active surface area (k/SA) per each sample in order to determine photocatalytic degradation efficiency.
From Table 2.1 Small Pt nanoparticles exhibited the highest amount of MB molecules degraded per SA and scaled reaction rate with SA at $1.4 \times 10^{16}$ molecules/cm$^2$ and $4.57 \times 10^{2}$ min$^{-1}$ cm$^{-2}$ respectively. Despite the larger SA value of Encapsulated Pt nanoparticles, their k/SA values show that photo-degradation is not as high as Small Pt nanoparticles. The same k/SA trend is observed with Medium Pt nanoparticles. The Bare TiO$_2$ k/SA value is observed to be higher than Encapsulated and Medium samples as well. By taking into account the normalized reaction rate and active surface area coverage, one can see that Small Pt nanoparticles are the most efficient in photodegrading MB molecules over time. An increase of Pt coverage seems to diminish the photocatalytic activity as evident by the lower k/SA values of Encapsulated and Medium Pt nanoparticles. Linsebigler et al explains that a large surface area of titania needs to be exposed in order for generated excited electrons and holes to migrate to the metal/titania contact at the Schottky barrier.$^{[37]}$

In the future we would like to perform similar experiments with other types of noble metals and TiO$_2$ morphology. Various noble metals have been known to prevent electron – hole recombination in order to increase TiO$_2$ photoactivity. Testing these metals with varying loading amounts on TiO$_2$ may show insight on the relationship between metal morphology and photocatalysis. Highly dispersed TiO$_2$ nanoparticles allow more sites for Pt deposition as well as sites for methylene blue photodegradation. The increased population may also accentuate the effects photodegradation compared to the low density of linear TiO$_2$ nanoparticles via UV-Vis.
2.5 Conclusion

In conclusion, Small Pt nanoparticles have been demonstrated to be the most efficient photocatalyst compared to other Pt morphologies on TiO$_2$. TiO$_2$ and Pt-TiO$_2$ nanoparticles with Small, Medium, and Encapsulated loading amounts of Pt were subjected to methylene blue photo-degradation in order to observe and compare degradation rates. Data from the experiment dramatically shows Pt-TiO$_2$ is more photo-active than blank TiO$_2$. In order to compare the Pt-TiO$_2$ morphologies the reaction rates were scaled in relation to a quantified active surface coverage (k/SA) of each sample to better understand reaction behavior. From the quantified data, Small Pt nanoparticles outperformed bare TiO$_2$ and larger Pt-TiO$_2$ morphologies by the highest k/SA value.

**Funding:** This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences through grant number: DE-FG02-96ER45576.

**Acknowledgment:** The authors thank the Laboratory for Electron and X-ray Instrumentation (LEXI) at UC Irvine for SEM, TEM, XPS and EDS work and service. The authors also thank the UC Irvine Laser Spectroscopy Facility for UV-Vis work and analysis.
CHAPTER 3: ELECTROPLATING COPPER ONTO TiO$_2$ NANOPARTICLES

3.1 Introduction

Copper doped TiO$_2$ nanoparticles have been studied for their photocatalytic enhancing properties. As a relevantly inexpensive metal compared to other noble metals, there has been much focus on the improvement and study of a Cu-TiO$_2$ system.$^{[45-48]}$ Most notably, much has been written about their charge-separation capabilities while associated with TiO$_2$ substrates.$^{[49]}$ One caveat of Cu deposition onto TiO$_2$ is the ease of Cu oxidation once exposed to atmospheric pressures and temperatures.$^{[50]}$ However, studies have shown that various oxidation states of Cu nanoparticles contribute to photocatalytic enhancement in tandem despite metallic Cu not being the most active component in certain cases.$^{[51, 52]}$

Although certain properties of Cu-TiO$_2$ photocatalysis have yet to be elucidated, the idea of fabricating a cheap photocatalytic material for environmental purposes is of much interest. Depositing Cu nanoparticles onto highly dispersed TiO$_2$ nanoparticles situated on HOPG will allow us to observe morphological changes on the surface of the substrate. In this article we will discuss the fabrication steps taken to deposit Cu nanoparticles onto TiO$_2$ substrates to observe Cu nucleation growth. This work is a product of collaboration with Prof. Reginald Penner’s laboratory group where fabricated TiO$_2$ nanoparticles were electroplated with Cu through step-potential deposition.
Figure 3.1: Electrochemical cell setup connected to a potentiostat (Gamry). Samples are submerged in the cell solution containing CuSO₄ and K₂SO₄ while surrounded by a home-made Faraday cage.
3.2 Experimental Procedures

3.2.1 TiO$_2$ Substrate Fabrication

Highly dispersed TiO$_2$ nanoparticles were fabricated via physical vapor deposition in an Edwards evaporation chamber under high vacuum. Fabrication steps were consistent with previous TiO$_2$ production steps with minimal differences in TiO$_2$ nanoparticle measurement yields. HOPG substrates were cleaved with Scotch tape and plasma cleaned in an FEI Magellan SEM in order to create defect sites for increased TiO$_2$ nucleation. Substrates were annealed to 800$^\circ$C and were placed in the pathway of evaporated Ti atoms from a Ti shot. A quartz crystal microbalance was used to monitor Ti deposition rate at 0.1 nm per minute and for a total of 1.2 nm thickness. Substrates were annealed at the same temperature for 2 hours in order to allow TiO$_2$ nucleation and formation. TiO$_2$ samples were then immediately prepared for Cu photodeposition or electro-plating.

3.2.2 Cu Photodeposition

Photodeposition experiments took place in a PEEK material cell where TiO$_2$ substrates were exposed to UV irradiation (365 nm) and Cu precursor salt solution CuNO$_3$ (Sigma Aldrich). Ar gas was bubbled through the solution for 20 minutes in order to occupy electron-hole sites and improve photoreduction of the precursor salt. Samples were irradiated for 30 minutes and 60 minutes in order to determine which irradiation time was best for Cu np production. Samples were washed with HPLC grade water (Sigma Aldrich), dried with nitrogen gas, and stored in a pressurized dessicator before characterization.
3.2.3 Cu Electrodeposition

TiO$_2$ samples were submerged in a 0.1M solution of CuSO$_4$ and K$_2$SO$_4$ and connected to a potentiostat (Gamry)(Figure 3.1). Electro-plating steps were repeated from a previous publication by Prof. Penner’s group.$^{[53]}$ Before electroplating, TiO$_2$ and HOPG control samples were soaked in a 1mM solution n-hexanethiol and ethanol (Sigma Aldrich) overnight. Samples were placed in an electrochemical cell consisting of 1mM K$_2$SO$_4$ and 1mM CuSO$_4$ as a Cu source. A copper wire was placed in the cell solution as a reference electrode. A potentiostat (Gamry) was used to apply a step potential to the TiO$_2$ either through an extended potential application time or in the form of a pulse of potential. We performed several experiments involving varying the potential power and deposition time in order to determine the best parameters for Cu nucleation. Potentials of |−100 mV|, |−500 mV|, and |−1 V| were applied to the TiO$_2$ sample. Extended potential application times ranged from 2 seconds to 10 seconds. Pulse application involves applying a potential in the millisecond time scale. Subsequent pulses were separated with 3 seconds of downtime. Samples were then washed with distilled water and then stored in a pressurized dessicator 24 hours before characterization.

3.2.4 Microscopy

Cu-TiO$_2$ samples were characterized by an SEM (FEI Magellan) for particle sizes. Before microscopy, samples were plasma cleaned in-situ of the SEM chamber in order to remove leftover dust from the surface for improved imaging. EDS analysis was also made in-situ of the SEM chamber with a higher beam energy of 0.40 nA.
3.3 Results and Discussion

Control experiments have shown that TiO$_2$ nanoparticles were required prior to electrodeposition in order for Cu particles to form. Figure 3.2 shows that bare HOPG had no observable Cu particle formation on the surface. There are remnants of material left on surface defects after electrodeposition attempts; however EDS analysis of this material yielded no Cu peaks or any other material. We assume that this material may have come from a combination of precursor and electrochemical salt and have deposited onto the surface despite atmospheric plasma cleaning.

The n-hexanethiol monolayer deposition was initially used to coat the surface of TiO$_2$ nanoparticles in order to prevent encapsulation from Cu material.$^{[53]}$ We have found that TiO$_2$ nanoparticles that were capped with n-hexanethiol and not were difficult to discern. Cu particles formed on the surface in a variety of sizes yet there were no instances Cu encapsulation on TiO$_2$ nanoparticles. EDS of TiO$_2$ nanoparticles yielded no Cu peaks on the surface of these TiO$_2$ nanoparticle aside from carbon at 0.28 keV, titanium at 0.45 and 4.51 keV, and oxygen at 0.52 eV (Figure 3.3). EDS analysis of the large crystalline particles on the microscale have been observed to be Cu from the exhibited peak values 0.93 keV. (Figure 3.4).
**Figure 3.2:** HOPG electrodeposited with Cu material for [-100mV] at 60 seconds. Resemblances of material being deposited onto HOPG surface defects have been observed, however EDS analysis reveals no specific peak bands relative to Cu or K.
Figure 3.3: EDS of Cu deposited TiO$_2$ nanoparticles. N-hexanethiol was not deposited as a monolayer on TiO$_2$ nanoparticles and has no effect on Cu nucleation morphology.
**Figure 3.4:** EDS analysis of Cu particles deposited onto TiO₂ substrates. One can see from the EDS spectra that a large Cu signal is observed when analyzing the larger microscopic particles.
We have observed that Cu particle nucleation size is related to the parameters applied by the potentiostat. 60 seconds of potentiostat application time at $-100\text{mV}$ have yielded a variety of Cu particle sizes ranging from nanometer to micrometer size thresholds. One can see these size ranges in Figure 3.5. Close inspection of TiO$_2$ surfaces revealed no Cu nanoparticles that were akin to sizes of Pt nanoparticles from previous studies. Some particles are more crystalline while other particles are more of an amorphous morphology. EDS of the larger particles were confirmed to be Cu. We have opted to reduce potential application time in an effort to reduce Cu particle growth.

Figure 3.5: Cu nanoparticles formed on the surfaces of TiO$_2$ nanoparticles after 60 seconds of $-100\text{mV}$ potential application. Note that these TiO$_2$ particles are smaller, however the size of TiO$_2$ does not affect Cu deposition from what we’ve seen.
We have lowered the electrodeposition time to 10 seconds in order to shrink Cu nanoparticle size. Overpotential was retained at $|\text{-100mV}|$. The resulting particles were observed to be significantly smaller than the microparticles observed after 60 seconds of electrodeposition. However, the Cu nanoparticles were still considered too large for photocatalytic enhancement to take place. From Figure 3.6, one can see that Cu nanoparticles were measured to be around 100 nm in diameter. While lowering the electrodeposition time has decreased Cu sizes, the particles are still too large. We have opted for a more intricate method of forming nanometer sized particles instead of continually lowering the electrodeposition time.

Figure 3.6: Cu nanoparticles formed on the surfaces of TiO$_2$ nanoparticles after 10 seconds of $|\text{-100mV}|$ potential application.
TiO$_2$ samples were subjected to Cu electrodeposition in a series of pulses. Each pulse consisted of applying |100mV| to the substrate sample for 5 ms. A total of 10 pulses were applied for a total of 50 ms of electrodeposition time. Each pulse was separated by 3 seconds to prevent Cu monolayer buildup. Figure 3.7 shows a sample of TiO$_2$ nanoparticles deposited with Cu nanoparticles following electro-pulse deposition. One can see that these Cu nanoparticles are much smaller in diameter compared to previous continuous electrodeposition times. On average, these Cu nanoparticles are ~23 nm in diameter; however the density of these particles is very low. Figure 3.8 shows that the density between TiO$_2$ and nucleated Cu nanoparticle population low, compared to the amount of adsorbed Pt or Ag nanoparticles from previous experiments.

**Figure 3.7**: Electrodeposited Cu nanoparticles via potential pulses were much smaller compared to an extended electrodeposition time.
Figure 3.8: Low dispersity of Cu nanoparticles after 10 pulses of |-100mV| potential.

Some modifications to the electrodeposition parameters were made to ensure a high population of Cu nanoparticle formation. According to the same publication by Ng et al, a higher potential will lead to more instances of Cu nanoparticle nucleation yet disregards spatial selectivity.[53] Since our TiO$_2$ dispersity is so high, the probability of Cu nucleation near or on TiO$_2$ substrates is high enough to warrant photocatalytic effects for TiO$_2$ band-gap radiation. The potential was increased to |-1 V| while retaining the number of pulses and time in-between pulses. One can see in the high resolution image, Figure 3.9, that there are an increased number of Cu nanoparticles forming on the surface of HOPG and TiO$_2$. Cu sizes have been observed to be ~30 nm in diameter and are relatively the same size as the TiO$_2$ nanoparticles in comparison. The Cu nanoparticles also appear to be more crystalline with less occurrences of an amorphous
structure. While the prospect of Cu-TiO\textsubscript{2} nanoparticles for application study seems promising, the aspect of Cu nucleation growth is still an area of behavior that has yet to be explored in depth. One way to observe Cu nucleation behavior is to electroplate Cu nanoparticles at a size range smaller in diameter compared to TiO\textsubscript{2} substrates. From these small Cu nanoparticles we will be able to determine whether or not Cu nucleation selectively prefers TiO\textsubscript{2} substrates or the TiO\textsubscript{2} / HOPG interface. Such information is vital for fabricating Cu-TiO\textsubscript{2} for applications.

**Figure 3.9**: High dispersity of Cu nanoparticle formation on TiO\textsubscript{2} substrates after increasing the step potential to [-1 V] for 10 pulses.
There are several techniques that we have performed for reducing Cu nucleation growth to determine Cu nucleation preferences. In order to accomplish this study, we have limited the number of pulses being applied to the TiO$_2$ sample to observe where Cu nucleation occurred without having Cu nucleate and encompass several TiO$_2$ nanoparticles as seen in previous results. We hypothesize that the initial pulse creates instances of Cu nucleation and each subsequent pulse allows more Cu reduction to occur which result in these nucleation sites to grow. One interesting observation we have witnessed when limiting the number of pulses is that Cu nucleation is dictated by the initial pulse and subsequent pulses may or may not affect nucleation growth. In Figure 3.10 the electrodeposition of Cu nanoparticles was limited to 1 and 2 pulses (A and B respectively). One can see in Figure 3.10.A that only 1 pulse is required to form Cu nanoparticles and that they roughly form the same size of Cu nps after 10 pulses. 2 pulses being applied to the TiO$_2$ sample results in similar-sized Cu nanoparticles (Figure 3.10.B). These Cu nanoparticles are too large, however by limiting the pulse length to 1 ms instead of 5 ms, we have observed initial stages of Cu nucleation occurring at TiO$_2$ sites or TiO$_2$/HOPG interfaces. Figure 3.11 shows the origin of these sites through red circles over the initial stages of Cu nucleation on TiO$_2$ or HOPG interfaces. Although the crystallization of Cu nanoparticles is apparent with the 1 ms pulse application, we believe this morphological result is a consequence of an outdated precursor solution.
Figure 3.10: Results of electrodepositing Cu nanoparticles onto TiO$_2$ through limited pulses. At 1 pulse Cu nanoparticles nucleated to around ~30 nm in diameter (A). At 2 pulses the size of Cu nps did not drastically change and remained roughly the same size as Cu nps forming after 1 pulse (B).
Figure 3.11: Cu nanoparticle growth sites on TiO$_2$/HOPG interfaces. Particular examples are circled in red.

3.4 Conclusion

Cu nanoparticles have been deposited onto the surface of TiO$_2$ nanoparticles adsorbed onto an HOPG substrate through step-potential electrodeposition. Opting for a step-potential electrodeposition method has been more successful in producing nanometer sized Cu particles. Increasing the potential to |−1 V| increases the population of Cu nanoparticles and applying a pulse of potential for a short amount time limits Cu growth to ~23-30 nm in diameter. Cu nanoparticle size is observed to be dependent on the initial potential pulse application. Cu nucleation has been found to nucleate on TiO$_2$ or TiO$_2$/HOPG sites after limiting the pulse duration to 1 ms.
CHAPTER 4: FABRICATING BI-METALLIC LOADED TiO$_2$
NANOPARTICLES THROUGH SEQUENTIAL PHOTODEPOSITION

4.1 Introduction

Single metal-loaded TiO$_2$ (M-TiO$_2$) nanoparticle properties have been well researched and documented. However, the aspect of loading different types of metal nanoparticles on a single TiO$_2$ substrate has yet to be studied extensively due to the difficulty of loading different species. As such, there are interesting properties that could arise from the introduction of a bi-metallic loaded TiO$_2$ nanoparticle system. The properties of one type of noble metal nanoparticle may compliment the effects of another noble metal species and in turn reveal desirable properties for enhanced photocatalytic properties. Our goal in this project is to fabricate a model bi-metallic loaded TiO$_2$ nanoparticle system in order to observe photocatalytic enhancements in future experiments.
Figure 4.1: Schematic of Au-Pt-TiO₂ nanoparticle undergoing free electron activation. Free electrons may be produced from the absorbance of visible light (rainbow arrow) via Au nanoparticles, while Pt nanoparticles may prevent electron-hole recombination. Pt and Au nanoparticles have been commonly deposited on our systems and their properties are well studied in literature. In this study we attempt to sequentially photo-deposit Pt and Au nanoparticles alongside one another on TiO₂ nanoparticle substrates. Figure 4.1 details a schematic of Au and Pt nanoparticles on TiO₂. The combination may enhance TiO₂ photocatalytic efficiency where both noble metal nanoparticle properties may complement each other. Au-TiO₂ nanoparticles are known to allow TiO₂ nanoparticles to absorb light in the visible spectrum, thus removing the need for powerful UV lamps for activating TiO₂. Pt-TiO₂ nanoparticles are known to prevent electron-hole recombination which results in the increased presence of free electrons and electron holes for adsorbed molecules to react to. Therefore Au-Pt-TiO₂ nanoparticles may increase photocatalytic efficiency with a decrease in activation energy requirements.
4.2 Experimental Procedures

Linearly arrayed rutile TiO$_2$ nanoparticles are deposited alongside step edges on freshly cleaved HOPG. Sequential deposition attempts were performed with Au nanoparticles initially deposited followed by Pt and vice versa. TiO$_2$ nanoparticles are placed in photochemical cell made of PEEK material and submerged in a precursor salt solution of 100 µM NaAuCl$_4$. Ar gas was bubbled into solution for 20 minutes in order to purge oxygen from the cell. TiO$_2$ nanoparticles were then exposed to UV light at 365 nm for 30 minutes in the presence of the Au precursor. After deposition the particles were removed and washed with HPLC-grade water and air-dried in a dessicator. After drying the particles were then annealed to 800 °C for 1 hour in an evaporator and placed back into the photochemical cell for Pt deposition.

Pt nanoparticles are sequentially deposited onto Au-TiO$_2$ nanoparticles by the same parameters for Pt deposition onto bare TiO$_2$ nanoparticles. A 1 µM K$_2$PtCl$_4$ precursor salt solution is placed in the cell where Au-TiO$_2$ nanoparticles are exposed to the solution. Ar gas is bubbled into the cell for 20 minutes followed by UV illumination for 32 minutes. Particles are washed with HPLC-grade water and dried in a dessicator followed by annealing up to 800 °C. The reverse deposition sequence was also performed to fabricate Au-Pt-TiO$_2$ nanoparticles where Pt was deposited first and then followed by a sequential Au deposition. Particles were characterized by SEM and EDS (FEI Magellan) and plasma cleaned in-situ in order to remove moisture and residue from the surface.
4.3 Results and Discussion

Two samples were prepared for sequential photodeposition: A bare TiO$_2$ nanoparticle sample deposited with Au nanoparticles and another bare TiO$_2$ nanoparticle sample deposited with Pt nanoparticles. One can see from Figure 4.2 that noble metal nanoparticles have been photo-deposited onto the surface of linearly arrayed nanoparticles. Au nanoparticles were observed to be distinct and spherical on TiO$_2$ surfaces. There are instances of where Au material has aggregated into larger clumps of Au and encompass multiple TiO$_2$ nanoparticles. A separate bare TiO$_2$ sample deposited with Pt nanoparticles were characterized and yielded similar observations with Au-TiO$_2$ nanoparticles. EDS spectra (Figure 4.2) shows that Au signal was observed at 2.12 keV among Ti and O signals on the Au-TiO$_2$ sample. The Pt-TiO$_2$ EDS spectrum yielded Pt signal at 2.0 keV among Ti and O signals. No Au or Pt signal was observed when EDS spectra was taken on HOPG surfaces. The Au nanoparticles on bare TiO$_2$ were measured to be 4.68 ± 1.34 nm in pseudodiameter. The Pt nanoparticles on bare TiO$_2$ were measured to be 4.74 ± 1.78 nm in pseudodiameter.
Figure 4.2: Top: An SEM image of Au-TiO$_2$ nanoparticles accompanied with an EDS spectra confirming the presence of Au material on TiO$_2$. Bottom: An SEM image of Pt-TiO$_2$ nanoparticles accompanied with an EDS spectra confirming the presence of Pt material on TiO$_2$.

Both samples were washed and annealed in order to remove any leftover precursor salt residue on nanoparticle surfaces. Sequential deposition was performed on both samples in a series of varying concentration amounts in order to determine an ideal concentration for bimetallic loading. The Au nanoparticle sample was exposed to a precursor salt solution of 1 µM K$_2$PtCl$_4$ and irradiated with UV light for 32 minutes. The Pt nanoparticle sample was exposed to the Au precursor solution of NaAuCl$_4$ 100 µM and irradiated for 30 minutes. These parameters were initially chosen because they have yielded metal nanoparticles adsorbed on bare TiO$_2$ through photo-deposition as shown in previous figures.
One way to confirm the formation of a bi-metallic TiO$_2$ nanoparticle was to observe specific particles before and after sequential deposition. This technique can be accomplished by leaving a surface mark on the surface as a landmark for relocating specific nanoparticles. SEM imaging in Figure 4.3 show Au-TiO$_2$ and Pt-TiO$_2$ before and after sequential deposition of Pt or Au nanoparticles respectively. The top row shows the particles in their initial state and the bottom row shows the same particle after it has been exposed to a precursor metal salt and UV irradiation.

An obvious observation can be made from comparing the Au-TiO$_2$ and Pt-TiO$_2$ nanoparticles with the Pt-Au-TiO$_2$ and Au-Pt-TiO$_2$ is that there was an absence of new individual nanoparticles forming on the surface of TiO$_2$. The post sequential nanoparticles were observed to retain the initial metal nanoparticles on TiO$_2$, however the particles were observed to be larger in diameter as well. This change of size is attributed to the deposition of precursor material forming a thin layer that encapsulates the entire particle as well as the initial noble metal nanoparticles. It is unclear if the material is precursor salt or purely metallic. This morphology is present throughout all the nanoparticles that have been observed on both samples after sequential deposition. EDS analysis of both samples confirms the presence of both Au and Pt material on TiO$_2$ while no metallic signal has been detected on bare HOPG surface. We suspect that the formation of a metal encapsulation over M-TiO$_2$ nanoparticles may be due to the parameters of deposition: precursor concentration and UV irradiation time.
Figure 4.3: SEM imaging of Au-TiO$_2$ and Pt-TiO$_2$ before and after sequential photodeposition to yield Pt-Au-TiO$_2$ (bottom left) and Au-Pt-TiO$_2$ (bottom right).

Separate samples of Pt-TiO$_2$ and Au-TiO$_2$ have been fabricated and exposed to the same concentrations of Au and Pt precursor salts respectively, but with an increase in UV irradiation time to 120 min. for Au deposition and 60 min. for Pt deposition. Previous experiments have shown that Au tends to form nanoparticles at a longer UV exposure time.
compared to Pt nanoparticles. By increasing the irradiation time we expected an increased likelihood of metal nanoparticles depositing alongside initial Pt and Au nanoparticles. Results of this experiment show that this was not the case. This could be due to an increased rate of free electron and electron-hole production which allow precursor salts to be continually reduced into metal ions for an increased rate of nanoparticle formation. Figure 4.4 shows before and after SEM images of Pt-TiO$_2$ undergoing sequential photodeposition with an Au precursor and extended UV irradiation time.
One can see that Au material completely encapsulates the original Pt-TiO₂ nanoparticles after sequential deposition. There was no evidence of Au nanoparticle formation alongside Pt nanoparticles. Au material was only found to be on Pt-TiO₂ nanoparticles and not on the HOPG surface through EDS. We suspect that 120 minutes of UV irradiation was too long of an irradiation time and allowed more Au to aggregate into an encapsulating material. Other Pt-TiO₂ samples were exposed to the same concentration of Au precursor salt but irradiated for 45, 60, and 90 minutes. It was found that all the samples at various UV irradiation times were found to be completely encapsulated with Au material with no evidence of Au nanoparticle formation. Au precursor concentrations were also increased and reduced to in order to form Au nanoparticles. Encapsulation of Pt-TiO₂ by Au material was only observed.
Au-TiO$_2$ nanoparticles were exposed to a platinum precursor solution and irradiated for 60 minutes. Figure 4.5 shows the before and after images of Au-TiO$_2$ deposited with Pt material. Platinum has been observed to encapsulate Au-TiO$_2$ nanoparticles after 60 minutes of deposition. The brighter particles situated on TiO$_2$ are remnants of Au nanoparticles. These particles increased in diameter post sequential deposition most likely due to the formation of Pt material on the surface. The morphology of these particles differ from the Pt-TiO$_2$ deposited with Au attempt in that there is not as much Pt material encapsulating the Au-TiO$_2$ nanoparticles. Material has also been found on the HOPG surfaces, however it is unclear what these residues consist of as EDS encounters difficulty when analyzing particles $<$5 nm. They are most likely un-reduced Pt precursor material aggregating and depositing onto the surface of HOPG. Due to the increased amount of Pt material encapsulating Au-TiO$_2$, further experiments were conducted with lower UV irradiation times in order to determine if Pt nanoparticle formation is dependent on exposure time. UV irradiation times were changed to 20 and 10 minutes and have been observed with similar results to longer irradiation times with encapsulation as an end result. Pt concentrations were altered for nanoparticle formation and experiments have shown a complete encapsulation of Au-TiO$_2$ nanoparticles regardless. Therefore it was determined that precursor concentration and UV irradiation time are not major factors in forming individual noble metal nanoparticles during sequential deposition.
Metal nanoparticle deposition and formation typically occurs on active sites or on site defects of bare TiO₂ surfaces. The initial presence of Pt or Au nanoparticles has been observed to affect the morphological outcome after sequential deposition of a different noble metal. Therefore the TiO₂ surface active sites, where metal nanoparticles form, may be a source of photodeposited metal nanoparticle morphology. Unfortunately characterizations of active sites are not easily defined as the interface between noble metal nanoparticles and TiO₂ surfaces are sources for active sites as well, leading to the complexity of determining reasons for metal
encapsulation.\textsuperscript{[57]} Another factor that must be considered are the morphological size, shape, and loading amounts of adsorbed metal nanoparticles which could affect rate of oxidation or reduction of precursor salts on M-TiO$_2$ surfaces.\textsuperscript{[10, 24, 58]} Nucleation of noble metal material after sequential deposition appears to grow into a film-like nature instead of aggregating into spherical nanoparticles. It has been observed that photochemical reaction activity on TiO$_2$ surfaces occur in little to no spatial relation to the adsorbed Pt nanoparticles.\textsuperscript{[59]} Therefore active sites all over the Pt-TiO$_2$ support may allow Au nucleation to occur at similar rates of aggregation, however the source of formation of a cover-like shell has yet to be pinpointed. We may infer that the charge-separation properties of Pt nanoparticles may increase the population of active sites for nucleation. This surplus may cause more Au atoms to nucleate at multiple sites instead of the majority of Au aggregating into nanoparticles due to fewer sites. Au-TiO$_2$ nanoparticles also exhibit similar properties of charge-carrier separation, however the relation between nucleation, surface active site population and charge-separation have yet to be studied.\textsuperscript{[60]} We suspect that similar surface active site properties are exhibited with Au-TiO$_2$ nanoparticles in order for Pt material to encapsulate after sequential photodeposition.
4.4 Conclusion

Sequential photodeposition of Pt or Au onto Au and Pt-TiO$_2$ respectively has yielded encapsulated nanoparticles. Increasing or lowering the concentration of the precursor salt has not affected the resulting encapsulated morphology. Altering the UV irradiation time may affect the morphology after sequential photodeposition, however this does not rule out the sequential deposition method but gives us insight to the behavior of depositing multiple species of metals onto TiO$_2$ substrates. These experiments are necessary in order to eliminate factors that are not contributing to forming individual metal nanoparticles. Other techniques, which are described in the next chapter, must be incorporated in the sequential deposition technique in order to fabricate a bi-metallic TiO$_2$ nanoparticle.
CHAPTER 5: OBSERVING SERS PHENOMENA OF BI-METALLIC LOADED TiO$_2$ NANOPARTICLES

5.1 Introduction

While metal nanoparticles doped onto TiO$_2$ substrates are ubiquitous in photocatalytic research, Ag nanoparticles in particular exhibit beneficial properties that excel in molecular detection.$^{[13]}$ The morphology and arrangement of these nanoparticles greatly influences the performance of molecular detection methods, especially for Raman spectroscopy.$^{[61-64]}$ Research has shown that nanoscale gaps in between linearly arrayed Ag nanoparticles can provide a significant enhancement in Raman signal via probe molecule.$^{[65]}$ However, the types of molecules being detected are limited due to only certain molecules chemically adsorbing onto silver. Therefore, there is a need in fabricating surface enhanced Raman (SERS) active materials to allow universal molecular detection.

This limitation can be remedied by the inclusion of different metal nanoparticle species alongside adsorbed Ag nanoparticles on TiO$_2$ substrates. For example, Pt nanoparticles deposited among Ag nanoparticles can act as adsorption sites for specific molecules that don’t specifically bind to Ag. Due to the close vicinity of Ag nanoparticles alongside Pt, the Raman signal enhancing effects may allow nearby molecules adsorbed on other metal species to be detected. In this study, we detail the fabrication steps required to form Ag-TiO$_2$ an Ag-Pt-TiO$_2$ nanoparticles. Molecular detection experiments via Raman microscopy were performed on these particles in order to measure Raman enhancement effects.
Figure 5.1: Raman scattering diagram of electron excitation from incident photon and subsequent scattered photon emission after electron relaxation into an energy level differing from the ground state.

Surface-enhanced Raman scattering (SERS) is a spectroscopic technique that is widely utilized for its non-destructive and high sensitivity detection.

Raman scattering, organic molecules absorb incident photons from a laser source (near Infra-red) which causes electrons (in a ground vibrational state) to become excited and relaxed in an almost instantaneous time frame. The excited state is so short-lived that is known as a “virtual state.” Electrons relaxing from the virtual state emit a photonic signal, known as a scattered photon, which can be detected in order to characterize specific molecules as detailed in Figure 5.1. Raman spectroscopy utilizes these scattered photons from excited electrons relaxing into a higher or lower energy state, known as inelastic scattering. Inelastic scattered photons can yield vibrational information coinciding with specific vibrational modes of particular molecules.
The intensity of these inelastic scattered photons is weak compared to the intensity of Rayleigh (elastic) scattered photons and therefore provides a challenge for characterization through Raman spectroscopy. Research has shown that the intensity of inelastic scattered photons can be enhanced with the inclusion of metal nanoparticles.\cite{70} The SERS diagram from Figure 5.2 details how metal nanoparticles of certain sizes can improve the weak signal through charge polarization. Visible or near-infrared radiation may influence localized charges to polarize, known as a localized plasmon, which causes an increase in electric field intensity that result in an increase in inelastic scattered photon intensity from adsorbed molecules on the surfaces of these metals. This enhancement is caused by the localized plasmon resonance frequency to be in sync with the radiation resonance and the plasmon oscillations to be perpendicular to the surface. It is important to note that localized plasmon resonances also enhance the incident light that causes electron excitation. Therefore, with each stage of enhancement characterized by $E^2$, SERS can be quantified as $E^4$ for the total enhancement of signal.

Figure 5.2: Metal nanoparticles undergoing charge polarization due to Raman influence.
Therefore the technique is ideal for determining chemical sensing capabilities. SERS active materials are usually Ag and Au metal nanoparticles that behave as antennas for an increase in Raman signal. Therefore, adsorbed organic structures on the surfaces of these metal nanoparticles can be detected via SERS mechanisms. A metal-oxide support structure with optimum noble metal nanoparticle sizes can provide a fundamental look into how SERS activity behaves with varying metal species and sizes. TiO$_2$ nanoparticles are an excellent support structure for noble metal nanoparticle loading due to its photocatalytic or electrochemical properties of reducing or oxidizing metal precursor salts to form distinct metal nanoparticles. By having multiple species of metal nanoparticles on TiO$_2$ supports, one can optimize the conditions and parameters for SERS and high resolution chemical sensing.

In this study, we detail the process of Raman experiments involving Ag-TiO$_2$ and bi-metallic loaded Ag-Pt-TiO$_2$ nanoparticles situated on highly oriented pyrolytic graphite. By sequentially photodepositing Pt and Ag onto TiO$_2$, we are able to load distinct noble metal nanoparticles on a single TiO$_2$ nanoparticle. Ag-TiO$_2$ nanoparticles were fabricated to quantify an enhancement factor (EF) related to SERS. In order to test the capabilities of enhanced Raman scattering of Ag nanoparticles, particles are subjected to thiophenol and cyclohexene adsorption as probe molecules. We sought to determine Ag nanoparticle enhancement through a bi-metallic loaded Ag-Pt-TiO$_2$ surface. Results show that an increase in SERS signal, or enhancement factor, is observed due to Ag nanoparticles functioning as enhancement antennas to nearby surface reactions and adsorbed organic probe molecules. Pt-TiO$_2$ and TiO$_2$ nanoparticles have been fabricated for enhancement comparisons.
4.2 Experimental Procedures

4.2.1 TiO$_2$ Fabrication

TiO$_2$ nanoparticles were fabricated onto ZYB grade, highly oriented pyrolytic graphite (HOPG, Momentive Performance). HOPG substrates were prepared by cleaving with tape and placed inside the Scanning Electron Microscope (SEM FEI Magellan XHR) for atmospheric plasma cleaning. Plasma cleaning the surface creates shallow defect sites that are preferable for TiO$_2$ nucleation during physical vapor deposition. The substrates were then immediately placed into an evaporator chamber (Edwards 306A). HOPG substrates were heated to 800°C in order to provide Ti adatom mobility for step edge decoration. Titanium shots were heated and vaporized in the chamber. The HOPG substrate is placed facing towards the Ti source in order for evaporated Ti to deposit onto the substrate surface. A thickness equivalent to 1.2 nm of TiO$_2$ film was measured to be deposited on the HOPG surface by a quartz crystal microbalance (Inficon) aligned alongside the substrate. Following deposition, samples were annealed for 3 hours in high vacuum prior to SEM imaging and use in photocatalytic experiments. After annealing, TiO$_2$ nanoparticles were observed to have an average pseudodiameter of 10.9 ± 4.6 nm through SEM imaging (Figure 5.5). Energy-dispersive X-ray Spectroscopy (EDS, Oxford EBSD) confirms the presence of TiO$_2$ through peaks observed at 0.523 (O) and 4.510 keV (Ti). Material composition was confirmed by X-ray Photoelectron Spectroscopy (XPS) where the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ showed binding energies of 459.7 eV and 465.2 eV respectively. TiO$_2$ nanoparticles were prepared for Transmission Electron Microscopy (TEM Philips/FEI CM-20) by cleaving the surface with Scotch tape and placing thin cleaved pieces onto a TEM grid. Thin samples were determined through a back-lit microscope to observe how well light passes through
the sample surface. TEM images confirmed the crystal structure of TiO₂ by the d spacing measurement of 3.2 Å. Fast Fourier Transform (FFT) measurement of the lattice fringes have been found correspond to the (110) phase of rutile TiO₂.

**4.2.2 Silver Deposition**

Ag-TiO₂ nanoparticles were fabricated by coating TiO₂ nanoparticles with AgIO₃ and exposing the coated TiO₂ to UV irradiation. TiO₂ decorated HOPG substrates were submerged in a solution of AgIO₃ and stirred for 2 hours. The AgIO₃ precursor solution was made by mixing NaIO₃ and AgNO₃ (Sigma Aldrich) at 5 and 2.5 wt% respectively. Samples were then removed and placed inside a PEEK photodeposition cell with 0.5 mL of HPLC grade water. Samples were irradiated with UV light (Bausch & Lomb) at 365 nm for 1 hour. After UV irradiation the samples were washed with HPLC grade deionized water in order to remove any residual leftover precursor salt on the surfaces in order to reveal Ag nanoparticles on TiO₂. Samples were then dried with nitrogen and placed in a vacuum dessicator (Fischer Price) for 24 hours before characterization. Samples were analyzed through SEM, EDS, XPS and TEM. From SEM imaging, Ag nanoparticles were measured to be 3.90 ± 1.9 nm in pseudodiameter (**Figure 5.5**). EDS confirms the species of Ag and TiO₂ through peaks observed at 2.964 (Ag), 0.523 (O) and 4.510 keV (Ti) (**Figure 5.3**). FFT analysis of the Ag nanoparticle lattice fringe reveals a d-spacing length of 2.3 Å, confirming the (111) plane of Ag metal (**Figure 5.4**). XPS confirms presence of Ag metal from the measured binding energies of Ag 3d₅/₂ and Ag3d₃/₂ of 368 and 374 eV respectively.
Figure 5.3: SEM of Ag-TiO₂ nanoparticles with EDS confirming the presence of Ag and TiO₂ species.
Figure 5.4: TEM analysis of Ag-TiO$_2$ nanoparticles depicting lattice fringe measurements.
Figure 5.5: Pseudodiameter histogram distribution of Ag and TiO$_2$ nanoparticles from Ag-TiO$_2$. 

Ag
Mean: 3.9 nm
SD: ± 1.9 nm

TiO$_2$
Mean: 10.9 nm
SD: ± 4.6 nm
4.2.3 Platinum Deposition

Pt particles were adsorbed onto the surfaces of the TiO$_2$ nanoparticles via photodeposition. An aqueous solution of 1µM K$_2$PtCl$_4$ salt (Sigma Aldrich) was placed in a PEEK photodeposition cell containing the HOPG substrate coated with highly dispersed TiO$_2$ nanoparticles pointed toward the UV source. K$_2$PtCl$_4$ serves as the precursor solution for Pt nanoparticle formation on the TiO$_2$ substrate. The salt solution was degassed with Ar (AirGas) for 30 minutes in order to displace and remove oxygen. UV radiation, (365 nm, 200 W Hg lamp) tuned to overcome the TiO$_2$ bandgap, was exposed to the salt solution and the TiO$_2$ nanoparticle coated HOPG for 32 minutes. Following the Pt photodeposition, the samples were washed gently with HPLC grade deionized water, dried with nitrogen, and air dried in a desiccator for 24 hours. SEM imaging of Pt nanoparticles resulted in a pseudodiameter of 4.74 nm. EDS confirms the presence of Pt species on TiO$_2$ through peaks observed at 2.048 keV. FFT analysis of the Pt nanoparticle lattice fringes reveal a d-spacing length of 2.3 Å, confirming the (111) plane of platinum. XPS confirms the presence of oxidized Pt metal from the measured binding energies of Pt 4f$_{5/2}$ 74 eV.

4.2.4 Sequential Silver Deposition

Silver nanoparticles were sequentially deposited alongside Pt-TiO$_2$ by coating Pt-TiO$_2$ with an Ag precursor solution. Jiang et al developed a method of depositing Ag nanoparticles on TiO$_2$ colloids by coating the substrate with an AgIO$_3$ precursor and exposing the coated particles to UV irradiation.\textsuperscript{[71]} We have utilized their method to photodeposit Ag nanoparticles alongside Pt nanoparticles on the same TiO$_2$ substrate (Figure 5.6). Pt-TiO$_2$ nanoparticles were annealed to
800°C in order to reduce PtO to Pt and were immediately submerged in AgIO$_3$ solution and stir coated for two hours. The coated sample is placed in a PEEK photodeposition cell, submerged in 1 mL of HPLC grade water, and exposed to UV irradiation for 60 minutes in order to form Ag nanoparticles. After UV irradiation the nanoparticles are washed with HPLC grade water in order to remove residual salts from the surface. Particles are dried with nitrogen and placed in an air dried desiccator for 24 hours before characterization. SEM imaging of Ag-Pt-TiO$_2$ nanoparticles resulted in Ag nanoparticles having a pseudodiameter of 8.90 ± 5.01 nm, which are larger compared to Ag nanoparticles photodeposited onto bare TiO$_2$. Pt nanoparticles were observed to have similar pseudodiameters to Pt-TiO$_2$ before Ag deposition.
Figure 5.6: Sequential photodeposition method of loading Ag nanoparticles onto Pt-TiO$_2$. Pt-TiO$_2$ nanoparticles were coated with AgIO$_3$ and exposed to UV irradiation. Redox reactions on the surface of TiO$_2$ allow Ag to nucleate alongside Pt nanoparticles.
Figure 5.7: Images are 75 x 75 nm. Left column: Pt nanoparticles deposited onto the surfaces of TiO$_2$ nanoparticles on HOPG. Right column: Image of Ag nanoparticles deposited onto the same Pt-TiO$_2$ nanoparticles from the left column.
Before and after SEM images (Figure 5.7) show that Ag nanoparticles were deposited onto the surfaces of Pt-TiO$_2$ nanoparticles. There is evidence that Ag nanoparticles are encapsulating some Pt nanoparticles and large surface areas of TiO$_2$. Some Ag nanoparticles were adsorbed onto the surfaces of multiple Pt-TiO$_2$ nanoparticles and the number of Ag nanoparticles observed in the sample area was much lower compared to Ag deposited onto bare TiO$_2$. Pt nanoparticles before and after Ag photodeposition largely retained their morphology and spatial positioning on TiO$_2$ nanoparticles. EDS analysis on various particles reveal major peaks observed at 2.964 (Ag), 2.048 (Pt), 0.523 (O) and 4.510 keV (Ti) (Figure 5.8). TEM analysis was not conducted on this sample due to the similar values in fringe lattice spacing for both Ag and Pt. Ag nanoparticles were measured to be $8.09 \pm \text{nm}$ in diameter (Figure 5.9).
4.2.5 Raman Intensity Measurement

Raman intensity was measured in order to determine SERS enhancement factor. Samples were annealed to 800°C in order to remove impurities and to reduce oxidized species of Ag and Pt. Annealed Ag-TiO$_2$ samples were immediately placed into a solution of thiophenol (Sigma Aldrich) for three hours. Samples were washed with hexane to remove residual thiophenol molecules and dried with nitrogen gas. Ag-Pt-TiO$_2$ nanoparticles were annealed to 800°C and submerged in cyclohexene (Sigma Aldrich) for three hours. Ag-Pt-TiO$_2$ samples were washed with hexane to remove residual cyclohexene and dried with nitrogen gas. Raman intensity of Ag bound thiophenol or Pt bound cyclohexene was measured with a Raman microscope (Renishaw) using a 532 nm laser at 30mW. Bi-metallic loaded TiO$_2$ nanoparticles were also submerged in a cyclohexene and hexane solution in order to further determine benzene detection.

**Figure 5.9:** Histogram of Ag nanoparticle pseudodiameter from Ag-Pt-TiO$_2$ nanoparticles.
capabilities. Annealed Ag-Pt-TiO$_2$ nanoparticles are submerged in a cuvette quartz cell containing the solution at room temperature. Raman microscopy lenses with a further confocal volume and point were used in order to detect benzene signal within a close vicinity of the nanoparticles.

Figure 5.10: Raman analysis of sample substrate after drying.
5.3 Results/Discussion

In order to characterize the enhanced Raman scattering field of Ag- and Ag-Pt-TiO$_2$ nanoparticles a series of probe molecules were used. Thiophenol and cyclohexene were deposited onto Ag- and Ag-Pt-TiO$_2$ nanoparticles respectively. Previous research has shown that thiophenol molecules exclusively bind to the surfaces of Ag nanoparticles at room temperature via the sulfur group in a vertical position (Figure 5.11).\textsuperscript{[72]} Therefore thiophenol is an ideal probe molecule to properly observe and quantify Raman scattering from activated Ag nanoparticles.

![Figure 5.11](image)

**Figure 5.11:** Thiophenol binds vertically and exclusively to the surface of Ag nanoparticles deposited onto TiO$_2$ support.
As expected, no thiophenol signal was observed when Ag nanoparticles are absent in the sample. **Figure 5.12** shows the enhanced Raman signal from thiophenol adsorbed onto Ag nanoparticles situated on TiO$_2$ nanoparticle supports (black) compared to a bare TiO$_2$ sample submerged in thiophenol (red). We attribute the rise in signal from 1020 to 1125 cm$^{-1}$ in the bare TiO$_2$ sample as a graphite phonon, not a thiophenol vibration signal. This graphite phonon is observed in control samples with no exposure to thiophenol. Pt-TiO$_2$ nanoparticles were also exposed to thiophenol and the resulting Raman spectrum did not yield peaks characteristic of thiophenol adsorption. Raman peaks observed at 999, 1020, and 1073 cm$^{-1}$ were assigned in-plane ring-breathing, the in-plane C-H bend, and the in-plane ring-breathing mode coupled to the C-S stretching mode of thiophenol, respectively.$^{[73]}$

![Figure 5.12: Raman spectrum of Ag-TiO$_2$ and TiO$_2$ nanoparticles coated with thiophenol and dried in air.](image)
A Raman enhancement factor (EF) was calculated for the case of thiophenol adsorbed onto Ag-TiO$_2$ nanoparticles by using Equation 1 where $N_{\text{ref}}$ and $N_{\text{SERS}}$ are the number of thiophenol molecules observed within the volume of Raman signal collection for a reference solution and the number of observed thiophenol molecules adsorbed onto Ag-TiO$_2$ nanoparticles within the laser collection area respectively. The EF calculation can be written as:

$$EF = \left( \frac{N_{\text{ref}}}{N_{\text{SERS}}} \right) \left( \frac{I_{\text{SERS}}}{I_{\text{ref}}} \right)$$  \hspace{1cm} (1)

$I_{\text{ref}}$ and $I_{\text{SERS}}$ is the measured intensity of the C-S stretching mode at 1073 cm$^{-1}$ for the reference solution of thiophenol and Ag-TiO$_2$ nanoparticles submerged in pure thiophenol respectively. Intensity values were normalized with respect to the collection time and laser power. The calculated Raman intensity of $I_{\text{SERS}}/I_{\text{ref}}$ yielded a ratio of 0.09. $N_{\text{SERS}}$ and $N_{\text{ref}}$ refer to the observable number of thiophenol molecules adsorbed to the surface of Ag-TiO$_2$ nanoparticles within the laser spot area and the number of molecules observed in the confocal volume of the laser in the reference solution in order to obtain a normal Raman spectrum, respectively. It is assumed that thiophenol molecules form an adsorbed monolayer encapsulating Ag after washing. The number of molecules in $N_{\text{SERS}}$ was calculated by taking into account the percentage surface area coverage of Ag nanoparticles (1.16%) in the laser spot size area (588,162.7 nm$^2$) to yield 6,868.6 nm$^2$ of Ag. The equilibrated surface area coverage of thiophenol ($\sim3.0 \times 10^{14}$ molecules/cm$^2$) in conjunction with the area of Ag-TiO$_2$ coverage can be used to calculate the number of adsorbed thiophenol molecules in the laser spot size area.$^{[74]}$ The number of adsorbed thiophenol molecules calculated was observed at 20,606. $N_{\text{ref}}$ was calculated by the confocal volume area ($V_c$) of laser analysis in the reference solution (Equation 2)

$$V_c = \pi^{3/2} \kappa \omega^3$$  \hspace{1cm} (2)
where $\kappa$ is defined as the resolution of the objective in the z direction (7.4) and $\omega$ is the radius of the laser spot size. $V_c$ comes out to be $1.12 \times 10^{-11}$ ml. The molecular weight and density of thiophenol can be used to calculate the number of molecules within the confocal volume: $6.6 \times 10^{10}$ molecules in ref. The calculated EF associated with thiophenol adsorbed on Ag-TiO$_2$ nanoparticles is $\sim 4.12 \times 10^5$. This EF value is comparable to another EF value associated with adsorbed thiophenol on linearly arrayed Ag nanoparticles.\[65\] Due to the size of Ag nanoparticles we believe the exact areas of SERS “hotspots” are assigned to areas where Ag nanoparticle population is denser than other areas. However, there has been research conducted on isolated and clustered Ag microparticles for enhanced Raman signal. Xiao \textit{et al} have found an average of $10^4$ enhancement associated with Ag particles of 1 µM. When combined with other Ag nanoparticles in the form of clusters, the enhancement has been increased by $10^2$, most likely due to the interaction between plasmonic effects of nearby particles.\[75\] Therefore to maximize enhancement one must be mindful of Ag nanoparticle size and gap distances between each particle. Such parameters must be taken into account for future experiments in determining optimum conditions for increasing EF. It is worth noting that the EF value is an average of enhancement in a specific area. Other areas within the laser spot size may have a higher or lower magnitude of enhancement but are all averaged in a resulting EF factor.
Figure 5.13: Diagram of cyclohexene binding to Pt nanoparticle surfaces on bimetallic-loaded TiO₂ nanoparticles.

In order to test the chemical sensing capabilities of SERS active Ag nanoparticles a bimetallic loaded TiO₂ nanoparticle system was fabricated. Ag-Pt-TiO₂ nanoparticles were fabricated on HOPG where distinct Ag and Pt nanoparticles are within close vicinity to each other (<5nm) (Figure 5.7). Platinum was chosen as the support nanoparticle due to its limited SERS activity.\textsuperscript{[15]} Cyclohexene was used as a probe molecule that binds exclusively to platinum surfaces.\textsuperscript{[76]} At near room temperature adsorbed cyclohexene will dehydrogenate into benzene on Pt surfaces, making it an ideal probe molecule to qualitatively determine Ag enhancement capabilities with nearby molecules (Figure 5.14).\textsuperscript{[77]} Nearby Ag nanoparticles, once activated by the Raman laser, may enhance the nearby signal intensity of benzene for detection. Because this hydrogenation reaction is taking place at room temperature, we expected to see a majority of Raman signal corresponding to the benzene molecule. There was no cyclohexene or benzene signal observed with Ag-TiO₂ nanoparticles after washing with hexane.
The resulting spectra (Figure 5.15) details several peaks after cyclohexene has been adsorbed on the surface Ag-Pt-TiO$_2$ and left to dry for one hour. Samples were then washed with hexane in order to remove residual cyclohexene. The peaks at 689 cm$^{-1}$ and 1170 cm$^{-1}$ have been assigned to benzene ring deformation and –CH bending modes respectively. The more significant peaks at 986 cm$^{-1}$, 1010 cm$^{-1}$, and 1061 cm$^{-1}$ have been assigned to the symmetric ring breathing mode, another ring deformation mode, and a C-H deformation mode of benzene. The appearance of the 1010 and 1061 cm$^{-1}$ bands are typically non-Raman active and suggests benzene adsorption onto Pt surfaces, resulting in the loss of molecular symmetry. We suspect that the resulting plasmon phenomena occurring on Raman induced Ag nanoparticles in combination with the close vicinity of Pt nanoparticles allow benzene molecules to be detected due to the radius of localized plasmon oscillations.
Figure 5.15: Raman spectrum of benzene adsorbed onto Pt nanoparticles in an Ag-Pt-TiO$_2$ nanoparticle system.

A Raman enhancement factor was calculated for adsorbed benzene in comparison to adsorbed benzene solution on HOPG. The 986 cm$^{-1}$ peak is used to calculate the EF value as the peak is observed in both benzene solution and adsorbed benzene. The number of benzene molecules was attributed to the surface area coverage of Pt nanoparticles instead of Ag. Note that this is a rough estimation of an EF value as signal is only observed from Pt located nearby Ag nanoparticles. The enhancement factor was calculated to be $\sim 1.4 \times 10^4$, an order of magnitude lower compared to thiophenol on Ag-TiO$_2$. There might be several reasons for the lower EF value, ranging from Pt particle vicinity within Ag plasmonic effects to the abundance of Ag nanoparticles available for intensity enhancing. One would hypothesize that there is an ideal gap distance between benzene adsorbed Pt nanoparticles and Ag in correlation to an optimum EF.
value. Ag nanoparticle sizes are also more varied when deposited onto Pt-TiO$_2$. The variation in diameter could affect plasmonic oscillation radius or activity leading to a loss of signal enhancement. This type of analysis would require additional experiments involving properly identifying particle species identity via Auger mapping through x-ray photoelectron spectroscopy. We conclude that his value is within reason due to the aforementioned reasons of Ag size variability and number of Pt nanoparticles within Ag plasmonic oscillation.

### 5.4 Conclusion

Ag-TiO$_2$ nanoparticles and Pt-Ag-TiO$_2$ nanoparticles were fabricated in order to observe SERS behavior through the exploitation of Ag nanoparticle antennas on TiO$_2$. Thiophenol and cyclohexene were used as probe molecules in order to determine Ag antenna capabilities. Thiophenol has been observed on Ag-TiO$_2$ nanoparticles through Raman microscopy. An enhancement factor has been calculated for Thiophenol adsorbed Ag-TiO$_2$ nanoparticles yielding $2.9 \times 10^5$. This value is comparable to a previous study performed by our lab and confirms the plasmonic enhancement properties associated with Ag nanoparticles. We have further tested the Raman enhancement properties of Ag nanoparticles through Ag-Pt-TiO$_2$ nanoparticles adsorbed with cyclohexene. Cyclohexene exclusively binds to Pt nanoparticles and forms benzene near room temperature. Benzene has been observed on the surfaces of Ag-Pt-TiO$_2$. We believe that benzene was bound exclusively on Pt nanoparticles and were detected due to nearby Ag nanoparticles. An EF value of $1.4 \times 10^4$ was calculated from the intensity of the 986 cm$^{-1}$ peak. Although intensity enhancement was observed on the sample surfaces, further experiments are necessary in order to determine specific conditions of Ag and Pt morphology for maximum enhancement capabilities.
**Funding:** This work is supported by the U.S. Department of Energy, Office of Basic Energy Sciences through grant number: DE-FG02-96ER45576.

**Acknowledgment:** The authors thank the Laboratory for Electron and X-ray Instrumentation (LEXI) at UC Irvine for SEM, TEM, XPS and EDS work and service. The authors also thank the UC Irvine Laser Spectroscopy Facility for UV-Vis work and analysis.


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APPENDIX A: HIGH RESOLUTION IMAGING OF NANOPARTICLES SUPPORTED ON HOPG

Imaging M-TiO$_2$ nanoparticles supported on highly oriented pyrolytic graphite consists of various characterization techniques. This chapter will describe methods associated with imaging nanoparticles using the scanning electron microscope (FEI Magellan) and transmission electron microscope ranging from sample preparation to imaging specific particles before and after wet experiments. All instruments used for sample characterization are held at LEXI.

A.1 SEM microscopy:

A.1.1 Sample preparation

Sample preparation for SEM microscopy involves a clean sample surface anchored onto an SEM stub holder.

1. Samples are typically placed in a vacuum desiccator 24 hours before any characterization.
2. Samples were then air dried with nitrogen gas in order to remove leftover moisture.
3. An SEM holder stub (Figure A.1) with copper clips is used to anchor the sample down for microscopy.
4. In order to achieve high resolution images with the SEM the samples must be plasma cleaned *in-situ* of the SEM. The plasma involved comes from the vented chamber of the instrument and will oxidize the sample surface, essentially damaging it. Therefore it is crucial to perform all experiments on the sample prior to plasma cleaning. Steps for plasma cleaning are listed below:
a. Double click on “Sample Cleaning” in the location menu tab.

b. Wait for the sample to move to the sample cleaning location. From the top menu tabs, select “Tools” and then “cleaning.” Plasma cleaning should start automatically.

c. Wait for cleaning to finish and double click on “Move to Last Location” to move the sample back.

Figure A.1: Sample loading onto SEM stub.
A.1.2 Imaging Specific Particles Before and After Experimentation

The SEM in conjunction with the nature of nanoparticles adsorbed onto HOPG allow users to image specific areas in order to monitor particle morphology. This is essential when determining particle nucleation before and after bi-metallic loading of TiO$_2$. However, one must practice the technique to locating specific particles after being accustomed to using the SEM instrument. The following steps will help guide a user to image specific areas of interest at high resolution.

1. Start by making a small, but obvious scratch onto the surface of your sample with a razor blade.

2. Locate the scratch mark itself through a low-resolution lens setting on the SEM. The scratch should be big enough to be viewable from the entire screen at this point. It is recommended to plasma clean the surface before high resolution imaging. If oxidation is of concern, one can re-anneal the sample at high temperatures by the evaporator before any experiments.

3. Perform the necessary steps to achieve high resolution imaging and choose an area that contains particles that are easy to discern. These particles should be on the edge or within view of a part of the scratch made on the surface earlier.

4. The surface scratches are visual key points that one must note in order to re-locate a specific area of interest. However, scratch marks made on the surface are prone to morphological alterations after experiments, especially after photodeposition. Therefore, choose an area that won’t necessarily change, such as large clumps of TiO$_2$, scratch marks that narrow to a needle point, or even microparticles of metal aggregates pictured below. Typically these features retain their appearances after
experiments, however there is no guarantee. One must play around and take images of multiple areas to increase the likelihood of imaging the same area.

5. Take a high resolution image of the desired location, typically at x650,000 magnification.

6. After taking a high resolution image, slowly decrease the magnification and take an image after every decrease. One can use the magnification wheel on the console to zoom out. NOTE: It is important to not move the window location during the zoom-out process.

7. Continue slowly zooming-out with the magnification wheel with subsequent imaging. One must take as many photos as they can from high resolution all the way to a low-resolution window in order to re-locate the area of interest.

8. If done correctly, one can use the series of images as a reference to relocate the scratch area from a microscopic scale to the nanometer scale in order to image the same area after an experiment. Below is a series of images that exemplify the technique. Starting from a high resolution area (Figure A.2 A) located near an aggregate of Pt particles; one continually zooms out while taking an image of each de-magnification.
Figure A.2: Example of images from a high resolution area to a zoomed out area in order to relocate a specific set of particles.

At image F, the user will have to switch to a TLD lens configuration in order to zoom out further in the microscopic scale to achieve image G. Eventually, the user will reach the maximum zoom configuration and be able to see visual landmarks of the surface scratch at image I. After experimentation the user will backtrack from the zoomed-out image all the way back to the high resolution area.
A.2 TEM Microscopy

A.2.1 Sample preparation

TEM sample preparation involves capturing a thin enough piece of sample to allow a particle imaging at high resolution as well as lattice fringe imaging and phase measurement. Note that this technique will destroy the sample surface so caution must be taken into consideration.

1. It is recommended to anneal or plasma clean the surface of the sample before peeling.

2. Thin samples are captured by peeling the surface of the sample as one normally would with Scotch tape. Except in this case one has to peel away long thin strips of the HOPG surface.

3. At MC2 there is a microscope located outside of the TEM room that features a back-lit lamp. Under the microscope with the back-light on, one can see how light passes through parts of the thin strip sample. Figure A.3 shows an example of a thin material where light is able to pass through. These ideal areas are where one can take high resolution images of nanoparticles.
4. Place the taped sample onto a plastic sample holder box with the thin film facing towards the user.

5. To image these areas one has to capture the thin area onto a TEM grid. The grid itself consists of two different grates. One side has large grid areas while the other has smaller squares. The nanoparticle side has to be facing toward the large grid area.

Figure A.3: Example of a thin area of HOPG.
6. Open a TEM grid with tweezers and slide it under the thin sample slice. Make sure the densely gridded area is placed right under the sample slice and not the open gridded area as shown in Figure A.4.

![Figure A.4](image)

**Figure A.4**: A TEM grid is placed underneath the taped HOPG slice.

7. Make sure that a piece of tape is stuck to the grid itself so that the HOPG slice won’t move.

8. Close the grid using a pair of tweezers. Under the microscope, take a razor blade and cut the area of tape and sample slice so that it fits onto the TEM grid (**Figure A.5**).
9. Place the grid open area face-down onto the TEM sample holder. One can use a vacuum needle located in the same room as the TEM to grab the grid without harming the surface.

10. Leftover tape on the TEM grid is ok as taped areas absorb most of the electron beam. This allows users to easily find the thin film area for analysis.
APPENDIX B: REDESIGN OF THE PHOTOELECTROCHEMICAL CELL

A photoelectrochemical cell was designed and fabricated in order to house a TiO₂ sample for photodeposition purposes. Initially designed by James Taing, the cell has been re-designed in AutoCAD to alleviate problems encountered during photodeposition. The cell is made of Polyetheretherketone (PEEK) material due to its stable and non-reactive properties and is constructed by the machine workshop located on campus in Rowland Hall.

The main improvement of the cell was to increase the distance between the sample surface and the point of entry for UV light. By increasing the cell height and inner-cell volume, the buildup of evaporated gas during Ar bubbling and photodeposition is alleviated. The exhaust port diameter has also been increased to increase the outflow of evaporated gas. The entry port for Ar bubbling has been shifted towards the bottom of the cell. These changes help prevent the entry-lens from fogging and obscuring the UV light pathway.
Figure B.1: Three dimensional view of PEEK Cell Model (1).
Figure B.2: Three Dimensional PEEK Cell Model (2).