NANOSTRUCTURED SILVER FOR APPLICATIONS IN SURFACE ENHANCED RAMAN SPECTROSCOPY AND PHOTOELECTROCHEMICAL REACTIONS

by

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ABSTRACT

Initial work focused on characterizing silver and its surface enhanced Raman spectroscopy (SERS) capabilities. Silver nanowires were chosen as an ideal material and scanning confocal microscopy studies were performed to identify hot spots. The silver nanowires were found to exhibit fluorescence blinking that was attributed to small silver clusters undergoing rapid interchange from $\text{Ag}^{0}$ to $\text{Ag}_2\text{O}$. Control of this blinking was accomplished through the removal of oxygen and through electrochemical control of the system. SERS was also recorded from these nanowires. Deconvolution of the SERS signal from the fluorescence was accomplished either by increasing the SERS analyte concentration or increasing the total number of “hot spots” in the focus volume.

Silver applications were studied by performing a SERS study of Rhodamine 6G (R6G) and Poly(3-hexylthiophene-2,5-diyl) (P3HT). A Tollens’ silver substrate was utilized as the SERS substrate and similar blinking effects were found to arise. P3HT was cast from 4 different solvents:dichloromethane, chlorobenzene, THF, and toluene. The solvent effects were studied, with kinking of the polymer noted in the non-chlorinated solvents. Single molecule studies in conjunction with polarization control indicated that the P3HT formed in an overlapping manner with only partial charge transfer within the molecule.

Finally silvers interactions with TiO$_2$ were studied. Micron scale single crystal anatase TiO$_2$ was synthesized by using HF in a hydrothermal process forming a truncated bipyramidal structure consisting of [101] and [001] faces. Fluorine was present in small amounts on the surface of the TiO$_2$ as confirmed by x-ray photoelectron spectroscopy (XPS). An annealing
process was used to remove the fluorine. Nitrogen doping was attempted, but was not found to occur in significant amounts. Visible light sensitivity was noted in annealed samples but did not occur in the bulk as demonstrated through photoelectrochemical measurements. Silver photoreduction directly on the surface of the TiO$_2$ crystals revealed visible light sensitivity at surface defects. No facial preference was noted for the silver growth through energy-dispersive X-ray spectroscopy (EDX) images. A secondary method of silver attachment through a linker molecule showed that on-resonance silver structures provided greater SERS enhancement dependent upon the direction of the linker molecule.
DEDICATION

I would like to dedicate this dissertation to my lovely wife DeAna. Without her support I could have never succeeded. Your faith in me has kept me motivated and inspired throughout the difficult times.
# LIST OF ABBREVIATIONS AND SYMBOLS

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>&lt;I&gt;</td>
<td>Mean Photoluminescence Intensity</td>
</tr>
<tr>
<td>AAO</td>
<td>Anodized Aluminum Oxide</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>APD</td>
<td>Avalanche Photodiode</td>
</tr>
<tr>
<td>BDT</td>
<td>para-Benzene Dithiol</td>
</tr>
<tr>
<td>CAF</td>
<td>Central Analytical Facility</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge Coupled Device</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>e</td>
<td>Elementary Charge of an Electron</td>
</tr>
<tr>
<td>$\epsilon_0$</td>
<td>Permittivity of Free Space</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EM</td>
<td>Electromagnetic Field</td>
</tr>
<tr>
<td>$E_p$</td>
<td>Energy of the Plasmon</td>
</tr>
<tr>
<td>G(Dt)</td>
<td>Temporal Autocorrelation Function</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s Constant</td>
</tr>
<tr>
<td>I(t)</td>
<td>Time-Resolved Fluorescence Intensity</td>
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<tr>
<td>ITO</td>
<td>Indium Tin Oxide</td>
</tr>
<tr>
<td>m</td>
<td>Mass of an Electron</td>
</tr>
<tr>
<td>m</td>
<td>Integer Multiple of $\tau$</td>
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<tr>
<td>MBZA</td>
<td>4-Mercaptobenzoic Acid</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>MPY</td>
<td>Mercaptopyridine</td>
</tr>
<tr>
<td>$n$</td>
<td>Conduction Electron Density</td>
</tr>
<tr>
<td>P3HT</td>
<td>Poly(3-hexylthiophene-2,5-diyl)</td>
</tr>
<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PSI</td>
<td>Pounds per Square Inch</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>R6G</td>
<td>Rhodamine 6G</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions per Minute</td>
</tr>
<tr>
<td>$s$</td>
<td>Seconds</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>SERS</td>
<td>Surface Enhanced Raman Spectroscopy</td>
</tr>
<tr>
<td>SHINERS</td>
<td>Shell-Isolated Nanoparticle-Enhanced Raman Spectroscopy</td>
</tr>
<tr>
<td>SM</td>
<td>Single Molecule</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Time Interval</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TERS</td>
<td>Tip Enhanced Raman Spectroscopy</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
</tr>
<tr>
<td>$\omega_p$</td>
<td>Plasmon Frequency</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
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ACKNOWLEDGMENTS

I would like to begin by acknowledging my research advisor, Dr. Shanlin Pan. He has provided the motivation, ideas, funding, and support allowing the work in this dissertation. Next I would like to thank my committee for providing guidance in my research efforts. I would especially like to thank Dr. Gregory Szulczewski who has provided additional support in interpretation of XPS spectra, and with the help of Alexandra Arnold, has performed a methylene blue degradation study presented within this dissertation. I would like to also acknowledge Dr. David Dixon and Mingyang Chen for performing theoretical computations on silver nanowires and their local electromagnetic field enhancements. Dr. Shane Street has provided significant contributions and discussions dealing with TiO$_2$ and linker molecules. Additional discussions and work were performed with Dr. Robert Bennett for the TiO$_2$ linker. Tyler McPherson helped perform work on the silver nanowire study. Karson Brooks performed significant contributions toward the P3HT study. Robert Holler collected all XPS data. Johnny Goodwin provided training and advice in performing all the SEM and TEM data collection. Financial contributions were made by the DOE, NSF and EPSCoR.
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CHAPTER 1
INTRODUCTION

Silver and its useful applications towards surface enhanced Raman spectroscopy (SERS) and photoelectrochemical methods is the key focus of this dissertation. As such, this chapter will attempt to provide a basic understanding of the fundamental knowledge and background of this topic. Initial discussion will include the development and implementation of Raman spectroscopy as well as the technique’s more recent integration with electrochemical methods. This will then be extended to providing a cursory understanding of plasmons and plasmonic structures for surface enhanced Raman spectroscopy. Then silver and its applications within the already fields will be detailed. Finally, the materials of interest for further study by utilizing silver will be detailed.

1.1 Raman Spectroscopy

Raman scattering is a form of inelastic light scattering discovered by Sir Chandrasekhara Venkata Raman in 1928\(^1\). The majority of scattered light undergoes Rayleigh scattering, which is an elastic process. Raman scattering is inelastic, with the electron undergoing promotion to a virtual energy state before undergoing light emission and relaxation to a different vibrational energy level from the original. This results in either a Stokes (red shifted) or anti-Stokes (blue shifted) shift of the emission dependent on whether the final vibrational energy level is at a higher or lower energy than the initial vibrational energy level. Since the energy difference is equivalent to the difference in the vibrational energy states, vibrational information is gathered.
The Raman spectrum has a different set of selection rules from IR spectroscopy, which allows for complementary vibrational data to be collected.

Raman spectroscopy provides definite advantages in chemical identification and sensing. First among these is its ability to “fingerprint” any compound dependent upon its unique vibrational energy. Second, Raman spectroscopy can be used with a wide variety of different light sources, from infrared through higher energy sources, with information about the Raman shift still being garnered. Third, since infrared light is not required, Raman spectroscopy can be performed on aqueous solutions, a problem normally difficult to overcome in IR spectroscopy. However, Raman spectroscopy has its own set of issues as a technique. First, the Raman interaction cross section is much smaller than the Rayleigh scattering cross section resulting in most of the light being elastically scattered. Since the important information gathered is based on the shift from the incident light, poor optical alignment and equipment can obscure the signal of interest. Second, as the incident light is moved into the visible spectrum the likelihood for fluorescence occurring is greater. Once again the fluorescence cross section is much greater than the Raman cross section and can obscure the signal of interest. Third, due to the low Raman cross section for most materials, either a large intensity of light is required or a great deal of collection time. Finally, a monochromatic light source is necessary for proper sampling since the Raman shift is the important measurement aspect of the technique.

Raman spectroscopy has seen its greatest gains through two major advances. The first of these was the creation of the laser, which provided a high power monochromatic source of light for Raman spectroscopy. This allowed for better signal resolution and higher throughput for Raman spectroscopy instruments. Further refinements, such as tunable and pulsed lasers, have provided a greater range of possible sample systems and types of analysis that can be performed.
The second major advance was the discovery of surface enhanced Raman spectroscopy (SERS) by Fleischmann, Hendra and McQuilan$^2$ and explained separately by Jeanmaire and Van Duyne$^3$, who introduced the electromagnetic theory of enhancement, and Albrecht and Creighton$^4$, who developed the chemical theory of enhancement. Since the discovery of SERS, the two theories have been reconciled to both contribute to the surface enhancement effect$^5,6$, though the proportion of enhancement caused by each is still debated. The electromagnetic theory states that the enhancement is caused by the surface plasmon interacting with the incident light$^7$. When the surface plasmon is on resonance with the incident light, the local electromagnetic (EM) field of the nanostructure becomes enhanced by the plasmon oscillation. The same electromagnetic field can enhance the light scattering from the sample of interest, giving a further enhancement. This two part enhancement from the plasmon provides the majority of the SERS enhancement. Metal nanostructures are often used as on-resonance plasmonic structures for SERS enhancement because of their ideal photophysical properties. The chemical enhancement method proceeds through the transfer of electrons from the SERS material to the sample of interest$^8$. The increased electron density provides more electrons for the scattering process and thus increases the Raman cross section of the material. In addition to the enhancement properties provided by SERS, the SERS material can also serve to quench fluorescence$^9,10$ through electron back transfer or FRET type pathways.

With these advancements, Raman spectroscopy saw resurgence in popularity and innovation in application$^{11-15}$. Among the new methods developed were Raman depth profiling$^{16-18}$, Raman antennae based sensors$^{19-21}$, and high throughput Raman flow cytometry$^{22-24}$. The method that has seen the most study, however, is that of single molecule surface enhanced Raman spectroscopy (SM-SERS)$^{25-27}$. First discovered by Nie and Emory$^{28}$ and separately by
Kneipp et al., SM-SERS takes advantage of the standard surface enhancement scheme to analyze single molecules of the analyte. In order to accomplish this, an appropriate SERS material, usually silver or gold in the visible region, is synthesized at the nanoscale to be maximally on resonance with both the incident laser and excident signal from the analyte. This can involve controlling the size, shape, and volume of the nanoparticles so as to create electromagnetic enhancement maximums known as “hot spots”. The extremely dilute analyte is then coated onto the SERS substrate, flowed over the SERS substrate, or placed in-situ with SERS particles to create a sample. The sample is then analyzed, usually through a confocal microscope, in such a way that only a single particle is visible within the area of spectrum collection. Further data discrimination methods are then applied to determine whether analyte particles are actually of a single molecule nature or not. This is possible due to the stochastic nature of a single particle undergoing Raman scattering, and provides features that are incapable of being probed in bulk sampling procedures. Thus unique information is capable of being garnered using a SM-SERS system of analysis.

1.2 Raman Spectroscopy and Electrochemistry

Electrochemistry is one of the oldest branches of formal analytical chemistry with luminaries such as Faraday performing some of the critical work. In their book Electrochemical Methods, Bard and Faulkner define electrochemistry as:

“Electrochemistry is the branch of chemistry concerned with the interrelation of electrical and chemical effects. A large part of this field deals with the study of chemical changes caused by the passage of an electric current and production of electrical energy by chemical reactions.”
that is an effective and thorough definition of the branch for this dissertation. As such, what will be focused upon is not the greater field of electrochemistry but the recent integration of electrochemistry with Raman methods.

The most common integrated methods focus on SERS sensing in electrochemical systems\textsuperscript{56}. This has included SERS studies that vary the electrode geometry\textsuperscript{57-59}, materials\textsuperscript{60-62}, and amount of surface activation\textsuperscript{63-66}. Such studies have focused primarily on identifying the effects on the SERS hotspots within the system\textsuperscript{67-71}, such as those performed by Willets and coworkers\textsuperscript{72,73} in using super-resolution techniques to perform co-localization studies of SERS hotspots with luminescence intensities. These studies have tried to formulate processes capable of creating electrodes appropriate to various systems. This has led to well defined electrode systems used in experiments to confirm theoretical calculations\textsuperscript{74-77}. Further work has been carried out by varying the electrochemical system\textsuperscript{78-80} to determine the effects of the system on the SERS intensity. These studies have been carried out even under single molecule conditions\textsuperscript{81,82} such as the Nile Blue/Rhodamine 6G bi-analyte study performed by Cortes et al\textsuperscript{83}. In this study the presence of single molecules of Nile Blue on an electrode was determined by sweeping the potential to reduce Nile Blue while leaving the Rhodamine 6G signal unaffected. Abrupt changes in the Nile Blue signal would alert researchers to the single molecule nature of the system, while the consistent signal from the Rhodamine 6g allowed identification and monitoring of the Raman hot spot.

Built upon SERS systems, two other major methods have been developed making use of electrochemical methods: Shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS)\textsuperscript{84-86}, and tip enhanced Raman spectroscopy (TERS)\textsuperscript{87-89}. SHINERS is a method originally developed by Tian and coworkers\textsuperscript{90}, where a Raman active core is synthesized with a
non-reactive thin shell. This allows for SHINERS particles to be coated onto an electrode and then for electrochemical reactions to be performed with Raman monitoring without unintended reactions with the coating particle. It also localizes the Raman active sites between the SHINERS particle and the electrode surface instead of allowing for intense hot spots to form between standard SERS nanoparticles. Various experiments have been performed by varying the core\textsuperscript{91,92}, shell\textsuperscript{93-95}, and electrode materials\textsuperscript{86,96,97}, as well as the electrochemical systems\textsuperscript{98-100} involved in the process. TERS uses a nanoscale AFM tip with an electrical bias applied to the tip\textsuperscript{101-103}. The applied bias generates an electric field that will only interact with a very small area near the surface of the electrode. Generated species only within the area can receive Raman enhancement, controlling the location of the hotspot. TERS has been used in biological systems\textsuperscript{104-106}, solid state catalysis\textsuperscript{107,108}, and metallic surfaces\textsuperscript{109-111}, with Zhang et al.\textsuperscript{112} recently performing single molecule mapping of \textit{meso}-tretrakis(3,5-di-tertiarybutylphenyl)-porphyrin on a silver substrate. However these systems are limited in that the tip enhancement is less than the standard colloidal mixtures and that aqueous systems have only just begun to be studied.

1.3 Plasmons

The critical aspect that links the Raman and electrochemical methods is the interaction of plasmons with an electromagnetic field\textsuperscript{113-115}. Plasmons are essentially a sea of electrons located on the conduction band of a structure. The electrons are free to move along the surface, and as a moving charge generates an electromagnetic field, each electron will generate a small electromagnetic field. When the electrons are free to move randomly, the electromagnetic fields will cancel out, but when the electrons are directed and moved en masse in the same direction the generated electromagnetic fields will constructively interfere. Controlling the electron movement can be accomplished by applying an electromagnetic field, as charged particles will move in the
direction of the applied field. With an oscillating field, such as light or an oscillating bias voltage, the electrons can be caused to oscillate generating their own oscillating electromagnetic field. As noted before, when such an electromagnetic field is generated on resonance with a wavelength of light, it can enhance the intensity of the light.

Two main factors control a plasmon: the geometric confinement\textsuperscript{116-118} and the electron density\textsuperscript{119-121}. The geometric confinement works on a quantum confinement principle. The electrons are bounded by their ability to traverse the plasmonic structure. This results in a practical upper limit of movement based on the length of the structure in the direction of the perturbation. Along with the rate that the electrons can traverse the structure this creates an ideal plasmon resonance for the structure in that direction. Thus tuning the size of the structure creates varied plasmonic resonance frequencies\textsuperscript{122} while tuning the shape can allow different resonances along different axis of the structure\textsuperscript{123}. Electron density in the conduction band determines multiple aspects of the plasmon, with the most obvious being absorption and scattering cross-sections\textsuperscript{124} as can be seen from the higher efficiency of nanoparticles in relation to quantum dots. However, electron density also directly affects the inherent plasmon frequency\textsuperscript{125}, which can cause reflection or transparency to incident light. This helps explain why certain materials are better at interacting with different energies of light, with the coinage metals’ electron density interacting well in the visible region. In order to calculate the plasmon frequency of a metal thin film one uses equation 1.1

\[ \omega_p = \sqrt{\frac{ne^2}{m \epsilon_0}} \]  \textsuperscript{1.1}

where \( \omega_p \) is the plasmon frequency, \( n \) is the conduction electron density, \( e \) is the elementary charge of an electron, \( m \) is the mass of an electron, and \( \epsilon_0 \) is the permittivity of free space. With all other factors being based on constants this means the controlling factor in the standard
frequency is the electron density. This information can then be used to estimate the plasmon energy by using the free electron model as in equation 1.2

\[ E_p = \hbar \omega_p \]  

where \( E_p \) is the energy of the plasmon and \( \hbar \) is Planck’s constant. This allows for an estimate of the appropriate wavelength of light for resonantly exciting the plasmon based upon the material used.

Electrochemical methods can indirectly interact with the plasmon through the growth and alteration of specific plasmonic structures and directly by altering the electron density and local electromagnetic field through an applied bias. Thus electrochemical techniques can improve or provide interesting interactions with SERS techniques through the plasmon necessary for the SERS enhancement.

1.4 Silver

Silver is a coinage metal with a plasmon frequency in the visible light range. This has led to it being used extensively in SERS experiments,\(^\text{126-131}\) with a roughened silver electrode being the first proof of SERS activity and a silver colloid providing the first proof of SM-SERS. Since then many different forms of SERS silver structures have been created including roughened and patterned electrodes\(^\text{132-134}\), and spherical\(^\text{135}\), pyramidal\(^\text{136}\) and bowtie\(^\text{137}\) nano-structures consisting of conglomerates\(^\text{138}\), dimers\(^\text{139}\) and trimers\(^\text{140}\). Further, due to its relative lack of reactivity with many common aqueous reactants, silver electrodes are often used as quasi-reference electrodes\(^\text{141-144}\), while Ag/AgCl is one of the more common reference electrodes\(^\text{145}\). Silver is also fairly easy to synthesize either as a coating\(^\text{146}\) or in colloidal form\(^\text{147}\). Both of these synthesis methods usually use an electrochemical reduction either through an applied bias or reducing
agent in conjunction with a silver salt in an aqueous solution to form the film or with an additional ligand to form the colloid.\textsuperscript{148}

Even with these multiple highly desirable aspects silver does have some fairly large drawbacks as a photoelectrochemical material. Silver undergoes an oxidation reaction with a standard oxidation potential of around -0.8 V, limiting the available electrode sweep range. When this is performed under an oxygen atmosphere, the oxygen can react with the silver ion to form Ag\textsubscript{2}O, which is electrochemically irreversible. The silver oxide does not have the preferential plasmonic and electrochemical properties, meaning that its formation is often undesirable. Ag\textsuperscript{0} can be reformed if it undergoes a photoreduction by UV or visible light\textsuperscript{149-151}, but the original shape of the structure is generally lost. This conversion is also generally incomplete as non-surface Ag\textsubscript{2}O is difficult to convert back to Ag. Further issues arise because all silver reduction processes lead to production of small silver clusters of less than 100 atoms\textsuperscript{152-157}. These clusters have quantized energy levels dependent upon their size, similar to quantum dots. This leads not only to size dependent light absorption by these clusters but also to fluorescence. Fluorescence, undesirable due to its ability to interfere with the Raman signal, is a complicated feature to remove from the spectra as the clusters undergo stochastic blinking under an oxygen atmosphere. Currently it is thought that this blinking, which occurs at time scales of greater than a few milliseconds, is caused by silver oxidation and reduction under an oxygen atmosphere\textsuperscript{150,158-161}.

Due to all of these aspects, better understanding of silver is needed. Thus the major goal of this dissertation is to garner information about silver and its interactions with materials. Of particular interest will be the photoelectrochemical interactions and SERS effects of
nanostructured silver. With the effects better understood, it is then hoped that better control can then be obtained of these effects.

1.5 Other Materials of Interest

1.5.1 Poly(3-hexylthiophene-2,5-diyl). Poly(3-hexylthiophene-2,5-diyl) (P3HT) is a common polymer dye used in photovoltaic cells. Most often it is used as a visible light sensitizer in conjunction with inorganic materials, such as TiO$_2$\textsuperscript{162-164} or ZnO\textsuperscript{165-167}, that have a bandgap which allows for only UV absorption. Often it is utilized in conjunction with 1-(3-methoxycarbonyl)propyl-1-phenyl[6,6]C$_{61}$ (PCBM) in bulk heterojunction geometries\textsuperscript{168-171} with conversion efficiencies reported up to 6.5\% by 2009 by Lee et al\textsuperscript{172,173}.

SERS has been demonstrated as an effective method to probe polymers\textsuperscript{174-176} and their interactions with solvents. Thus utilizing silver to probe the solvent properties of P3HT would allow for a useful application. In addition the effects that arose during the initial silver work could be compared for both bulk and single chain situations to see how the polymer SERS spectrum is affected.

1.5.2 Titania. Titania (TiO$_2$) is a metal oxide being extensively researched for use in photocatalysis\textsuperscript{177} and photoelectrochemistry cells\textsuperscript{178}. Anatase TiO$_2$ has a bandgap around 3.2 eV\textsuperscript{179}, providing it with UV light sensitivity but barely any visible light sensitivity as seen from the absorption spectrum in Figure 1.1\textsuperscript{180}. As such, much of the work with TiO$_2$ has involved trying to provide visible light sensitization through doping\textsuperscript{181-183} or surface modification\textsuperscript{184-186}. For example, Liu\textsuperscript{187} et al. have recently produced a red boron-nitrogen co-doped microsphere with a bandgap that reaches as low as 1.94 eV on the surface, while Gratzel\textsuperscript{188,189} and coworkers have demonstrated multiple different dyes in conjunction with TiO$_2$ capable of making dye-sensitized solar cells. Further work has focused on effectively mapping the preferred charge
transfer pathways\textsuperscript{190-192} of the various crystal types of titania,\textsuperscript{193-196} including a study performed by Lian and coworkers that uses CdSe/CdS quantum dot modified AFM tips to probe the facial heterogeneity of the charge transfer at the surface of a TiO\textsubscript{2} crystal.

![Figure 1.01](image.png)

**Figure 1.01.** Example UV-vis absorption spectrum of undoped TiO\textsubscript{2} and nitrogen doped TiO\textsubscript{2} with the nitrogen doping showing an increase in the visible absorbance. Figure used with permission from reference 180 and IOP Publishing. It is protected under a CC BY-NC-SA license.

In this dissertation the interactions of silver and TiO\textsubscript{2} are of interest, as TiO\textsubscript{2} with plasmonic nanostructures has become a popular area of research\textsuperscript{197-199}. Thus the silver effects that were found to be present, such as the fluorescence blinking and SERS capabilities, will be studied in order to determine how the presence of TiO\textsubscript{2} will affect the system. This should provide additional insight into the construction of the plasmonic photocatalyst that have already been developed.

**1.6 Dissertation Focus**

This dissertation will thus focus on combining spectroscopy, microscopy and electrochemical techniques in order to study silver. As can be already seen, Chapter 1 covered a brief introduction to the topic, along with an idea of the importance of the work towards the
greater field. Chapter 2 details the experimental techniques used throughout the research. This includes the instrumentation and details of its use along with any synthesis methods required.

Chapter 3 begins looking at how combining Raman and electrochemical techniques can be used to study plasmonic heterogeneities in silver. This is a critical chapter in establishing the understanding of how the techniques from chapter 2 are actually applied and how the subject is advanced. It will include discussions of the difficulties faced in properly determining effects, and the conclusions drawn from the probing of silver, including the stochastic blinking behavior observed. Chapter 4 extends the work to a practical application by utilizing the silver SERS properties to look at single molecule and bulk SERS behavior of P3HT. Importantly, the affect that the addition of the polymer has on the silver behavior will be noted. Chapter 5 explains the interaction of silver and titania through spectroscopic and electrochemical methods. It will focus on how plasmons silver structures in both direct and indirect contact for a metal-metal oxide system, and the important conclusions that can be drawn from this information. Chapter 6 provides the conclusions of the dissertation and how to further extend the work. It will detail a few systems that could be further studied and developed to improve both the fields of sensors and photovoltaic devices through the knowledge gleaned about silver.
CHAPTER 2
EXPERIMENTAL

This chapter will outline all the experimental procedures used in the dissertation. The chapter will begin by outlining all the materials preparation procedures including the slide preparation, silver synthesis and TiO$_2$ synthesis. Next optical techniques will be discussed including confocal microscopy, fluorescence and absorption spectroscopy with an emphasis on Raman spectroscopy techniques. Electrochemistry techniques are then looked at with specific discussion of cyclic voltammetry and wavelength response. Electron microscopy techniques used in the materials analysis will then be discussed, focusing mainly on scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Finally x-ray techniques, including X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), will finish the experimental section.

2.1 Materials Preparation

2.1.1 Slide Cleaning Procedure. Bare or ITO coated glass cover slips were placed in a staining jar with 0.45 M KOH in either ethanol or isopropanol and sonicated for 10 minutes. The solution was then removed and deionized water was added before sonicating for an additional 10 minutes. This process was then repeated with both isopropanol and deionized water separately. The slides were then blown dry by nitrogen before undergoing UV-ozone treatment on both sides for 10 minutes. The slides were then stored in a clean slide box until use.

2.1.2 Silver Nanowire Synthesis. Nanowires were either synthesized or purchased from Seashell Technologies, with the purchased wires having a mean diameter of 89 nm and a mean length of
7.5 μm. Two primary synthesis methods were used to produce the silver nanowires: the polyol reduction method and the alumina template method. While stirring, 5 ml of ethylene glycol was heated to 160°C in disposable glass vials in an oil bath before 40 μL of a 4 mM CuCl$_2$·H$_2$O/ethylene glycol solution was added. The solution was allowed to heat for 15 min. Then 1.5 mL of 114 mM (monomer concentration) polyvinylpyrrolidone (PVP) in ethylene glycol and 1.5 mL of 94 mM AgNO$_3$ in ethylene glycol were added to the solution. After 10 minutes, the stirring was stopped and the reaction was allowed to continue for about 1 hour, at which point the solution became gray and wispy. The product was collected by centrifugation, rinsed with acetone and water, and stored in 2-propanol. The anodized aluminum oxide (AAO) template method, 1 cm diameter AAO templates with 100 nm pores were purchased from Whatman. Graphene oxide was coated onto one side of the template through vacuum infiltration, which provided a conductive substrate on one side of the template to allow for electrodeposition. The graphene oxide was synthesized from purified natural graphite (SP-1, Bay Carbon) using the Hummers$^{200,201}$ method in conjunction with hydrazine reduction. The silver wires were electrodeposited into the pores by using a CHI 760C biopotentiostat (CHI, Austin, TX) with a platinum counter electrode and a silver quasi-reference electrode with a 10 mM Ag$_2$SO$_4$ in 0.1 M Na$_2$SO$_4$ solution. For 5 minutes a 0.5 mA constant cathodic current applied while stirring. The template was then cleaned by ultrasonication in a DI water bath for 15 minutes to remove excess silver particles. The template was then dissolved by shaking for 5 minutes in a 3 M NaOH solution. The silver wires were collected by centrifugation and washed with DI water before being stored in 2-propanol.

2.1.3 Silver Colloid Synthesis. Silver colloids were synthesized$^{202}$ by adding 9 mg of AgNO$_3$ to 50 mL of DI water in a three neck flask. The solution was brought to a boil and then 10 mL of
1% weight sodium citrate dehydrate in water was added. The solution was then allowed to boil for an additional 30 minutes while stirring. A color change from yellow to gray was observed. After cooling, aggregation was induced by the addition of 10 μL of 10 mM NaCl and the solution was stored in DI water.

2.1.4 Silver Mirror Reaction. In order to make fully coated slides for SM-SERS experiments, the Tollens\textsuperscript{203} silver mirror reaction was used to coat glass slides. A 15 M NaOH solution was added to 150 mL of 0.1 AgNO\textsubscript{3} until all the brown precipitate was dissolved. Then 75 mL of 0.8 M KOH was added to the solution, with formation of a precipitate. 15 M NaOH was added drop wise to dissolve the precipitate. Addition of 0.5 mL of the AgNO\textsubscript{3} solution with 0.5 mL of 0.5 M dextrose in water initiates the reaction. This solution is stirred and drop-coated onto the glass slide.

2.1.5 Gold Deposition. Gold modification was performed on the silver by an electroless deposition method. For the silver nanowires, 100 μL of the Ag NW solution was added to 3.0 mL of DI water in order to dilute the wire concentration. Then 50 μL of 1.0 M PVP in water was added to the solution while stirring. After 5 minutes, 100 μL of 20 mM FeCl\textsubscript{3} in DI water was added drop wise to the solution. Stirring was continued for an additional hour followed by addition of 50 μL of 0.1 M AuCl\textsubscript{3} to the reaction. Gold deposition on the Ag NWs was confirmed by a color change in the solution. The wires were coated by centrifugation and rinsed by DI water. The Ag NWs were dispersed in 2-propanol until used.

2.2 Single Crystal TiO\textsubscript{2} Synthesis.

2.2.1 Synthesis. Synthesis of the single crystal TiO\textsubscript{2} begins by adding 64 mg of titanium (IV) oxysulfate hydrate to 40 mL of 120 mM hydrofluoric acid in a Teflon lined acid digestion vessel. The vessel is placed in the oven at 180° C overnight. After allowing the vessel to cool, the
solution is centrifuged in an Ultra-8V (LW Scientific) centrifuge at ~3300 rpm. The supernatant is disposed of in the unwanted chemicals containers, and the precipitate is collected and dispersed in water. The resultant solution is centrifuged in an accuSpin 400 (Fisher Scientific) centrifuge at 10000 rpm for 10 minutes. The precipitate is then collected and dispersed in water again, before repeating the centrifugation. The resultant precipitate is then collected and dispersed in isopropanol and the centrifugation is repeated. This should result in any leftover hydrofluoric acid being completely removed from the crystals. Finally the precipitate is collected and dispersed in deionized water and the crystals are allowed to gravimetrically separate. This should result in better overall size dispersion control of the single crystals. The precipitate is collected and dispersed in water and vacuum filtered through a size 0 filter paper (Whatman). It was rinsed multiple times with deionized water, and then allowed to dry.

2.2.2 Annealing. The annealing process was initiated in order to remove the fluorine present on the surface of the TiO$_2$ crystals, and to possibly introduce a dopant into the TiO$_2$ crystal structure. Single crystal TiO$_2$ and P25 TiO$_2$ were placed in a quartz boat with a quartz cover slip over top and placed in a tube furnace (Thermolyne, Thermo Fisher). For annealing under oxygen, the tube furnace was left open to air and heated to 500°C for 1 hour at a 15°C/min ramp rate. For annealing under ammonia, the tube furnace was purged by alternating vacuum and nitrogen atmosphere three times before being left under a nitrogen atmosphere. An ammonia mixture (67% ammonia, 33% argon) was flowed through the tube furnace at 4 psi while being ramped at 15°C/min until reaching and being held at 500°C for 1 hour. The sample is allowed to cool to less than 100°C before stopping the ammonia flow. Carbon doping was performed by purging the furnace by alternating vacuum and nitrogen atmosphere before leaving under a nitrogen atmosphere. The sample was heated at a ramp rate of 50°C/min up to 1000°C and held
for 1 hour. At 700°C the methane mixture (33% methane, 67% argon) at a pressure of 4 psi was flowed through the furnace. The furnace was allowed to cool to 350°C before the methane flow was stopped and a nitrogen flow begun. A multi-part annealing procedure was also performed, with first the annealing under air occurring and then annealing under ammonia occurring, with final temperatures varying between 500°C and 700°C.

2.2.3 Silver Growth. Direct deposition of silver on the TiO₂ surface was accomplished using photoreduction of Ag⁺. Briefly, 1 mg of TiO₂ was dispersed in a 2 mL solution of 0.1 mM AgNO₃ in 1 to 1 volume water/methanol. The methanol will act as a sacrificial hole scavenger to increase the rate of the reaction on the TiO₂ surface. While stirring, the solution is illuminated by either UV (254 nm) or visible (>400 nm) light for 10 minutes. The solution is then centrifuged, vacuum filtered (Whatman size 0), and rinsed with DI water. The collected precipitate is then allowed to dry and stored in a glass vial.

2.2.4 Linker Attachment. Two primary linker attachments were performed using 4-mercaptobenzoic acid (MBZA) and para-benzene dithiol (BDT) to link single crystal TiO₂ and silver nanoparticles. For the MBZA the linker orientation was varied. The first of these has the sulfur attached to the TiO₂ and the carboxyl attached to the Ag. This is accomplished by adding 10 mg of the TiO₂ and 10 mg of MBZA to 4 mL of ethanol and stirring for 2 hours. The sample is then centrifuged, dispersed in DI water and centrifuged again for 10 minutes at 10,000 rpm. The precipitate is then added to a solution of 1 mL of ethanol and 1 mL of Ag colloid solution. The sample was stirred for 2 hours and then centrifuged. The precipitate was collected, dispersed in DI water and centrifuged again. The precipitate was stored in a glass vial after being allowed to air dry. In order to attach the sulfur to the silver and the carboxyl group to the TiO₂, 1 mL of Ag colloid solution was added to 10 mg of MBZA and 4 mL of ethanol. The solution was stirred
for 2 hours before the precipitate was collected through centrifugation. The precipitate was dispersed in DI water and centrifuged again at 10,000 rpm for 10 minutes. The precipitate and 10 mg of TiO$_2$ were then added to 2 mL of ethanol and stirred for 2 hours. The sample was then centrifuged; the precipitate was collected and dispersed in DI water before being centrifuged again. The precipitate was allowed to dry in air and stored in a glass vial until use.

2.3 Optical Techniques

2.3.1 Photoluminescence Imaging and Spectrum Collection. An Olympus IX-71 Inverted Microscope with a Nano-View 200-2/M nanopositioner (Mad City Laboratories, Madison, WI) mounted on top was used for scanning samples. One of three lasers, a 488 nm self-contained argon-ion laser (Edmund Optics Inc.), a diode pumped 532 nm laser (CrystaLaser) or a 633 nm He-Ne laser (Thorlabs, Inc.), was used for excitation in conjunction with a x100 numerical aperture oil-immersion objective (NA = 1.3). Appropriate Rugate Notch filters (Edmund Optics Inc.), dichroic filters (Edmund Optics Inc.), and long pass filters (Chroma Technology, Brattleboro, VT) were used in line to insure a mono-wavelength laser and to remove scattering. Avalanche photodiodes (APD, SPEM-AQRH-15, Perkin-Elmer) were used to collect the photoluminescence signal. A 50 nm pinhole was placed in the laser line before the microscope with the APD aperture acting as the secondary pinhole to complete the confocal geometry. A PC 6602 card (National Instruments Inc.) was used in conjunction with Labview 8.5 (National Instruments Inc) for data collection and control of the APD and nanopositioner. An example schematic is shown in Figure 2.01. Fluorescence and Raman spectra were collected by placing a beam splitter in line with the excident light, allowing a portion to travel to the APD with the rest directed into a monochromator (Acton SP-2558, Princeton Instruments, Trenton, NJ) and collected at a liquid nitrogen cooled charge coupled device (CCD) (Acton Spec-10:100B,
Princeton Instruments, Trenton, NJ). Samples were prepared by drop coating or spin coating onto ITO coated, bare or indexed cover glass (No. 1 22 mm², Corning).

2.3.2 Surface-Enhanced Raman Spectroscopy. Samples were prepared by first cleaning glass or ITO slides. Then one of three methods is used to prepare the SERS substrate: In the first of these, the Tollens silver mirror reaction is performed on the glass slide. The slide is then either drop coated or spin coated with the analyte of interest. For single molecule samples the concentration of the analyte solution is ≤10 nM. The second method makes use of colloidal silver nanoparticles, which are synthesized using the methods described above. Prior to adding the NaCl to cause agglomeration the analyte solution with a concentration of ≤10 nM for single molecule is added to the colloid solution. The resulting agglomerated colloidal solution is then

**Figure 2.01.** Schematic of the scanning confocal instrument. The laser is interchangeable. A secondary APD and band pass filters can be inserted to do separate imaging by wavelength.
either drop coated or spin coated directly onto the slide. The third method uses the nanowires or colloids synthesized as above. The nanostructures are drop coated or spin coated onto the slides. After drying the nanostructure, coated slides are then drop coated with ≤10 nM analyte solution for single molecule samples. SERS measurements were performed using the confocal microscopy imaging system discussed above. Initially areas containing SERS capable structures are identified by bright field microscopy. Samples were then further identified using the laser excitation and confocal imaging. The areas of highest intensity are focused on and the intensity trajectory and Raman spectrum are recorded.

2.3.3 Absorption Spectroscopy. Absorption spectroscopy is carried out using a SpectraVis-plus UV-Vis spectrometer (Vernier) with a 1 cm quartz cuvette.

2.4 Electrochemistry Techniques

2.4.1 Cyclic Voltammetry. For cyclic voltammetry (CV) experiments a CHI-760C was used to vary the bias. The working electrode is dependent upon the system, but is usually ITO, with a platinum counter electrode and either a Ag/AgCl reference or Ag quasi-reference electrode with a 0.1 mM NaOH electrolyte solution. In order to employ cyclic voltammetry in conjunction with optical spectroscopy, a home-built electrochemical cell was employed. The Teflon cell with a bottom portion made to accommodate the ITO coated glass slides was mounted atop the microscope using edge clips.

2.4.2 Wavelength Response: Samples were prepared by mixing 1 mg of TiO$_2$ with 1 mg of gelatin (Korr) in 10 mL of DI H$_2$O. The resulting solution was thinly drop-coated onto a cleaned ITO slide and allowed to dry. Other samples were prepared by mixing 1 mg of TiO$_2$ with 1 mg of Nafion and drop coating onto an ITO slide. The slide was then heated at 100°C for 60 minutes. Samples for the wavelength response were placed in a home built glass electrochemical cell with
0.1 M NaOH and a Pt counter electrode. A Mercury-Xenon Lamp (Newport) was used as the illumination source with a Spectrometer (Thorlabs, Inc.) used to scan the wavelength. A Keithley 2400 sourcemeter is connected to the sample and data is collected in conjunction with the Labview 8.5 (National Instruments Inc) program.

**Electron Microscopy Techniques**

2.5.1 *Scanning Electron Microscopy.* SEM images were taken using the JEOL 7000 FE SEM located at the Central Analytical Facility (CAF) at the University of Alabama. Samples were prepared by drop coating directly onto cleaned silicon, ITO coated glass, or indexed cover glass. For the non-conductive substrates, the sample was coated with gold by sputtering prior to imaging.

2.5.2 *Transmission Electron Microscopy.* TEM images were acquired using an FEI Tecnai F-20 transmission electron microscope equipped with a CCD camera for scanning transmission electron microscopy (STEM), high angular annular dark field (HAADF) detector and EDAX® energy-dispersive X-ray spectroscopy (EDX) located at the CAF at the University of Alabama. Samples were prepared by drop coating directly onto a holey carbon backed 200 mesh copper TEM grid (Electron Microscopy Sciences), which could be either indexed or not.

**X-Ray Techniques**

2.6.1 *X-ray Diffraction.* XRD data was collected with help from Jue Wang using the Bruker D8 located at the CAF at the University of Alabama. All samples were in powder form atop a glass slide during sampling.

2.6.2 *X-ray Photoelectron Spectroscopy.* XPS data was collected with help from Rob Holler using the Kratos Ais 165 XPS/Auger system located at the CAF at the University of Alabama. All samples were in powder form and held in place by scotch tape.
CHAPTER 3
SILVER NANOWIRES

Chapter 3 will focus on elucidating the photo-interactions of silver. While many similar studies have previously been conducted\textsuperscript{204-207}, this chapter will focus particularly on silver nanowires. Silver nanowires were chosen because of several beneficial aspects. First, silver nanowires have a nanoscale diameter. This allows for plasmon interactions\textsuperscript{208-211} with visible light that lead to SERS interactions such as those discussed in chapter 1. Second, the wires can have aspect ratios that allow for lengths on the micron scale. The longer lengths allow for easier imaging of the wires when utilizing an optical microscope, as the wire is longer than the diffraction limit of the light. Third, silver nanowires have been fabricated in optically transparent meshes\textsuperscript{212-214} that could be used in photocatalysis and photoelectrochemical cells. Despite this, nanowires have received less study than nanoparticles. Elucidating the similarities or differences in these structures is critical for understanding the effects when eventually applied to these systems.

Initial discussion will focus on silver’s inherent fluorescence\textsuperscript{215-217} and photoluminescence\textsuperscript{218-220} capabilities. The study will focus on how to identify and control the fluorescence and its stochastic blinking through geometric, optical, and electrochemical means. Next, the link between the areas of highest fluorescence intensity or “hot spots” and the highest intensity Raman signal will be investigated. Similar techniques to the fluorescence intensity control will be investigated for the Raman hot spots.
3.1 Silver Fluorescence and Control

3.1.1 Silver Fluorescence. Using the purchased silver nanowires from Seashell Laboratories, initial work focused on the imaging capabilities of the instrument. Figure 3.01 shows a confocal microscopy image of the silver nanowires. It can be noted in the image that the diameter of the nanowires appears greater than the SEM confirmed nanowire diameter (Figure 3.02).

Figure 3.01. SEM (A) and scanning optical microscopy (B) images of the purchased silver nanowires show that the wires can be easily imaged with their micron lengths allowing for easy identification.

Figure 3.02. The scanning confocal image of silver nanowires (A) shows variance of the intensity from along the length of the wires and where wires cross. Taking a photoluminescence spectrum (B) at the marked portion of the nanowire reveals a broad fluorescence background. All excitation was at 488 nm. The diameter of the nanowires appears greater than the SEM confirmed nanowire diameter (Figure
This apparent increase in nanowire size is due to the diffraction limit of light, which is roughly estimated at $\frac{1}{2}$ the wavelength of the light. With the excitation laser used being 488 nm in these images that places the diffraction limit at roughly 250 nm. It can also be seen that the photoluminescence is not uniform across the length of the wire. The areas of highest intensity serve as photoluminescence “hot spots”. Just from the shown image, it initially appeared that hot spots could be generated from geometry control of the silver nanowires, as the intensity near the point of crossing appears to vary. Further images (not pictured) support this conclusion as hot spots are regularly generated at wire junctions. Probing the photoluminescence spectrum of the wires (Figure 3.02) shows a broad fluorescence is generated at the wire hot spots with a peak of around 525 nm.

**Figure 3.03.** The intensity trace of a single hot spot (A) shows large increases in the intensity upon increased excitation power. The time resolved photoluminescence spectrum (B) shows large fluctuations in the fluorescence peak. All excitation was conducted at 488 nm.
The overall fluorescence intensity response (Figure 3.03 A) shows two interesting characteristics. First, the background fluorescence intensity is dependent upon the excitation laser intensity. Second, large intensity bursts are overlaid on the background fluorescence. This fluorescence “blinking” behavior occurs in a stochastic manner. The blinking also shows excitation intensity dependence, with higher intensity and faster blinking occurring with greater excitation intensity. Time-resolved fluorescence spectra (Figure 3.03 B) were collected every 1 s and show the same stochastic blinking behavior. In the spectrum it can be noted that the blinking behavior intensity is primarily due to fluctuations in the highest intensity fluorescence peak and not intensity fluctuations in the background. Importantly these fluctuations appear to be very long in time, being observable at the relatively long time of 1 s. This indicates that the physical process that causes the on/off of the blinking occurs on a longer timescale than typical charge transfer processes and is likely a large scale inter-conversion of the sample.

Dickson and coworkers have noted many examples of this phenomenon on various silver samples\textsuperscript{150,158-161}. The fluorescence is attributed to small silver clusters of less than 100 atoms, which can be formed through high intensity photo-excitation of silver oxide. These clusters behave similarly to small fluorescent molecules. The blinking effects are attributed to inter-conversion between the small Ag\textsuperscript{o} clusters and Ag\textsubscript{2}O when under both an oxygen atmosphere and photo-excitation as shown in Equation 3.01.

\[
\begin{align*}
\text{PL On} & : 2\text{Ag} + 2\text{OH}^- \rightarrow \text{H}_2\text{O} + \text{Ag}_2\text{O} + 2\text{e}^- \\
\text{PL Off} & : \text{hv} + \text{O}_2 \\
\end{align*}
\]

\text{Eq. 3.01}
To better understand the stochastic blinking effect the temporal auto-correlation function was used. In order to do this the photoluminescence intensity trace is expanded and a threshold is used to determine the On and Off states of the photoluminescence as seen in Figure 3.04 A. This allows for a full count of the occurrence of the blinking, with Figure 3.04 B showing the results. As can be noted, the majority of the occurrences are at the lowest intensity, with a significant drop off of total occurrences as the intensity increases. From this, the auto-correlation function

Figure 3.04. The intensity trajectory (A) was taken at 50 mW excitation power with the blue line indicating the threshold for ON/OFF counting statistics. The occurrence histogram (B) shows burst frequency information. The temporal auto-correlation function (C) shows exponential decay behavior.
can be calculated to find the fluorescence blinking memorization of the initial state. The temporal autocorrelation function, \( G(\Delta t) \), can be expressed as:

\[
G(\Delta t) = \frac{\sum_{i=0}^{M-m} I(i\tau)I(i\tau + m\tau)}{\langle I \rangle^2 (M - m)}
\]

where \( \Delta t = m\tau \) (where \( 0 \leq m \leq M \)), \( \tau \) is a time interval, \( m \) is an integer multiple of \( \tau \), \( I(t) \) is the time-resolved fluorescence intensity with \( M+1 \) data points ranging from \( t = 0 \) to \( t = M \), and \( \langle I \rangle \) is the mean PL intensity. As seen in Figure 3.04 C, the autocorrelation indicates a fast exponential decay, lacking the periodicity representative of a correlated state. The autocorrelation was extended to multiple wires and helped confirm that different wires show significantly different behavior, as seen in table 3.1. The average decay time constant was 0.81 s, but the individual wires decay time constants varied from 2.19 s to 80 ms, further confirming the spontaneous loss of the initial state due to the Ag\(^0\) to Ag\(_2\)O to Ag\(^0\) inter-conversion discussed earlier. The alteration of the structure causes the loss of the memory of initial states.

**Table 3.01.** Table of the temporal auto-correlation and threshold variables for 6 wires

<table>
<thead>
<tr>
<th>wire #</th>
<th>( \tau_{\text{Ag}} ) (s)</th>
<th>( m_{\text{on}} )</th>
<th>( m_{\text{off}} )</th>
<th>( \langle I \rangle ) (cps)</th>
<th>( I_{\text{threshold}} )</th>
<th>( I_{\text{max}} )</th>
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<td>3150</td>
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<td>1.60</td>
<td>2937</td>
<td>3070</td>
<td>9280</td>
</tr>
<tr>
<td>5</td>
<td>0.27</td>
<td>2.70</td>
<td>1.57</td>
<td>182</td>
<td>250</td>
<td>1616</td>
</tr>
<tr>
<td>6</td>
<td>0.53</td>
<td>2.40</td>
<td>2.08</td>
<td>1201</td>
<td>1245</td>
<td>8178</td>
</tr>
<tr>
<td>avg</td>
<td>0.81 (0.78)</td>
<td>2.44 (0.20)</td>
<td>1.87 (0.23)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In order to further confirm the autocorrelation results, the On/Off occurrences were measured and studied. Importantly, the distributions lack Poisson behavior, indicating that the behavior is not due to shot noise. Noticeably, as seen in figures 3.05 A and B, the occurrences of
Figure 3.05. The occurrence histogram by time for the On (A) and Off (B) and their corresponding autocorrelation plots (C and D).
both the On and Off states are highest at the shortest times. However, while the On states show more overall occurrences, at longer times the Off states begin to dominate. On states completely disappeared by 50 ms, while Off states appeared at up to a few seconds. This is further confirmed by the probability density plots (Figures 3.05 C and D) that were fit to a power law distribution. A greater slope appears for the On states as confirmed by the power constants, m, in Table 3.1. A broad distribution of values, with the On power exponent spanning 2.2 to 2.7, while the Off power exponent spans 1.6 to 2.2, further confirming the disordered nature of the photoluminescence blinking behavior.

3.1.2 Fluorescence Control. Believing that the cause of the fluorescence blinking behavior was the interactions of oxygen with silver clusters, it was decided to remove oxygen from the system. Thus the silver nanowires were coated with poly(methyl methacrylate) (PMMA) after being coated onto the glass slide. Multiple hot spots appeared on both a regular silver nanowire and a coated silver nanowire as seen in Figures 3.06 A and C. In both images, the hot spots vary greatly in intensity, as confirmed by the intensity trajectories shown in Figure 3.06 B and D. However, while the non-coated wires show the blinking effect, the coated wires lack the blinking behavior. Additional experiments were carried out under a nitrogen atmosphere and showed similar results. This further confirms the silver cluster interactions with oxygen, with its removal eliminating the blinking behavior.

With the ability to control the silver fluorescence blinking behavior by removing oxygen, other control methods were desired. Being aware of the inherent link between the oxidation and reduction of the silver clusters and its blinking behavior, it was decided to try electrochemical methods. Thus, using the photoelectrochemical set-up described in chapter 2, cyclic voltammetry (CV) was performed on the sample while measuring the photoluminescence. The voltage was
Figure 3.06. Scanning confocal images of bare silver nanowires (A) and PMMA coated silver nanowires (C) with accompanying intensity traces of the indicated spots (B and D, respectively) are shown under 50 mW 532 nm excitation.
swept from -0.15 to 0.45 V (vs Ag/AgCl) starting at 0.15 V. The resulting CV and intensity trace can be seen in Figure 3.07. The CV shows the silver oxidation reaction at around 0.28 V and the reduction occurring around 0.05 V. Importantly, if upon oxidation the silver reacts with ambient oxygen to form Ag₂O then the process becomes electrochemically irreversible. Thus both the reduction and oxidation responses become lessened as the system is cycled. The photoluminescence shows a large decrease after the first oxidation that is not recovered and is not shown in the photoluminescence traces in Figure 3.07. However, as can be seen from the second (blue) and third (red) photoluminescence traces, a distinct decrease in the photoluminescence occurs at the silver oxidation peak. A slight increase in the intensity occurs
immediately after the reduction peak and continues as the voltage is swept back to the negative. While the Ag₂O reduction back to Ag⁰ is electrochemically disallowed, it can be performed using photodecomposition, which occurs under the laser illumination. As the voltage is swept to the positive again the photoluminescence decreases at the silver oxidation peak. However, when swept back to the negative, the photoluminescence does not recover this time.

![Figure 3.08](image.png)

**Figure 3.08.** The applied square wave potential (A) is modulated between 0.45 V and 0.00 V while the photoluminescence is collected using the standard photoelectrochemical set-up. Photoluminescence intensity traces (B) of fresh and oxidized wire that have been self normalized show that the oxidized wire can regain photoluminescence intensity under light illumination.

A square wave potential experiment was performed in addition to confirm the oxidation causes the decrease in the photoluminescence. Figure 3.08 A shows the results of the experiment. The very sharp decrease in the photoluminescence can be seen while the first positive potential is applied. A slight recovery occurs when the potential is switched to zero, showing the photodecomposition occurring. Switching the potential back to the positive causes a photoluminescence decrease to occur; sweeping back to zero once again shows only a small increase in the photoluminescence. After this the photoluminescence plateaus, with little difference seen in the overall intensity. To ensure that the observed decrease in intensity isn’t due to fluorescence bleaching and that the recovery is repeatable, a fresh Ag nanowire and an
oxidized Ag nanowire are illuminated for an extended time. The fresh nanowire shows a slight increase in the overall intensity, likely due to surface Ag$_2$O being decomposed to Ag$^0$. The oxidized Ag wire however shows a large increase in the intensity; though a full recovery back to the original intensity does not occur. This confirms that the small silver clusters are actually undergoing physical changes to and from Ag$_2$O and that besides controlling the presence of oxygen, electrochemical methods can be used to control the fluorescence.

Figure 3.09. SEM images of silver nanowires produced using the polyol reduction method (A) and the AAO template method (B) with the accompanying photoluminescence spectrum, which shows the first set of Raman peaks from the PVP surfactant.
The next major step was to investigate if the fluorescence blinking only occurred on the purchased silver nanowires or if it extended to other structures, as seen by Dickson and coworkers. As such two other nanowires were investigated, wires synthesized through the polyol reduction method\textsuperscript{221,222} and wires synthesized through the anodized aluminum oxide (AAO) template method\textsuperscript{222,223}. These wires have significantly different lengths and diameters with the AAO template showing shorter wires in general, as seen in Figure 3.09 A and B. The photoluminescence spectrum (Figure 3.09 C) of each wire, collected using 532 nm excitation, still shows a broad fluorescence background. However, the silver wires produced through the polyol reduction method show two intense peaks overlaid atop the fluorescence background; these peaks result from the Raman signal from the PVP surfactant, and were the first SERS peaks observed in this study. The two wires were easily imaged (Figure 3.10 A and B) and show hot spot like those seen in the purchased wires. The intensity traces of the wires (Figure 3.10 C) show the same blinking behavior indicating that the small silver clusters are present regardless of

![Figure 3.10. Scanning confocal microscopy images of the polyol (A) and AAO (B) produced silver nanowires can still be collected. The resulting intensity traces (C) show similar stochastic blinking behavior to the purchased silver nanowires.](image)
the wire type. While formal studies weren’t conducted detailing the blinking effects on silver nanoparticles or silver coated slides, visual observation confirms that blinking does occur on these samples.

3.2 Silver SERS Capabilities

3.2.1 Raman Signal Enhancement. With the fluorescence hot spots and the methods to control them investigated, the Raman capabilities needed to be studied. As already stated, the surfactant Raman signal was visible on the wires produced through the polyol reduction method. Since the purchased wires were known to have surfactant, it was believed that improving the grating resolution would allow for observation of the signal. As can be seen in Figure 3.11 A, the overall SERS signal can be seen superimposed atop the fluorescence signal. When taking the time resolved spectra with 1 s spectra collection, as seen in Figure 3.11 B fluctuations in the signal intensity do occur. However, the increases in intensity appear to be due to background signal fluctuations instead of Raman signal fluctuations. Thus the blinking effect appears to be

Figure 3.11. The Raman spectrum (A) of the purchased silver nanowires show the Raman peaks overlayed atop a broad fluorescence background. The time resolved Raman spectrum (B) indicate that the fluctuations in the Raman intensity are due to background fluorescence fluctuations.
dependent only on the fluorescence from the silver clusters. However, it is difficult at this point to separate the Raman signal from the fluorescence, so further studies were required.

![Figure 3.12](image)

**Figure 3.12.** Bright field images of the same set of silver nanowires in water (A) and in a 1.0 mM MPY solution (B) with line graphs of the intensity overlaid at the bottom of the image indicate that the MPY solution has higher overall intensity at the nanowires. The intensity traces of the circled nanowires (C) show greater intensity fluctuations for the wire in water. The statistical analysis of the two images

Due to the difficulty in separating the Raman signal from the fluorescence signal, several methods were employed to deconvolute the signals. The simplest method employed was to increase the amount of Raman analyte molecule. The surfactant used for the silver synthesis does not completely coat the silver nanowire. Thus, in order to increase the Raman signal by
increasing the total coverage, mercaptopyridine (MPY) was introduced into the system. The MPY replaces the PVP in the system and is capable of completely coating the wires. This is somewhat supported by the total SERS signal shown in the bright field images in Figure 3.12, with mean counts for the PVP coated system around 611 ± 10 while the MPY coated wires have a mean intensity of 1152 ± 584. While these numbers do not significantly differ, the wire signal in comparison to the background is significantly higher. Further the MPY coated wires have a higher overall intensity when summed across the whole wire. This is further supported by the line intensity trace across both images, which shows that the MPY coated wires have higher intensities relative to the background than the PVP coated wires. The intensity traces of the individual wires as seen in Figure 3.12 C show that the fluorescence blinking is the main contributing factor to the overall intensity, whereas the MPY coated wires have much smaller fluctuations. The reduction in intensity fluctuations is caused by the increase of the Raman analyte resulting in the Raman signal dominating the system. This is further confirmed by the statistical analysis of the samples seen in Figure 3.12 D, which shows the MPY coated wires having both a higher frequency of counts and a lesser slope; once again confirming the increase in Raman intensity due to the greater number of analyte particles being present. Slow fluctuations in the overall intensity do occur in the MPY solution, but these are primarily due to silver nanowire diffusion due to the lack of covalent attachment. Increases in the laser excitation intensity resulted in higher Raman signals for the MPY while the greater excitation resulted in fluorescence intensity increases and more fluorescence blinking in the PVP coated wires.

While the addition of analyte does improve the signal, other methods would be preferred as the analyte concentration can’t always be increased. Thus it was decided to probe how the geometry could control the number of Raman hot spots in the system. As such four different sets
of wires were imaged and probed: a single wire, a crossed set, a bundle of wires, and a wire conglomerate. By adding MPY to each of the systems and collecting the Raman spectrum the differences in the intensity of the Raman peaks can be attributed to the number of hot spots. As seen in Figure 3.13 the Raman spectrum for the case of the single silver nanowire provides baseline normalization. The crossed wires showed a small increase in the overall Raman intensity. This is likely due to an increase in the hot spots generated at the wire crossing site. Wire bundles also show a slight increase in the intensity, but not as intense as the crossed wires. The intensity difference points to the parallel bundles generating less intense hot spots than those

**Figure 3.13.** Bright field images of a single (A), crossed pair (B), bundle (C) and conglomerate (D) of nanowires in a MPY solution with their accompanying Raman spectra. The laser spot is visible as a high intensity area on the wire in the bright field images.
seen in the crossed wires. This could be due to the use of circularly polarized excitation, but could also be caused by distinct differences in the distance and layout of the generated hot spots. The largest enhancement is seen in the silver nanowire conglomerate, which should have the highest number of generated hot spots, due to the large number of wire crossing sites. Thus it confirms that the overall Raman signal is directly linked to the number of Raman hot spots present in the focus.

![Figure 3.14](image.png)

**Figure 3.14.** The bright field image of none (A), a few (B), and a conglomerate (C) of polyol method nanowires without purification and the accompanying Raman spectrum. The Raman peaks of MPY receive the greatest enhancement in the conglomerate case.

3.2.2 *Raman Spectra of Nanostructure Decorated Silver Nanowires.* A secondary method using unpurified silver nanowires and gold decorated silver nanowires was employed to confirm that the increase in hot spots sites increases the overall Raman signal. In both cases these wires should have a greater number of hot spots generated by nanoscale silver or gold near the larger
Figure 3.15. (A) The Raman spectrum of adenine at a single (1), parallel (2), crossed (3), and end to end (4) set of nanowires indicate that pairs of wires have higher Raman intensity. (B) The Raman spectrum of cytosine at a crossed set (1) and single nanowire (2) confirm the trend. (C) The Raman spectrum of guanine at three different sites on a pair of crossed nanowires shows that the Raman intensity is site specific. (D) The time-resolved Raman spectra of thymine at the same hot spot at 30 (1), 60 (2), 90 (3), and 120 s (4) show that the hot spots are undergoing alterations in the intensity due to diffusion in the system.
wire surface. It must be noted that for the gold decorated silver nanowires, that the change of material to gold may be the cause of any signal enhancement. These sites should generate high intensity SERS hot spots, which can be confirmed by introducing a Raman analyte. In the case of the unpurified nanowires, MPY was introduced into the system. Looking at sites without nanowires shows a broad background signal with no Raman peaks present, as seen in Figure 3.14. Changing the focus to crossed wires shows a significant increase in the Raman signal and an overall reduction in the fluorescence background, with the agglomerate structure showing significantly larger overall enhancement. Once again, the increase in hot spots results in larger overall Raman enhancement. Further, the reduction of fluorescence likely occurs from these same Raman hot spots partially quenching the fluorescence and leads to the dominance of the Raman signal. Due to the thiol functional group having covalent interactions with silver, it is possible that the Raman enhancement could simply be a charge transfer based enhancement. To insure that the enhancement is due to the plasmon enhancing the local electromagnetic field, DNA bases were used as the Raman analyte. As can be seen in Figure 3.15, a single wire coated with adenine shows little SERS enhancement, but changing the wire geometry to a parallel set of wires showed significant enhancement. Cytosine shows similar behavior, with a crossed set of nanowires giving a much larger enhancement than the single wire case. Guanine and thymine also show large enhancement in the crossed wire geometry, indicating that the enhancement is not simply due to a charge transfer interaction through a covalent bond but due to the large electromagnetic field enhancement. Making use of the adenine with a gold decorated silver nanowire provided a method to increase the overall number of hot spots without introducing a secondary wire while keeping the electromagnetic effect as the primary method of enhancement. A single purified silver nanowire showed little to no enhancement of the adenine Raman
spectrum, as seen in Figure 3.16. The introduction of gold nanostructures caused a significant enhancement of the overall Raman intensity in the single nanowire case. Looking at a crossed set of gold decorated nanowires shows an even greater enhancement. The overall increase in enhancement is attributed to the combination of more hot spots as well as an increase in the total surface area allowing more interactions with the adenine present in the solution. As stated previously, the enhancement could be primarily to interactions with the gold instead of silver in this instance and cannot be completely discounted with the experiment performed.

Figure 3.16. Bright field images of a bare silver nanowire (A), a gold decorated silver nanowire (B), and a pair of gold decorated silver nanowires (C) with their accompanying Raman spectra in an adenine solution. The TEM image (D) of the gold decorated nanowire shows the high density of gold particles on the silver nanowire.
Figure 3.17. Calculated 3D representations of the electromagnetic field intensity of two 80 nm diameter crossed silver nanowires with varied dipole-dipole distance and nanowire length under different polarization angles of 488 nm excitation.
Figure 3.18. 2D XY summations of the local electromagnetic field of a pair of 80 nm diameter, 1400 nm long crossed nanowires with 488 nm excitation into the plane and the polarization at 0° (A), 45° (C), or 90° (E). The 3D representations of these results with (B), (D), and (F) corresponding to (A), (C), and (E), respectively.
Figure 3.19. The 2D local electromagnetic field intensity summed across the x-axis of two 80 nm diameter, 1400 nm long parallel silver nanowires calculated with 488 nm excitation along the z-axis and a polarization angle of 0° (A), 45° (C), and 90° (E). The corresponding 3D representations for (A), (C), and (E) are provided by (B), (D), and (F) respectively.
3.2.3 Polarization Dependence. With the hot spots playing a key role in the enhancement and hot spots capable of being generated by wire-wire interactions, it was decided that a theoretical study would provide insight into the enhancement effect. Many theoretical studies of the plasmon effects on the local electromagnetic field have been previously performed, with most utilizing finite difference time domain calculations to do studies of waveguides and various nanoparticles. These studies have provided estimates of the local electromagnetic (EM) field enhancements based upon variance in the distance, material and shape of the particles. What has been less utilized is the discrete dipole approximation (DDA) method, which can give superior estimates of the effects on the local EM field at the cost of increased calculation complexity and time. However, some DDA calculations have been performed, such as the study by El-Sayed detailing the differences in the effect on the electromagnetic field dependent upon the distance between the nanoparticles.

With Dr. David Dixon’s and Dr. Mingyang Chen’s support a DDA calculation was performed on two different sets of silver wires: a crossed set and a parallel set. To our knowledge, this was the first DDA calculations performed on silver nanowires. For varied dipole-dipole distances and lengths of the wires, as seen in Figure 3.17, the shape of the plot of the electromagnetic field intensity does not change drastically. Thus using the 80 nm diameter and 1400 nm pair of crossed wires and varying the polarization angle of the incident light from 0° to 45° to 90° in the xy plane, summed plots in the z plane can show the highest intensity electromagnetic enhancements caused on the wires as seen in Figure 3.18. It can be seen from these plots that the highest intensity areas occur at the wire crossing site, indicating the capability of hot spot generation. Similar plots for parallel wires with a 5 nm gap, as seen in Figure 3.19, indicate that the intensity of the electromagnetic field is highly dependent on the orientation of
the polarization angle, with the highest intensities occurring when the polarization is perpendicular to the longitudinal axis of the wires. Referencing back to the crossed wires, polarization dependence of the electromagnetic field is clearly apparent though the exact trend is difficult to understand with the current data set. Thus it could be predicted that the polarization angle could play a very important role in the overall SERS enhancement. Due to experimental difficulties in making a well defined geometry with the Ag nanowires, the theoretical calculations serve more as a qualitative explanation of the experimental results. However, this leads to the acknowledgement that other nanostructures such as spheres interacting with the nanowires should have similar behavior. Thus a preliminary study of an unpurified set of wires with MPY was investigated for polarization dependence. As seen in Figure 3.20 the wires were first imaged by bright field microscopy before using scanning confocal microscopy to identify the areas of highest intensity. A total of 8 spots were selected and the intensity was tracked for each as the image was scanned using different incident polarization angles. Due to an issue with the dichroic mirror not reflecting the same intensity of light at different polarizations, the overall intensity decreased as the incident polarization angle was swept. Each spot shows similar behavior to earlier imaging, with various spots displaying different base intensities. The majority of spots imaged show the same trend of a gradual decrease in the overall intensity. However,
spots 2 and 6 showed an increase in the intensity at certain polarizations. While the exact polarization effects were not capable of being identified in this experiment, it did provide a significant confirmation of the effects occurrence.

3.3 Conclusions

Silver hot spots were identified in silver nanowire systems as expected from the literature. Fluorescence can occur at these sites with blinking behavior as noted previously by Dickson and coworkers. The fluorescence is attributed to small silver clusters with blinking effects occurring due to chemical changes between Ag° and Ag₂O. The work performed shows that these clusters can be controlled through the removal of oxygen from the system, supporting the previous assertions in the literature. Electrochemical methods are shown as an effective way to control this fluorescence and blinking, extending the total means of controlling the system. Existence of these small silver clusters makes identification of low concentrations of Raman analytes difficult in the system, though not insurmountable. By increasing the total number of hot spots, the Raman signal was shown to increase. These hot spots are generated in the same way that the hot spots are created in the fluorescence study, though later work by Willets and coworkers has revealed that the location is slightly different for the Raman and fluorescence enhancement maximums. Finally it is seen through theoretical calculations and confirmed by experimental work that the incident polarization plays a large role in the overall Raman signal enhancement.
CHAPTER 4
SILVER FILM UTILIZATION IN SERS

Chapter 4 will focus on the results of SERS probes performed on a Tollens silver substrate. Previous work\textsuperscript{241-245} has determined that the Tollens silver substrates makes a good SERS substrate with many Raman hot spots, but does not provide a well defined geometry. For this study, the SERS measurements will be collected on the small molecule Rhodamine 6G (R6G) and the polymer dye poly(3-hexylthiophene-2,5-diyl) (P3HT). The R6G serves as a well-studied, idealized probe to confirm the general system SERS capabilities. P3HT, a common dye for dye sensitized solar cell systems, will then be studied to provide utilization of the silver film. The SERS study will probe bulk and single chains of the polymer to note the effects of solvent on the multiple chromophores. Similar studies have been performed in the literature\textsuperscript{246-247}, with Rothberg and coworkers\textsuperscript{175,248,249} performing a thorough study of poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) Fortunately, the previous silver work still provides sufficient methods and insight in how to examine the P3HT through SERS methods.

4.1 Bulk and Single Molecule Measurements

In order to perform SERS experiments, a SERS substrate was generated on a glass slide by using the Tollens silver mirror reaction as described in Chapter 2. The resulting nano-textured SERS slide is uniformly covered with silver and moderately brown in color but still partially transparent. The slides were examined using a scanning electron microscope to discern the silver morphology (Figure 4.01A). The absorbance of the silver (Figure 4.01B) shows the optical density of the SERS substrate is around 1.18 at its plasmon absorption maxima of 445 nm. This
was found to be the optimal silver coverage and resonance condition for the single molecule study. In order to confirm the viability of the Tollens silver mirror reaction substrate for SM-SERS, the background SERS signal of the bare silver substrate was examined first. Many “hot spots” were located on the sample emitting primarily silver fluorescence, but two Raman peaks at around 1258 and 1344 cm\(^{-1}\) were present. These peaks were attributed to nitric acid not being fully removed by the washing step. It should be noted that previous reports in the literature have indicated various contaminants,\(^{250}\) such as atmospheric carbon, being present on single molecule substrates indicating that such contaminants are fairly common. As can be seen in Figure 4.01C,
after coating with R6G a single “hot spot” was chosen using the confocal microscopes scanning capabilities. As noted in chapter 3, while the fluorescence and Raman “hot spot” are not always correlated, high photoluminescence intensity areas are likely sites of SERS enhancement. The Raman spectra of the single molecule R6G is consistent with the SERS spectra of the ensemble. Some Raman peaks disappear from the single molecule spectra because the single molecule Raman is sensitive to the molecular orientation. The ensemble SERS spectra of P3HT and single molecule P3HT coated from THF are compared in Figure 4.01D; similar consistency in the SERS spectra can be observed for ensemble and single polymer chains of P3HT SERS. The C=C symmetric ring stretch of P3HT at 1459 cm\(^{-1}\) is reported in the literature\(^{251}\) as being the most intense band, and appears in all measurements, though slightly blue shifted for SERS spectra. The blue shift is likely due to the partial oxidation state of the polymer chain upon the photoinduced charge transfer at a hotspot and is consistent with previous report.\(^{251}\) The C=C anti-symmetric ring stretch normally located at 1498 cm\(^{-1}\) appears to be absent. This band, which is normally used to help determine the conjugation length of the polymer, is thought to actually still be present but difficult to deconvolute from the broad symmetric ring stretch and background fluorescence. It should be noted that both panel C and D include no fluorescence background from silver substrate as the fluorescence signal was background subtracted from the SERS spectra.

As shown in Figure 4.02 A and B, images of the light scattering of the SERS substrate containing many hot spots were recorded but only a few spots were found to contain single molecule Raman signatures. As noted earlier this is due to inherent silver fluorescence likely due to the small silver clusters discussed in the single wire work. The time evolution of single molecule R6G spectra (Figure 4.02 C) shows a high rate of intensity fluctuation indicative of
single molecule behavior as well as possible movement of the molecule. Differences in the peak intensity can be accounted for through variance in the angle of scattering, molecular orientation changes, and differences in the excited molecular motion. The identifying peaks at 1392 and 1541 cm\(^{-1}\) are present confirming the presence of the R6G.\(^{252-254}\) In comparing the various acquisitions in a single molecule of R6G over 4 minutes (Figure 4.02 C), the intensity of the acquisition is initially moderate for the first acquisition; however, after the first acquisition the intensity increases significantly. This remains relatively stable throughout many acquisitions, decreasing slightly with each subsequent acquisition. However, after 150 s, the intensity decreases significantly, and the intensity further decreases at 210 s and remains low for the
remainder of the collection period. On the other hand, the spectra of single P3HT molecules from chlorobenzene show that the molecule’s Raman signal is much more stable throughout many acquisitions. As seen in Figure 4.02 D, the relative intensity remained increasingly stable throughout the eight 30 s acquisitions. This lack of blinking in the molecule can also be seen in the molecule’s trajectory, which shows a stable slightly downward sloping line. The trajectory does show several intense, short-lived peaks; however, these peaks are likely due to the minute variations of orientation of the molecule or charge transfers occurring in the sample. Unlike in R6G, these events in P3HT do not affect the overall stability of the molecule, and, therefore, P3HT is much more stable than R6G, which is attributed to P3HT being a conjugated polymer. This is not completely unexpected as the polymer can have multiple chromophores capable of either performing scattering or absorption with energy transfer to a single primary chromophore. Thus, even in the single molecule case for a conjugated polymer, the system can be thought of as being more akin to the silver nanowire system with complete coverage of the reporter molecule as opposed to the sparsely covered situation. Additionally, the hydrophobic side chain may help minimize the photo-oxidation of the polymer backbone in air further increasing the stability.

4.2 Solvent Effects

Figure 4.03 A shows the single molecule Raman spectra of P3HT cast from four different solvents onto the SERS active silver substrate. The C=C symmetric ring stretch of P3HT around 1459 cm\(^{-1}\) appears for all solvents while dramatic differences for other Raman peaks exist. The differences in the Raman spectra from solvent to solvent is likely due to conformation differences of the P3HT polymer caused by solvent memory during the coating process. For dichloromethane, the SM-SERS peaks match well with the ensemble confirming the identity of the P3HT. Importantly peaks such as the C-S-C bond at 683 cm\(^{-1}\) and the C-H bond at 1210 cm\(^{-1}\)
are markedly absent in almost all the spectra, a common phenomenon in single molecule Raman studies where particular bands apparent in the ensemble are absent in the single molecule. Other peaks like the C=C bond at 1521 cm\(^{-1}\) are present in the shown spectra but absent in other measured spectra, indicating not only SM behavior but also implying that the orientation along the varied silver surface is not uniform when casting the single molecule. This should further indicate that local variability will occur with variances in the polarization angle of the incident light, with that aspect being further probed below. The peak at ~1498 cm\(^{-1}\) is related to the backbone of the polymer and can be used to indicate the conjugation of the polymer chain. In past cases, lower intensities and sharper peaks in this region have indicated more highly conjugated polymers with less overall flexibility along the backbone. Further the intensity ratio of the 1459 cm\(^{-1}\) over the 1498 cm\(^{-1}\) peak gives an inverse relationship with the conductivity of polythiophene films, and is a value worth noting in the single molecule systems. However, due to the high background fluorescence it is extremely difficult to find the anti-symmetric stretch band, without which the ratio cannot be calculated. The Raman signature of single P3HT...
molecule cast from the other three solvents (chlorobenzene, THF, and toluene) are shown in Figure 4.03 A. It was found that each single molecule run corresponds well with its ensemble measurements, showing some variance much as dichloromethane showed variance. Further, P3HT single molecules from each solvent demonstrate slightly different spectra. Similar studies have been performed on bulk samples of P3HT. Peaks appear in some of the toluene and thf spectra at ~650 cm\(^{-1}\) that are not present in the other two solvents and that correspond closely with the distorted conformation around the inter-ring single bond also known as a kink in the polymer. This is thought to be due to the presence of chlorine causing solvent memory. In addition, samples coated from dichloromethane do not exhibit a peak at 997 cm\(^{-1}\), which appears in each of the other solvents and is due to the C-C between the ring and alkyl chain. This is believed to be due to solvent memory influencing the side chains folding parameters upon the silver surface causing them to preferentially lay perpendicular with the surface and thus not be enhanced by the silver surface plasmon.

The single molecule trajectories of P3HT were compared with the ones of R6G as shown in Figure 4.03 B. The intensity trajectories of P3HT from all kinds of solvent are fairly stable over the whole time period. As shown in chapter 3 and noted earlier this would normally indicate several molecules being present with blinking behavior indicating a single molecule. However, previous studies done by SERS with polymers have suggested that the polymer can be thought of as having multiple specific chromophores. Other studies have indicated that it is possible to have both a system of non-isolated chromophores that exhibit energy transfer to the lowest energy level chromophore and isolated chromophores along the same polymer chain that fail to transfer energy. The ability to energy transfer between these chromophores causes distinct broadening of the photoluminescence background that is overlaid on the Raman signal.
The stair step nature of the intensity trajectory indicates that multiple chromophores are likely exhibiting Raman signals indicating a low level of intra-molecular conjugation. The majority of intensity trajectories for P3HT molecules from each solvent indicate similar low amounts of conjugation to that seen in dichloromethane. However, not all intensity trajectories showed the normal stair step decrease in intensity and thereby indicate the possibility that high levels of intra-molecular conjugation have occurred in some single molecule experiments. This appears to be largely solvent independent within the observed solvents, and may be more a function of the local surface. This is dramatically different from single molecule trajectories of R6G that show rapid stepwise changes in the trajectories due to changes in the molecular orientation and/or local heating before becoming photobleached. We found no such behavior for bare SERS substrate, except very short bursts in fluorescence background from small silver clusters that emit strong luminescence, which can undergo dynamic changes because of the local photochemical reaction of silver oxide and silver as discussed previously.

The trajectories shown in Figure 4.03 include both Raman and the silver background fluorescence. To further demonstrate the solvent dependence and dynamic changing in the local field enhanced Raman spectra, time evolution Raman spectra are shown in Figure 4.04. Consistent with results of trajectories in Figure 4.03, Raman spectra of P3HT from all solvents measured are fairly stable over the whole time period in comparison to single molecule R6G. The appearance of particular bands also provides strong proof of actual single molecule activity, since it is a common occurrence for some bands not visible in the ensemble to be visible in the SM spectra. For example, Raman bands in THF at 724 cm\(^{-1}\) of the C-S-C band appear initially but disappear over time, indicating that the local area is likely undergoing heating and thus the SM is undergoing conformational shifts over time. Additionally local silver sites could be
generating and destroying silver clusters. These findings hold for more than 20 molecules probed.

4.3 Polarization Dependence

Stable single polymer Raman spectra allow for the study of the polarization dependence of the Raman intensity of a molecule. The SERS enhancement of the polymer is dependent upon the polarization of the incident light and its interactions with the orientation of the molecule and the local plasmonic field, which can be directly linked to the local surface geometry. In order to accomplish this, a half plate is placed in the laser line attached to an electric motor with known
acceleration and velocity. The plate is rotated from 0° to 90° then back to 0° with the cycle being repeated three times. This alters the polarization angle of the incident light so that its effects may be tracked.

Figure 4.05. (A) photoluminescence intensity trajectories of several selected hotspots (1-5) on silver substrate in comparison to a P3HT thin film at various laser polarization angle. (B) single molecule P3HT intensity trajectory shows definite modulation due to the differences in laser intensity. Fluorescence modulation on ensemble P3HT intensity trajectory is shown in each figure to show changes in the laser intensity on the sample surface.

One of the major difficulties when performing this sort of experiment is that the dichroic mirror used in the microscope will not reflect all polarization angles equally. Therefore the first experiment was performed with a thin film of P3HT with no silver to correct the actual light intensity in the laser focal volume. This leads to a situation where the P3HT is homogenous on the glass, and no differences in local geometry of the substrate should affect the overall output light. Figure 4.05 A shows the sinusoidal intensity traces taken of the P3HT thin film while the polarization angle is altered. The fluctuations in intensity are fairly uniform and despite some photo-bleaching due to the photoluminescence signal having significant fluorescence, lead us to believe that the dichroic mirror is having a standardized effect on the power of the incident light at the sample. The laser intensity modulation by the dichroic is about 10% of the total laser
intensity. With the nature of the dichroic’s effect on the light intensity determined, it is now important to see if an uniform effect would occur on a nanostructured silver substrate. As such, Figure 4.05 A shows five traces taken of the silver scattering photoluminescence. The usual blinking phenomenon seen in silver is present and overlaid on a stronger background intensity modulation. The blinking phenomenon arises from the stochastic bursts of photoluminescence caused by the silver clusters as detailed in chapter 3. With the experiment being performed under air, one also expects that oxidation of the silver structures can cause bleaching. Photoreduction of the structures can still occur in this system but at a much reduced rate at other points causing reappearance of the silver photoluminescence. This modulation appears in all of the samples but is not uniform across the film in either time or intensity from spot to spot as shown in Figure 4.05 A. The lack of uniformity in the modulation for some of the hotspots indicates that local field enhancement at some hotspots of the nanostructured silver substrate is strongly dependent on the geometry of the local silver nanostructure instead of the incident light intensity. Such local structural dependence of the surface enhancement is critical for single molecule Raman enhancement. Other spots probed show strong correlation between the background fluorescence of silver and incident light intensity modulation. This is not unexpected since the silver has been reported as enhancing the intensity several orders of magnitude due to the local field effect. The difference in intensity spectrums is further supported by the silver mirror process, which leaves a poorly defined system. Thus one would expect to see multiple different intensity spectrums dependent upon the poorly defined, but strongly enhancing local field.

Finally single molecule P3HT samples are analyzed while the polarization angle of the incident laser is changed as shown in Figure 4.05 B. Overall, uniformity is not seen in the trajectory of the SM-Raman signal upon the change of polarization angle of the incident beam as
the total collected light scattering signal of P3HT is overwhelmed by the background fluorescence signal of silver substrate as shown in Figure 4.02 D and Figure 4.05 A. Most P3HT molecules investigated on the nanostructured silver surface show light scattering that seems to consistently follow the trend of the laser intensity as polarization angle changes with the local field effects appearing to have no effects. Because the silver substrate is poorly defined it cannot be ruled out that the local field may primarily be in resonance along the maximum polarizations of the incident laser, but is thought to be unlikely to continuously occur. Thus the polymer chains themselves are likely not laid out flat along a single axis on the surface and instead are folded in many different directions and possibly overlaid upon themselves. This leads to chromophores being excited along multiple different axes, and not just when the substrate’s local field and incident laser are primarily interacting, and thus leading to the laser intensity modulation playing such a large role in the excitement of the molecule.

4.4 Conclusions

This chapter showed that single molecule spectra could be collected on the Tollens silver substrate for R6G, confirming previous assertions in the literature. SM-SERS measurements were performed on P3HT in order to show the applicability of the system to more complex problems. The results show the presence of multiple chromophores, which allow a higher stability and less overall blinking when compared to the R6G. Time resolved spectra indicated some fluctuation in these chromophores under excitation. Further work indicated that solvent effects are apparent with particular bands being absent, and this data provides additional insight into the folding structure of the molecule dependent upon its solvent memory when only a single molecule is present. This data provides additional information for the construction of models of the initial step in the film formation. Finally, the photoluminescence background of
nanostructured silver substrate and single molecule Raman scattering show only weak polarization dependence. The collection of the polarization data is poor due to the undefined nature of the substrate causing a strong photoluminescence background. However, it was noted that it is likely that the polymer does form in a folded pattern with various chromophores showing preferential polarization on the nanostructured silver surface.
CHAPTER 5
SILVER DECORATION OF SINGLE CRYSTAL TiO\(_2\)

Chapter 5 will concentrate on decorating micron sized TiO\(_2\) single crystals with silver structures in order to probe the surface of the TiO\(_2\). The goal is to determine the interactions of the silver at the surface and determine the interactions between the silver and the TiO\(_2\). This is an especially interesting system for study, as the literature has put forth improved photocatalysts based upon TiO\(_2\) decorated with plasmonic structures\(^{266-269}\). Initial work in the chapter will detail the synthesis of a well defined micron sized single crystal TiO\(_2\) and the annealing procedures used to try to improve the photosensitivity. The TiO\(_2\) structures will then be well characterized before silver is decorated onto the surface through two separate methods: a direct reduction and a linker attachment. The silver decorated TiO\(_2\) will then be probed to see if the silver structures maintain similar behaviors to the silver nanowires and Tollens substrate utilized in previous chapters.

5.1 Characterization

TiO\(_2\) was synthesized as described in Chapter 2. The resulting structure was a white powder at the macroscopic level, and a truncated bipyramid at the microscopic level with a width of between 2 and 3 microns, as can be seen in the SEM image in Figure 5.01. The thickness of the crystals varied greatly between runs, but was at a minimum of several 100 nm. The as synthesized crystals’ surfaces were relatively smooth though a large pit or nanoparticle of a few 10s of nm would sometimes be found on the surface. TEM images (Figure 5.01 B) of the edges of the crystal indicate a single crystal structure. TEM of the center of the crystals was impossible.
to perform because of the thickness of the crystals. The truncated bipyramidal structure is indicative of the anatase phase of TiO$_2$ with the eight side faces corresponding to the [101] face.
and the two top/bottom sides corresponding to the [001] face. XPS of the crystals (Figure 5.02) showed that in addition to titanium and oxygen, fluorine was present. The literature\cite{270} indicated that much of this fluorine would be surface bound, so annealing procedures, described in Chapter 2, were put in place to remove the unwanted fluorine. Post annealing, the XPS spectrum (Figure 5.03) shows a large but not complete removal of fluorine from the system. This indicates that there is likely some deeply trapped fluorine in the bulk of the crystal. Interestingly, it was important that the annealing process occurred in a quartz boat, otherwise silicon could be found in the system. The crystals maintained their shape after annealing, though some agglomerations of multiple crystals could now be found. The surfaces of these crystals were still largely smooth though additional pitting was introduced into the system.

\textbf{Figure 5.03.} The XPS spectra of the annealed sample shows a reduction in the fluorine peak. This is supported by the expansion of the fluorine spectra (B). The expansion of the nitrogen spectra (C) shows that nitrogen is still present in the system.
Satisfied that the as synthesized and annealed crystals could be successfully employed in the study, an attempt was made to dope the crystals with nitrogen as described in chapter 2. Initial doping attempts centered on a combined removal of fluorine and introduction of nitrogen under an ammonia atmosphere. As before, the XPS spectrum (Figure 5.04) indicated that the fluorine was reduced but not completely removed. Nitrogen was indicated as being present in the system, but not at a greater percentage than the nitrogen seen in the annealed samples. Thus if nitrogen doping has occurred in the sample, it is below the limit of detection for these samples.

The samples structural changes are nearly identical to those seen in the annealing process. Trying to introduce more nitrogen into the crystal, the doping procedure was performed after the annealing process was completed. The XPS spectrum (Figure 5.05) of these crystals shows almost complete removal of the fluorine but no additional nitrogen present, even when increasing the normal doping temperature from 500°C to 700°C. The macroscopic crystals underwent a

Figure 5.04. The XPS spectra of the ammonia doped crystals shows that the fluorine is reduced but still present. This is supported by the fluorine spectra expansion (B). The nitrogen spectra expansion (C) shows that nitrogen is present in the system, but this could be due to the nitrogen already present in the as-synthesized sample.
Figure 5.05. The XPS spectra of the annealed then doped crystal samples performed at 500°C (A) and 700°C (B) show little to no fluorine and nitrogen. This is supported by the expansion of the fluorine and nitrogen spectra for the 500°C (C,D) and 700°C (E,F) samples.
color change from white to charcoal colored in the 700°C sample, but no change was observed at 500°C. P25 samples that were run concurrently with the annealing and doping processing of the crystals do show significant percentages of nitrogen present in their XPS spectra (Figure 5.06).

For the P25 samples, greater nitrogen doping occurs in the higher temperature situation. It is thought that for the single crystal system, the nitrogen doping only occurs at the surface of the crystal. Considering that the surface only makes up a small fraction of the overall material in the single crystal system, there may simply not be enough nitrogen present to create a significant signal. Thus, while nitrogen may be present on the surface of the crystals, it was not definitively confirmed. However, for the P25 samples, the grain boundaries of the rutile and anatase structures allow for infiltration of the nitrogen into the whole of the structure. Further, even if the doping is only occurring at the surface of the P25, the increased surface area would account for
an increase in the total nitrogen present. SEM images (Figure 5.07) of the samples show similar results to the annealed samples, though a rise in the number of agglomerates does occur. No major structural differences are seen at the higher doping temperatures.

**Figure 5.07.** The SEM images of the annealed then doped samples for 500° C (A) and 700° C (B) show more roughness than the as synthesized samples but the anatase crystal phase is maintained.

**Figure 5.08.** XRD of the as synthesized (black) corresponds to anatase phase TiO₂. The air annealed (red) and ammonia doped (fuchsia) samples show an almost perfect match to the as-synthesized sample.
To confirm the SEM visual analysis XRD (Figure 5.08) was performed on all the samples. The XRD confirmed that the as synthesized samples were in the anatase phase. The annealed samples and doped samples showed little to no change, indicating that the heating was not causing a crystal morphology change. This is largely unsurprising, as the literature\textsuperscript{271-273} indicates that the anatase to rutile phase transition occurs at 600°C or above. XRD was also performed on the annealed then doped samples, as seen in Figure 5.09, with the as-synthesized sample presented for reference. Once again little change is seen between the XRD spectrums for the single crystals, even when doped at 700°C. P25 samples are also presented in the XRD spectrum. P25 is a mixture of rutile and anatase phase and thus will exhibit properties of both. The 700°C doped P25 sample exhibits less anatase and more rutile character than the 500°C

\textbf{Figure 5.09.} XRD of the as synthesized and the annealed and doped at 500°C and 700°C show an anatase pattern. The doped P25 samples at 500°C and 700°C show anatase and rutile phases as being present.
doped P25 sample, indicating that a physical transformation has occurred. The single crystal 
TiO$_2$ doped at 700$^\circ$C likely undergoes this change as well, but much like the nitrogen coverage, 
the percent of the crystal undergoing the transformation is extremely small. P25 likely undergoes 
the change more easily with its higher surface area allowing for more heating interactions with 
the ambient atmosphere. The single crystals likely undergo some transformation to rutile, and if 
allowed to stay under temperature for long enough, complete intra-conversion would be likely. 
Raman spectra (Figure 5.10) of all the samples show the three characteristic anatase TiO$_2$ peaks, 
further supporting that the bulk of the samples are in the anatase phase.

![Raman Spectra](image)

**Figure 5.10.** Raman spectra of the as-synthesized (black), annealed (red), and ammonia doped 
(green) samples show the three peaks characteristic of anatase TiO$_2$.

To test for the light sensitivity of the TiO$_2$ crystals, light and dark IV curves were 
gathered using the photoelectrochemical set-up described in chapter 2 under AM 1.5 excitation. 
The resulting graphs for the as-synthesized, annealed and doped samples can be seen in Figure 
5.11. A light response is seen indicating that the TiO$_2$ samples are photosensitive, but
conclusions about the bulk charge transfer capabilities were difficult to draw due to the difficulty in sample preparation. The relatively large size of the crystals meant that a film had to be used to immobilize the crystals on the ITO surface. The film had to be thin in order to be transparent to light and permeable to water to allow the water splitting reaction to occur. In order to accomplish this, only a very sparse coating of TiO$_2$ was used, and little control of the amount of TiO$_2$ in the excitation area was had. Additional wavelength response experiments were performed on the various TiO$_2$ samples using the photoelectrochemical system described in chapter 2 in order to determine the UV and visible light sensitivity. For the as-synthesized, annealed and doped

![Figure 5.11](image1.png)

**Figure 5.11.** The IV response curves for the as-synthesized (A), annealed (B), and ammonia doped (C) samples show that an increase in the current does occur once light is shined on the sample.

![Figure 5.12](image2.png)

**Figure 5.12.** Background wavelength response curves for the (A) as-synthesized (black), annealed (red) and ammonia doped (green) show essentially no shift. (B) The annealed then ammonia doped samples at 500° C (black) and 700° C (red) show similar behavior.
sample the largest peak appeared around 345 nm and tailed only slightly into the visible region as seen in Figure 5.12 A. Figure 5.12 B shows the photowavelength response of the annealed/doped samples run at 500°C and 700°C. These samples were immobilized in a nafion thin film instead of a gelatin film due to trouble with the film properly adhering to the ITO slide. Once again, the primary peak is centered around 345 nm with only a slight tail into the visible region. The lack of a red shift when looking at the modified samples indicates that the bulk of the material has undergone little to no transformation, and that any sites capable of interacting with visible light are very few. Indeed, looking at this data alone, it was not expected that any visible light sensitivity existed for the modified samples. Thus, Dr. Greg Szulczewski and Alexandra Arnold provided support to the project by performing photodegradation of methylene blue in the presence of TiO$_2$. For as-synthesized samples, the photodegradation process occurred at the highest rates under UV excitation. Under the visible excitation, the degradation occurred at a much slower rate, as observed in Figure 5.13A, but at a still greater rate than the degradation occurred when no TiO$_2$ was present. This held true for the various modified samples, which still showed the UV excitation leading to higher degradation rates. However, when comparing the visible degradation rates, the modified samples showed a higher initial degradation rate than the as synthesized samples. This indicates that a small number of interstitial sites, likely on the surface of the crystals, were generated. These interstitial sites are likely to be either oxygen vacancy or nitrogen doping sites, as discussed by Diebold and coworkers$^{274-275}$ as well as others$^{276,277}$. 


Interactions with Silver

5.2.1 Deposition of Silver. Silver, as discussed in the previous chapter, has an interesting set of properties that could allow it to be used to probe the facial charge transfer properties of the TiO$_2$ crystals. As such, it was decided to use silver as both a direct and indirect probe of the TiO$_2$ by growing it directly on the face of the TiO$_2$ by using either visible or UV excitation, with the process outlined in chapter 2. Initial work focused on determining the optimal growth time to make the silver easily visible under optical observation. As can be seen in the SEM images in Figure 5.14, even the shortest growth times under UV excitation result in silver growth on the TiO$_2$. However, extremely long growth times did result in silver obscuring the faces completely and in separation of the silver from the faces. Thus a growth time of 10 minutes was settled upon to allow optical imaging without causing overgrowth and silver separation.

Figure 5.13. The degradation of methylene blue occurs at a greater rate under UV excitation compared to visible light excitation (A). When the TiO$_2$ is compared between as-synthesized, annealed, and ammonia doped samples under visible light excitation (B), the degradation occurs initially at a greater rate for the annealed and doped samples.

5.2 Interactions with Silver
Before optical experiments were carried out, the as-synthesized, annealed, and doped samples with silver grown under UV and visible excitation were imaged using SEM, as seen in Figure 5.15. Under visible illumination, all the samples showed direct silver growth on the surface of the TiO$_2$ except for the as-synthesized samples. Instead dendritic silver structures were found in the images, indicating that the silver growth had occurred in the solution instead of directly on the surface. EDX images for the samples with direct silver growth were then overlaid on SEM images of the same crystals. Then using ImageJ, the percent coverage of silver for each face was calculated. The results, presented in Table 5.1, indicate that within error the [101] and [001] faces of each individual sample show similar growth. There is a large error involved with this calculation as EDX is not the most sensitive of detection methods and the facial aspects have been manually assigned. Further, between separate samples, the data cannot be compared as the UV and visible light excitation power could not be effectively controlled from sample to sample.

**Figure 5.14.** The SEM of the as synthesized samples at with silver grown directly on them for 10 (A) or 20 (B) minutes show that silver is present in both samples. However, the 20 minute sample shows significantly larger silver structures which makes it difficult to localize the silver structures.
Figure 5.15. The SEM images for the Ag grown by UV excitation on the as-synthesized (A), ammonia doped (C), and annealed (E) TiO$_2$ with their respective (B,D,F) silver EDX images. The SEM and Ag EDX images for the Ag grown by visible light excitation is shown only for the ammonia doped (G,H) and annealed (I,J) samples as the as-synthesized samples do not show silver growth under visible excitation.
Table 5.01. The atomic percent silver coverage by TiO$_2$ face

<table>
<thead>
<tr>
<th>Sample</th>
<th>{001}</th>
<th>{101}</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Synthesized, UV</td>
<td>0.07 (0.04)</td>
<td>0.09 (0.04)</td>
</tr>
<tr>
<td>Annealed Air, UV</td>
<td>0.03 (0.03)</td>
<td>0.03 (0.02)</td>
</tr>
<tr>
<td>Annealed Air, Visible</td>
<td>0.06 (0.02)</td>
<td>0.06 (0.03)</td>
</tr>
<tr>
<td>Annealed Ammonia, UV</td>
<td>0.12 (0.07)</td>
<td>0.2 (0.2)</td>
</tr>
<tr>
<td>Annealed Ammonia, Visible</td>
<td>0.03 (0.02)</td>
<td>0.03 (0.02)</td>
</tr>
</tbody>
</table>

In order to observe the in-situ silver effects, the samples were imaged using a bright field microscope while under a deionized water solution. The resulting movies were observed, and it was noted that without silver present on the samples, the TiO$_2$ exhibited no blinking effects, but instead showed a constant bright image. Samples with silver on the TiO$_2$ surface showed similar blinking effects localized on “hot spot” areas of the TiO$_2$. Due to the appearance of these blinking sites only after the inclusion of silver and the stochastic nature of the blinking, it is reasonable to assume that the “hot spots” are generated by the deposited silver. Knowing that the silver is the fluorescence source, it is clear that the TiO$_2$ does not cause complete quenching. A statistical study of the difference in blinking behavior was not performed for the silver on TiO$_2$ so no further conclusions can be drawn about the effects of the TiO$_2$ on the silver blinking behavior.

Figure 5.16. The scanning confocal images of the [001] face (A) and [101] face (B).
To further investigate the facial growth aspects samples were imaged using the confocal scanning microscope after silver deposition. It can be seen in Figure 5.16, the resolution of the depth of field is such that the [101] and [001] faces can be preferentially resolved. Additionally silver that is present on the samples can be imaged from the photoluminescence hot spots. However, the resolution is such that the individual silver structures cannot be fully resolved, and structures that lack a high intensity response are not seen. Additionally, the resolution of the [001] face is lower than the [101] face in the image. The resolution difference is not the same between every sample due to difficulties arising from the manual control of the microscope focal point and in identification of the surface focus. It must be noted that all samples are initially identified by bright field imaging and that the focal depth is manually set based upon user experience with the confocal imaging instrument. Further, more possible sample is in the depth of field when focusing on the [001] face, as the sample is thicker at these points. Using the UV lamp as the photoelectrochemical excitation source and the 633 nm laser as the imaging excitation source, scanning confocal images were taken as the silver was grown in-situ. As seen in Figure 5.17 these images were taken in air, under the AgNO₃ solution, and then after 10, 20, and 30 seconds of illumination. All images are for the same piece of TiO₂ though some movement was seen due to the TiO₂ not being bound to the substrate. Prior to UV illumination, the signal to background is small for the TiO₂ sample. However, after just 10 seconds, the TiO₂ signal increases drastically and the image resolution is much higher. When focusing on the [101] faces, the resolution is once again higher than when focusing on the [001] face up until the photoelectrochemical excitation had reached 20 seconds. At this time and beyond the resolution seems to be non-dependent on the faces. It is thought that this is due to the silver particles reaching a size and concentration that they dominate the signal and making identification of the
Figure 5.17. Optical imaging of the [001] and [101] faces as silver is grown on the TiO$_2$, beginning with the sample under air, then liquid, extending the excitation from 0 to 30 seconds.
focus depth on the sample faces a simpler procedure. Also beginning in the 20 second excited samples, silver grown in the solution can be seen in the images.

Noting that the silver nano-structures cannot be individually resolved by optical means alone, samples were imaged by combined SEM and optical microscopy methods. By dispersing the silver coated TiO$_2$ crystals on a gridded substrate and then optically imaging the particles, well dispersed particles could be identified by SEM or TEM. For gridded glass substrates, this involved coating with a gold thin film prior to SEM imaging. However, this led to difficulty in identifying silver particle locations on the TiO$_2$ structures. TEM grids were then employed to satisfactorily provide a conductive labeled grid surface for particle identification. The holey carbon backing of the TEM grids caused some light dispersion and a lessoning of the optical resolution of the samples. However, optical methods could still be used to image the samples with the SEM now being capable of performing imaging as well. While the identification of the individual crystals was successful, the loss of optical resolution made identifying the accompanying hot spot structures unsuccessful as the co-localization between the two imaging methods became untenable. This problem was further compounded by an inability to definitively resolve whether the optical scans were probing the upper or lower side of the TiO$_2$ crystals, while it was known that the SEM scans could only probe the upper side of the crystals.

5.2.2 Silver-Linker-TiO$_2$ Structures. In order to probe the crystals through a different structural set-up than with the directly grown silver, silver nanoparticles were bound to the TiO$_2$ by using a linker molecule, 4-mercaptobenzoic acid (MBZA) or 1,4-benzenedithiol (BDT). The conjugated structure of the linker molecule allows electron transfer between the TiO$_2$ and silver. For the MBZA the difference of the end molecules creates an inherent dipole within the structure that
may interfere with electron transfer between the TiO$_2$ and silver. In order to control the dipole direction, it was attempted to attach the thiol either preferentially to the Ag or TiO$_2$, as seen in Figure 5.18. The synthesis with the thiol attached to the silver is simple as the thiol preferentially binds to the silver. However, the thiol binding to the TiO$_2$ is more difficult and requires that the thiol be bound to the TiO$_2$ prior to the addition of the silver. Lombardi and coworkers$^{278-281}$ have indicated in the literature that this is a possible attachment procedure, though no XPS data or Raman supporting this assertion is shown. The exact process is detailed in the experimental section. For the BDT, the preferential silver binding can cause silver agglomerates to form when the silver colloid is bound first. Further, it is important to note that the TiO$_2$ used in these samples must be annealed or doped samples as the fluorine on the as-synthesized samples blocks the binding sites on the TiO$_2$. For this study only the annealed samples were used.

**Figure 5.18.** A cartoon of the possible linker attachment scheme for the MBZA. (A) shows the TiO$_2$/MBZA/Ag scheme and (B) shows the Ag/MBZA/TiO$_2$ scheme.
Figure 5.19. Raman spectra of the bulk BDT, TiO$_2$/BDT, Ag/BDT, TiO$_2$/BDT/Ag, and Ag/BDT/ TiO$_2$ structures. Noticeably the Raman spectra for the TiO$_2$/BDT and Ag/BDT/ TiO$_2$ samples show very little signal corresponding to the BDT.
Figure 5.20. Raman spectra of the bulk MBZA, TiO$_2$/MBZA/Ag and Ag/MBZA/TiO$_2$ structures.
Raman spectra were taken on the BDT and MBZA bound silver/TiO$_2$ structures with 533 nm excitation to see what effects would arise. Figure 5.19 shows the Raman spectra for bulk BDT and the TiO$_2$/BDT, Ag/BDT, TiO$_2$/BDT/Ag, and the Ag/BDT/TiO$_2$. As can be seen, the Raman signals for the BDT show up very clearly on the Ag/BDT and TiO$_2$/BDT/Ag structures. In both cases it is thought that the silver is providing a significant SERS enhancement. For the TiO$_2$/BDT very little signal is seen from the BDT, which is likely due to poor coverage on the TiO$_2$ surface coupled with the strong signal from the TiO$_2$ making identification difficult. The Ag/BDT/TiO$_2$ shows essentially no Raman signal from the BDT, which is likely due to a lack of silver and BDT being still present in the sample. Instead, it is likely that the BDT caused linkage between the silver nanoparticles or have doubly bound to the silver surface prior to the addition of the TiO$_2$. Thus after TiO$_2$ is added, no bonds are likely formed between the TiO$_2$ and BDT present on the silver. Thus all the silver and BDT is washed away during the rinsing step of the synthesis.

The Raman spectra for MBZA, TiO$_2$/MBZA, Ag/MBZA, TiO$_2$/MBZA/Ag and Ag/MBZA/TiO$_2$ are shown in Figure 5.20. For these samples the MBZA Raman signal can be seen in all the spectra. The intensity varies from sample to sample and cannot be compared directly across samples as the total coverage of the MBZA on each sample is unknown. Of special note in the MBZA spectrum are the peaks at 1080 and 1592 cm$^{-1}$ that correspond to the ring deformation and the peak at 1184 cm$^{-1}$ that corresponds to the C-H stretching. The ring deformation peaks should see greater enhancement due to charge transfer increasing the polarizability along the axis between TiO$_2$ and the silver nanoparticle. The C-H stretch, which has its bond not primarily along this axis, should not undergo a significant enhancement dependent upon charge transfer. Thus the 1184 cm$^{-1}$ peak can be used to normalize against the
<table>
<thead>
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<th></th>
<th>Peak Position (cm(^{-1}))</th>
<th>Intensity (counts)</th>
<th>Intensity normalized</th>
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<tr>
<td>40 nm Ag/MBZA/TiO(_2)</td>
<td>1080 ±1.8</td>
<td>300 ±230</td>
<td>2.65</td>
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<tr>
<td></td>
<td>1184 ±2.9</td>
<td>106 ±63</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1592 ±1.8</td>
<td>700 ±480</td>
<td>6.21</td>
</tr>
<tr>
<td>TiO(_2)/MBZA/40 nm Ag</td>
<td>1079.1 ±0.64</td>
<td>1300 ±470</td>
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<tr>
<td></td>
<td>1185.5 ±0.67</td>
<td>370 ±170</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1591 ±1.3</td>
<td>2400 ±970</td>
<td>6.52</td>
</tr>
<tr>
<td>60 nm Ag/MBZA/TiO(_2)</td>
<td>1074 ±1.4</td>
<td>330 ±360</td>
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</tr>
<tr>
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<td>1184 ±1.1</td>
<td>240 ±230</td>
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<td>1593 ±2.1</td>
<td>500 ±660</td>
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<td>800 ±360</td>
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<td>1182.8 ±0.83</td>
<td>300 ±68</td>
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<td>1587 ±1.2</td>
<td>1300 ±560</td>
<td>5.10</td>
</tr>
</tbody>
</table>

**Table 5.02.** Table displaying the intensities and normalized intensities of the Raman modes of interest using different size Ag colloid and linker arrangements.

1080 and 1592 cm\(^{-1}\) peaks in order to determine relative enhancement while removing the dependence on coverage. Table 5.02 shows the normalized intensities for the Ag/MBZA/TiO\(_2\) and TiO\(_2\)/MBZA/Ag structures with 40 nm and 60 nm silver nanoparticles used. For the 40 nm silver nanoparticles, the normalized intensity difference between the TiO\(_2\)/MBZA/Ag and Ag/MBZA/TiO\(_2\) structures is within error, indicating that no real enhancement difference is seen.
However, for the 60 nm silver, the Ag/MBZA/TiO\textsubscript{2} structure shows peaks that are roughly half the normalized intensity of the TiO\textsubscript{2}/MBZA/Ag structure. It is thought that this is due to bringing the silver more on resonance with the excitation laser, as is supported by the UV/Vis absorption spectra in Figure 5.21. For the Ag/MBZA/TiO\textsubscript{2} the hot electrons are likely allowed to transfer along the linker from the Ag to the TiO\textsubscript{2}, reducing the total polarizability of the molecule induced from the presence of the plasmonic silver. For the TiO\textsubscript{2}/MBZA/Ag structure, the hot electrons are likely blocked from transferring, instead remaining in the silver nanoparticle. This leads to greater enhancement than the Ag/MBZA/TiO\textsubscript{2} case.

![Absorption Spectrum](image)

**Figure 5.21.** The absorption spectrum of the 40 nm diameter Ag nanoparticles (black) has a higher absorption in the blue range but less in the visible range compared to the 60 nm diameter Ag nanoparticles (red).

### 5.3 Conclusions

It was shown that single crystal anatase TiO\textsubscript{2} could be grown through a hydrothermal process. The resulting crystals were coated with a layer of fluorine on the surface that could be removed through annealing processes and doping could be performed. The doping and annealing processes showed little to no effect on the absorption spectrum of the bulk of the sample.
However, the removal of the fluorine did introduce surface defect sites that could be directly probed by silver growth. These defect sites allow for visible light absorption and silver growth on the surface. No preference was seen between the two different anatase faces present in the crystals. Further work was done by introducing a linker molecule, MBZA or BDT, to attach silver nanoparticles to the TiO$_2$. By observing the Raman peaks, it appeared that a reduction of possible total enhancement arises dependent upon excitation wavelength and linker alignment. Particular arrangements that allowed hot electron transfer from the TiO$_2$ to the Ag but blocked the back transfer gave the highest SERS enhancement when the silver was brought on resonance with the incident light. Unfortunately facial differences were not capable of being probed as the methodology available to identify the individual silver sites by face did not allow for both electron microscope and optical microscope recognition of the same site.
CHAPTER 6

CONCLUSIONS AND PERSPECTIVES

Chapter 6 provides a summary of the previous chapters. Particularly the aspects of silver, the focus of this study, studied throughout chapters 3, 4 and 5 will be brought together. Applications of the silver towards garnering knowledge of other materials, like P3HT and TiO$_2$, will be summarized. Following this, future experiments and how these experiments expand upon the current work will be discussed.

6.1 Conclusions

The main focus of the dissertation is studying plasmonic silver structures and understanding silvers behavior in conjunction with other materials. In order to do this, optical and electron microscopy techniques were used as the primary methods of analysis, with a specific focus on SERS capabilities. Thus silver nanowires were chosen as an ideal material for in depth study due to ease of optical identification, while maintaining plasmon resonances in the visible light region. The silver nanowires exhibited interesting photoluminescence properties, primarily exhibiting a strong fluorescence signal that underwent blinking. This was attributed to small silver clusters of a few silver atoms, which are capable of giving off fluorescence signals. The blinking effects are due to a combination of general stochastic effects and also to rapid changes of the silver cluster from Ag$^0$ to Ag$_2$O and back again. The fluorescence blinking effects seen in the nanowires were also apparent in the Tollens’ silver substrate and photoreduced silver. Of particular interest was that the blinking effect did not completely disappear when the silver was present on the TiO$_2$. As TiO$_2$ and silver can undergo electron transfer in either direction, it is
important to note that possible electron transfer from the silver to TiO$_2$ does not cause complete quenching of the fluorescence blinking.

The SERS effects and the location of the hotspots were investigated, with it being found that the fluorescence signal could be overcome by using large concentrations of the SERS analyte. Additionally it was noted that the fluorescence hot spots did not correspond to the SERS hot spots, confirming previous reports in the literature$^{72,240}$. Thanks to theoretical support from Dr. Dixon and Dr. Chen as well as literature on SERS structures, it was decided to perform a polarization study of the SERS hot spots. Some polarization dependence was noted on the silver wires though the exact dependence was not able to be deconvoluted from the data due to experimental difficulties. Further work utilizing P3HT polarization dependence showed possible dependence, though the uncharacterized nature of the substrate made exact determination of the dependence effects impossible.

The work was then extended by showing an application of the plasmonic silver structure to a small Raman active molecule, R6G, and a large polymer, P3HT. Bulk and single molecule SERS measurements were performed and showed good agreement of the spectra, though some peaks were not apparent in the single molecule spectra. R6G demonstrated the stochastic blinking behavior consistent with its SM-SERS spectra. P3HT was found to be very stable in the single chain spectra, which was attributed to multiple chromophores giving the Raman signal. This was supported by the stair step intensity traces exhibited by the single molecule P3HT samples, which indicated that single chromophores were becoming no longer Raman active. Four different solvents were investigated and the P3HT was found to exhibit different Raman spectra dependent upon the solvent. Certain solvents led to the appearance of peaks around 650 cm$^{-1}$, which is indicative of a kink in the polymer. Dichloromethane, one of the solvents used, causes
the peak at 997 cm\(^{-1}\) to disappear, which is attributed to the C-C ring-alkyl chain bond not receiving enhancement. Thus it was concluded that the solvent effects could be probed at the single chain level.

Finally, a silver-TiO\(_2\) system was studied to determine what effects may arise due to the materials interactions. This work was begun in order to better understand the many photocatalysts that are attempting to apply plasmonic structures to improve the photocatalytic properties\(^\text{282-284}\). Initial work focused on the synthesis process of a well characterized anatase TiO\(_2\) through a hydrothermal method. The synthesized crystals take on a truncated bipyramidal shape with only [101] and [001] faces present and a micron size. However, the as-synthesized crystals have fluorine on the surface of the TiO\(_2\) that needs to be removed to better simulate the standard TiO\(_2\) used in dye sensitized solar cells and photocatalysts. Thus TiO\(_2\) underwent an annealing process that removed the fluorine. Using a similar process ammonia doping was also attempted on the TiO\(_2\), but if any nitrogen was doped into the sample it was a very small amount and was likely surface localized. To improve the doping amount, the annealing and doping processes were performed sequentially at various temperatures though little to no doping was still apparent, despite P25 showing ready doping. The difference in the doping amount was likely due to the grain boundaries within the P25 allowing infiltration of the nitrogen into the structure.

Through various experiments, the bulk and individual UV and visible light sensitivity were probed. The bulk for all the samples was found to be UV but not visible light sensitive. However, visible light sensitivity was seen to be present in small amounts for all the annealed and doped samples. This was attributed to the introduction of defect sites on the surface of the sample. Following this, silver was deposited directly on the TiO\(_2\) samples by light excitation. The silver confirmed the UV sensitivity of all the samples, and the visible sensitivity of only the
annealed and doped samples. Further with the direct reduction of silver on the TiO$_2$ it was possible to examine preferential sites of silver reduction through EDX. Within the limits of detection, it appeared that the faces showed similar amounts of silver reduction. Two linker molecules were then utilized to attach silver to the TiO$_2$ without utilizing a direct reduction. The two linker molecules, BDT and MBZA, have different dipole properties and may show different effects dependent upon the orientation of the linker. It was noted that the highest SERS intensities occurred when the TiO$_2$ could perform electron transfer to the silver while the silver colloid was more on resonance with the excitation wavelength.

6.2 Future Experiments

The most logical experiment to perform would be to combine the micron-scale TiO$_2$ and P3HT into a photovoltaic device. However, two major issues arise when considering this experiment. The first of these is that the micron size of the anatase crystals causes some issues for the device with nano-scale particles being more commonly used. This is due to a combination of charge diffusion path length and difficulties in immobilizing the larger micron crystals on the electrode surface. The immobilization problem can be overcome through experimental design, but was already seen as a difficulty in the photoelectrochemical experiments performed. The second major issue is that no major impetus exists to perform the experiment currently. The literature has many examples of P3HT/TiO$_2$ devices already, and little contribution to the greater scientific conversation would likely result.

Superior experiments to perform would focus on more fully exploring the properties of the TiO$_2$. The first of these would involve gathering additional data about the facial preference for the photoreduction of silver. This could be accomplished through a simple experiment already using the methods currently employed to deposit silver and image silver on the TiO$_2$. By
simply reducing the rate of silver reduction through the removal of the sacrificial reagent in the silver growth solution and maintaining good control of the growth time and excitation intensity the amount of silver deposited can be greatly reduced. With the reduction of rate, the number of Ag seed particles initially reduced on the TiO$_2$ should be decreased, with further growth occurring mainly at the already reduced silver. Then instead of counting percent coverage from EDX images, the number of silver reduction sites could be counted for many crystals to determine the preferred reduction face through the use of counting statistics.

Considering that the visible light sensitivity of the TiO$_2$ only occurs after the introduction of color centers through annealing or doping, trying to improve the doping methods could be effective in increasing the visible light sensitivity. The simplest experiment to attempt would be to vary the length of time for the doping. As was already noted, the P25, which is of nanoscale size, showed significant nitrogen doping. Thus it would reason that increasing the reaction time may allow for more nitrogen doping in the micron sized crystals. But the doping process should not just be limited to nitrogen. The literature has already indicated other n-type dopants such as carbon$^{294}$ and hydrogen$^{295}$ that could serve to effectively sensitize the TiO$_2$ to visible light. The carbon doping process would involve using a carbon containing gas, such as methane, and flowing it over the TiO$_2$ in the tube furnace with heating. This has already been attempted but currently the carbon appears to be forming an outer coating on the TiO$_2$, as seen in the SEM image in Figure 6.01. Thus the carbon doping process still needs to be optimized prior to continuing the experiments with the carbon doped TiO$_2$. Hydrogen doping could be performed through the use of ammonia in much the same way that nitrogen doping is currently attempted. However, the temperature for the hydrogen doping needs to be increased significantly when using ammonia.
Other experiments with TiO$_2$ could also provide additional insights and experimental design. One of the more notable methods that has been utilized by other experimentalist is to use embedded plasmonic structures to improve photocatalysts. Interestingly anatase TiO$_2$ can have the [001] face preferentially etched by using hydrofluoric acid$^{296}$ while controlling the pH. The etched surface tends to be highly roughened, providing many high surface energy sites for Ag photoreduction as evidenced by the preferential photoreduction at the edges of the crystals from the previous work. Thus deposition of plasmonic nanoparticles that could then be covered by TiO$_2$, would be feasible. This would provide a plasmonically enhanced micron scale TiO$_2$ single crystal for analysis. Thus photocatalytic reduction studies such as the photoreduction of silver on the surface of these plasmonically enhanced TiO$_2$ structures could be compared to as synthesized and doped TiO$_2$ samples. Other methods of utilizing silver and TiO$_2$ could involve making use of the combination of TiO$_2$ and silver to make a Raman antennae structure. This would involve utilizing the photoreduction of silver directly onto the TiO$_2$ in order to generate a seed particle. Then the silver could be grown in a 1-dimensional method to form long wires extending from the surface of the TiO$_2$. Ideally these wires would consist of nano-scale diameters with micron-scale lengths, similar to the wires utilized in chapter 3. Making use of the nano-scale aspects of the wire, SERS could be performed on the far end of the silver nanowires from the TiO$_2$, while UV

Figure 6.01. SEM of the carbon doped TiO$_2$. 
light was shined on the TiO$_2$ crystals to induce electron doping into the silver. This additional electron density should cause an overall increase in the local EM field enhancement, even if it would also be expected to slightly shift the resonance wavelength. Indeed, probing the differences in the absorbance wavelength of the nanowires with and without applied UV excitation on the TiO$_2$ may provide insight into the total electron transfer into the silver structures.

Moving away from experiments utilizing TiO$_2$, the polymer dyes could receive significant investigation. Using the same methods already described while utilizing other dyes could provide additional information about the solvent effects of these dyes and the interactions with a silver substrate. Other experiments could utilize the monomers of polymer dyes capable of performing linking properties with the TiO$_2$ and silver colloids. Then utilizing the same methods as for the small molecule linkers, the monomers and their capability to allow preferential electron transfer could be probed. Finally similar to the photocatalyst with embedded plasmonic structures, the polymer could be embedded in the TiO$_2$ and covered to create a self contained micron size UV/Visible light absorber. The actual coverage of the polymer with TiO$_2$ is likely to be an extremely difficult proposition without destroying the polymer.
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### APPENDIX

**Table 1A.** Table of the Raman peaks for 4-Mercaptopyridine.

<table>
<thead>
<tr>
<th>DFT</th>
<th>Experimental</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1005 (28)</td>
<td>1049.74</td>
<td>Ring stretch/deformation</td>
</tr>
<tr>
<td>1084 (8)</td>
<td>-</td>
<td>Ring stretch/deformation</td>
</tr>
<tr>
<td>1121 (18)</td>
<td>1139.179</td>
<td>C-S stretch</td>
</tr>
<tr>
<td>1234 (7)</td>
<td>1255.087</td>
<td>CCH bend</td>
</tr>
<tr>
<td>1280 (3)</td>
<td>-</td>
<td>Ring stretch/deformation</td>
</tr>
<tr>
<td>1332 (4)</td>
<td>1323.129</td>
<td>CCH bend</td>
</tr>
<tr>
<td>-</td>
<td>1537.362</td>
<td>Unassigned</td>
</tr>
<tr>
<td>1610 (15)</td>
<td>1620.094</td>
<td>CC double bond str</td>
</tr>
<tr>
<td>-</td>
<td>1751.934</td>
<td>Unassigned</td>
</tr>
<tr>
<td>-</td>
<td>1830.802</td>
<td>Unassigned</td>
</tr>
</tbody>
</table>
Table 2A. Table of the Raman peaks for Adenine

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Experimental</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>723 (28)</td>
<td>-</td>
<td>Ring stretch</td>
</tr>
<tr>
<td>820 (1)</td>
<td>804.693</td>
<td>Ring torsion</td>
</tr>
<tr>
<td>857 (1)</td>
<td>-</td>
<td>CH out-plane wag on 5-ring</td>
</tr>
<tr>
<td>896 (2)</td>
<td>-</td>
<td>N-C-N bend</td>
</tr>
<tr>
<td>942 (4)</td>
<td>-</td>
<td>5-ring stretch</td>
</tr>
<tr>
<td>1005 (5)</td>
<td>1025.737</td>
<td>NH$_2$ Rock</td>
</tr>
<tr>
<td>1078</td>
<td>-</td>
<td>Mix of CNH bend and NC str</td>
</tr>
<tr>
<td>1238 (11)</td>
<td>-</td>
<td>Mix of ring breath and NH$_2$ rock</td>
</tr>
<tr>
<td>1264 (22)</td>
<td>1251.183</td>
<td>Ring stretch + CN str</td>
</tr>
<tr>
<td>1335 (10)</td>
<td>-</td>
<td>Ring stretch + CN str</td>
</tr>
<tr>
<td>1356 (18)</td>
<td>-</td>
<td>Ring stretch + CN str</td>
</tr>
<tr>
<td>1366 (72)</td>
<td>-</td>
<td>Ring stretch</td>
</tr>
<tr>
<td>1416 (25)</td>
<td>1369.409</td>
<td>NCH bend + CN str</td>
</tr>
<tr>
<td>1434 (4)</td>
<td>1440.000</td>
<td>CC str + CN str (on bridging C)</td>
</tr>
<tr>
<td>1498 (13)</td>
<td>-</td>
<td>CN str</td>
</tr>
<tr>
<td>1513 (82)</td>
<td>1522.234</td>
<td>CN str (in 5-ring)</td>
</tr>
<tr>
<td>1605 (4)</td>
<td>-</td>
<td>NH$_2$ bend (scissor)</td>
</tr>
<tr>
<td>1636 (24)</td>
<td>1618.222</td>
<td>CN and CC str</td>
</tr>
<tr>
<td>1660</td>
<td>-</td>
<td>C-NH$_2$ str</td>
</tr>
</tbody>
</table>
Table 3A. Table of the Raman peaks of Cytosine.

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Experimental</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>768 (31)</td>
<td>-</td>
<td>Ring stretch</td>
</tr>
<tr>
<td>-</td>
<td>823.152</td>
<td>Unassigned</td>
</tr>
<tr>
<td>-</td>
<td>1068.000</td>
<td>Unassigned</td>
</tr>
<tr>
<td>1120 (10)</td>
<td>-</td>
<td>CCH bend + CNH Bend + CC str + CN str</td>
</tr>
<tr>
<td>1208 (8)</td>
<td>1202.234</td>
<td>CCH bend + CNH bend + CC str + CN str</td>
</tr>
<tr>
<td>1261 (15)</td>
<td>-</td>
<td>CN str</td>
</tr>
<tr>
<td>-</td>
<td>1300.000</td>
<td>Unassigned</td>
</tr>
<tr>
<td>1350 (6)</td>
<td>1373.334</td>
<td>CC str + CCH bend</td>
</tr>
<tr>
<td>1439 (6)</td>
<td>1450.000</td>
<td>CC str + CN str</td>
</tr>
<tr>
<td>1498 (5)</td>
<td>1499.492</td>
<td>C-NH2 str</td>
</tr>
<tr>
<td>1566 (21)</td>
<td>-</td>
<td>Ring str kekule</td>
</tr>
<tr>
<td>1626 (10)</td>
<td>1605.111</td>
<td>NH2 scissor</td>
</tr>
<tr>
<td>1684 (16)</td>
<td>1668.000</td>
<td>CC str</td>
</tr>
<tr>
<td>1757 (33)</td>
<td>1739.026</td>
<td>CO str</td>
</tr>
</tbody>
</table>
Table 4A. Table of the Raman peaks of Guanine

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Experimental</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>625 (28)</td>
<td>-</td>
<td>Ring stretch</td>
</tr>
<tr>
<td></td>
<td>730.475</td>
<td>In phase ring stretching</td>
</tr>
<tr>
<td></td>
<td>823.000</td>
<td>Unassigned</td>
</tr>
<tr>
<td>945 (6)</td>
<td>-</td>
<td>CN2 bend</td>
</tr>
<tr>
<td></td>
<td>975.520</td>
<td>NH str + NC str</td>
</tr>
<tr>
<td>1043 (4)</td>
<td>-</td>
<td>CN str</td>
</tr>
<tr>
<td>1065 (7)</td>
<td>-</td>
<td>CN str</td>
</tr>
<tr>
<td></td>
<td>1210.080</td>
<td>CN str + NH str</td>
</tr>
<tr>
<td>1301 (21)</td>
<td>1272.000</td>
<td>NCH bend</td>
</tr>
<tr>
<td>1328 (5)</td>
<td>-</td>
<td>NCH bend</td>
</tr>
<tr>
<td>1360 (6)</td>
<td>1368.000</td>
<td>CC + CN str on the bridging C</td>
</tr>
<tr>
<td>1384 (96)</td>
<td>-</td>
<td>CN str + CNH bend</td>
</tr>
<tr>
<td>1438 (16)</td>
<td>1451.920</td>
<td>CC + CN str</td>
</tr>
<tr>
<td>1509 (124)</td>
<td>1513.000</td>
<td>CN str</td>
</tr>
<tr>
<td>1553 (27)</td>
<td>1586.350</td>
<td>CN str</td>
</tr>
<tr>
<td>1602 (16)</td>
<td>-</td>
<td>NH2 scissor mixed with other str</td>
</tr>
<tr>
<td>1609 (98)</td>
<td>-</td>
<td>NH2 scissor mixed with other str</td>
</tr>
<tr>
<td>1652 (52)</td>
<td>-</td>
<td>NH2 scissor mixed with other str</td>
</tr>
<tr>
<td>1782 (51)</td>
<td>1731.640</td>
<td>CO str</td>
</tr>
<tr>
<td></td>
<td>2226.000</td>
<td>Unassigned</td>
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**Table 5A.** Table of the Raman peaks of Thymine

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Experimental</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>623.000</td>
<td>Unassigned</td>
</tr>
<tr>
<td>735 (18)</td>
<td>723, 759</td>
<td>Ring str</td>
</tr>
<tr>
<td>802 (5)</td>
<td>-</td>
<td>Ring str</td>
</tr>
<tr>
<td>-</td>
<td>872.193</td>
<td>CN str + NH str + CC str</td>
</tr>
<tr>
<td>963 (5)</td>
<td>-</td>
<td>Ring str</td>
</tr>
<tr>
<td>910 (1)</td>
<td>-</td>
<td>CH out-plane wag</td>
</tr>
<tr>
<td>-</td>
<td>1069.690</td>
<td>CCH3 rocking</td>
</tr>
<tr>
<td>-</td>
<td>1286.000</td>
<td>Ring str + CH bend</td>
</tr>
<tr>
<td>1367 (29)</td>
<td>-</td>
<td>CC str + CCH bend</td>
</tr>
<tr>
<td>1406 (9)</td>
<td>1413.980</td>
<td>CH3 deformation</td>
</tr>
<tr>
<td>1495 (21)</td>
<td>-</td>
<td>CN str + CNH bend</td>
</tr>
<tr>
<td>-</td>
<td>1547.000</td>
<td>Unassigned</td>
</tr>
<tr>
<td>-</td>
<td>1629.450</td>
<td>Unassigned</td>
</tr>
<tr>
<td>1700 (40)</td>
<td>1668.000</td>
<td>CC str + CCH bend</td>
</tr>
<tr>
<td>1743 (53)</td>
<td>-</td>
<td>CO str</td>
</tr>
<tr>
<td>1787 (22)</td>
<td>-</td>
<td>CO str (C in –NCN-)</td>
</tr>
<tr>
<td>-</td>
<td>1823.000</td>
<td>Unassigned</td>
</tr>
</tbody>
</table>
### Table 6A. Table of the Raman peaks of Rhodamine 6G

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Experimental</th>
<th>Assignment</th>
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<tbody>
<tr>
<td>-</td>
<td>623.000</td>
<td>Unassigned</td>
</tr>
<tr>
<td>735 (18)</td>
<td>723, 759</td>
<td>Ring str</td>
</tr>
<tr>
<td>802 (5)</td>
<td>-</td>
<td>Ring str</td>
</tr>
<tr>
<td>-</td>
<td>872.193</td>
<td>CN str + NH str + CC str</td>
</tr>
<tr>
<td>963 (5)</td>
<td>-</td>
<td>Ring str</td>
</tr>
<tr>
<td>910 (1)</td>
<td>-</td>
<td>CH out-plane wag</td>
</tr>
<tr>
<td>-</td>
<td>1069.690</td>
<td>CCH3 rocking</td>
</tr>
<tr>
<td>-</td>
<td>1286.000</td>
<td>Ring str + CH bend</td>
</tr>
<tr>
<td>1367 (29)</td>
<td>-</td>
<td>CC str + CCH bend</td>
</tr>
<tr>
<td>1406 (9)</td>
<td>1413.980</td>
<td>CH3 deformation</td>
</tr>
<tr>
<td>1495 (21)</td>
<td>-</td>
<td>CN str + CNH bend</td>
</tr>
<tr>
<td>-</td>
<td>1547.000</td>
<td>Unassigned</td>
</tr>
<tr>
<td>-</td>
<td>1629.450</td>
<td>Unassigned</td>
</tr>
<tr>
<td>1700 (40)</td>
<td>1668.000</td>
<td>CC str + CCH bend</td>
</tr>
<tr>
<td>1743 (53)</td>
<td>-</td>
<td>CO str</td>
</tr>
<tr>
<td>1787 (22)</td>
<td>-</td>
<td>CO str (C in –N=NC-)</td>
</tr>
<tr>
<td>-</td>
<td>1823.000</td>
<td>Unassigned</td>
</tr>
</tbody>
</table>
Table 7A. Table of the Raman peaks of poly(3-hexylthiophene-2,5-diyl)

<table>
<thead>
<tr>
<th>Ensemble</th>
<th>Single Molecule</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>592</td>
<td>614</td>
<td>Ring deformation</td>
</tr>
<tr>
<td>719</td>
<td></td>
<td>C-S-C deformation</td>
</tr>
<tr>
<td>754</td>
<td>742</td>
<td>Ring deformation C-S-C</td>
</tr>
<tr>
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