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Publication Date
2014

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RIVERSIDE

Fundamental Study and Practical Applications of Composite Colloidal Nanostructures

A Dissertation submitted in partial satisfaction
of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

by

James Andrew Goebl

December 2014

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Acknowledgements

First, I would like to thank my advisor, Prof. Yadong Yin, for his training and mentoring throughout my graduate career. I have learned so much in my time in his lab, and I am in his debt for the opportunity to study under him.

I would also like to thank my co-authors for their contributions to the research presented in this dissertation, including Dr. Qiao Zhang and Dr. Le He for their work on the marker experiment project (published in Angewandte Chemie), Yiding Liu, Sandy Wong, and Prof. Serkan Zorba for their assistance on the magnetic mirrors research, as well as Dr. Jibong Joo and Michael Dahl for their help with the photocatalysis project (published in Catalysis Today).

I am also greatly appreciative of the fellow lab members I have worked with over the years, as well as the undergraduate and high school researchers who assisted me with my work.

I am also grateful for assistance at the UCR microscopy facility from the staff at CFAMM, Dr. Krassimir Bozhilov and Steven McDaniel. I would also like to acknowledge the help of Krisanto Pranata with using the ICP instrument in the UCR Chemistry Department.

Finally, I would like to thank the institutions responsible for financially supporting this work, including the National Science Foundation (award number 1308587), the U.S. Department of Energy (DE-FG02-09ER16096), and the Cottrell Corporation for Science Advancement, as well as UCR for the DYP fellowship.
In recent years, nanomaterials, defined as materials with a size of < 100 nm in at least one dimension, have attracted widespread interest due to their promise in many applications. Due to their small sizes, nanoparticles exhibit unique properties not found in their bulk counterparts, such as superparamagnetism in magnetic nanoparticles, as well as quantized plasma oscillations, leading to well-defined extinction peaks, in metal nanoparticles. Although many fabrication techniques exist to produce these unique materials, colloidal nanomaterials are of particular importance due to their low cost and ready scalability, and their easy suspension in solutions. Current research focuses on improving syntheses and developing new types of materials with novel properties, as well as studying the underlying mechanisms behind their growth in solution.

One area of investigation involves producing composite nanomaterials, which contain two or more different nanoscale components. By making a composite material, it is
possible to produce a material which possesses the properties of all of its components, or even a material with entirely new properties. Composite materials can also be produced as intermediates, often with one material acting as a sacrificial template which is later removed, to produce a material with a morphology unattainable with conventional synthesis.

In this work, a variety of uses have been explored for colloidal nanoscale composites. First, the mechanism for the seeded growth of 2D silver nanoplates was studied through a marker experiment. Prior to growth, a thin layer of gold was deposited on the plate edges, which defined the original boundary of the nanoplate seed, allowing easy observation of the direction of growth and making it possible to explain previously observed shape transitions during this process. In later work, gold microplates were conjugated to amine-terminated magnetic nanoparticles to create a material which was both anisotropic, magnetic, and highly reflective. This composite was studied as a micron-size actuated mirror system, which was found to have a fast magnetic response and good optical contrast between the “on” and “off” states. Finally, a gold-titania core-shell composite was developed, which proved resistant to high-temperature sintering and was able to photocatalytically produce hydrogen from ethanol.
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Chapter 1

Introduction to Composite Colloidal Nanomaterials

1.1 Background of Colloidal Nanomaterials

1.1.1 Nanomaterials Fabrication

Nanomaterials have attracted great interest in recent years due to their many unique features, including fluorescence, superparamagnetism, surface plasmon resonance, and catalytic efficiency. These properties have in turn been leveraged for a variety of applications, including analyte detection, cancer thermotherapy, biological imaging, and photonics. The unique properties of nanomaterials are derived from their small sizes, which by definition must be < 100 nm in at least one dimension. As materials shrink in size, they approach the quantum regime, which leads to properties not seen in their bulk counterparts. For instance, when CdSe is reduced to sizes below 5 nm, it can exhibit quantum confinement of excitons, producing a size-dependent fluorescence and becoming a “quantum dot.” Similar nanoscale effects can also be seen in magnetic nanomaterials, which exhibit superparamagnetism below a critical size in the nanometer range, as well as in nanoscale metal particles, which exhibit both size and shape dependent changes in their optical extinction due to the coupling of plasma oscillations on their surfaces with incident light.

In order to produce such materials, typically one of two general approaches is used, top-down or bottom-up. Top-down synthesis involves starting with a bulk material and reducing it into nanoscale pieces or features. Common examples include ball-milling,
which a bulk material is simply ground into a nanopowder, and photolithography, in which the starting material is covered with a patterned mask and is selectively etched, after which the mask is removed to leave behind a material with nanoscale features. Bottom-up synthesis produces nanomaterials in reverse fashion, by combining atoms in a precise manner until a defined nanostructure is formed. Deposition techniques, such as sputtering, chemical vapor deposition, and molecular beam epitaxy all fall under this category, as well as electrochemical synthesis.

While these methods are all effective for producing nanostructured materials, and are widely used both in research and industry, they share one critical disadvantage: high cost. Most of these techniques require sophisticated equipment to successfully produce nanomaterials, and such fabrication is often performed in a clean room. Photolithography typically requires numerous templating and etching steps, and deposition techniques often require long periods of time to produce significant amounts of material, as they typically involve only depositing a few atoms at a time. The complex nature of these processes can also cause difficulty in scaling them up to produce industrial quantities of nanomaterials. While this drawback is acceptable for high-value products like microchips, it is impractical for many other useful goods like optical coatings and paints, which must be produced in larger amounts.

1.1.2 Colloidal Nanomaterials Synthesis

Fortunately, an additional method, which has not yet been mentioned here, holds the key to resolving these issues: colloidal synthesis. The colloidal synthesis of nanomaterials is more rudimentary than the aforementioned techniques, in that it
generally involves no other equipment beyond what is found in a typical chemistry or biology laboratory. In order to synthesize bulk solids, a reaction to produce the desired compound is simply performed in solution to yield large, polydisperse particles of the product. However, producing nanoscale materials is more difficult, as the stability of a solid particle greatly decreases as its size is reduced,\(^{15}\) as shown in Equation 1.1:

\[
E_p = E_b (1 - d/D)
\]

Where \(E_p\) is the cohesive energy of the particle, \(E_b\) is the bulk cohesive energy, \(d\) is the diameter of one atom of the particle, and \(D\) is the overall particle diameter. At large to moderate values of particle diameter, the cohesive energy of the particle remains close to that of the bulk, but at extremely small sizes, typically of just a few nanometers, the particle cohesive energy begins to plummet and the particle becomes unstable. This resultant instability is due to the extremely high surface area of nanoparticles, which causes a large portion of their constituent atoms to be located at the surface. Unlike the atoms in the center of the material, which are fully bonded to adjacent atoms in a continuous network, the atoms on the material surface are exposed and have dangling bonds.

To rectify this stability issue, the energy at the nanoparticle surface must be lowered, and this is typically accomplished by using a surfactant.\(^{16}\) A surfactant is a compound which lowers the energy of an interface between two phases; in this case, the solid colloidal particle and the surrounding liquid solution. Usually, least one end of the surfactant is able to coordinate with the dangling bonds on the nanoparticle surface, with the other end being highly soluble (either hydrophobic or hydrophilic) in the reaction.
solvent. Ultimately, the solution-phase synthesis of a material in the presence of an appropriate surfactant allows the fabrication of a stable colloid which can be suspended in the surrounding solution.

Colloidal nanomaterials possess major advantages over nanomaterials produced by other means. Because they can be synthesized in solution, often in a single processing step, common chemistry equipment is all that is necessary to produce colloidal particles. Furthermore, although there are some challenges involved, scaling up these processes is often a matter of simply increasing the volume of the system while making minor changes to the reaction formulation. Because these nanomaterials are colloids, they can be handled in solutions and are more easily incorporated into applications in which dispersability is required, notably biological systems. The final major advantage of colloidal synthesis is that it can be used to produce structures which are simply not obtainable with other methods, due to the unique properties of colloidal systems. Overall, colloidal nanomaterials, largely due to their low cost and easy scalability, possess significant advantages over classes of nanomaterials, which is the driving force behind ongoing research into their synthesis and applications.

1.2 Types of Colloidal Nanomaterials

At the present stage of development of the field of colloidal nanoparticle synthesis, colloidal nanoparticles comprising almost every material have been produced, featuring a broad array of properties. It is now genuinely possible to choose an element on the periodic table and quickly develop or find in the literature a synthesis for nanoparticles containing that element, often with numerous shapes and sizes. Thus, covering all of the
common types of colloidal nanomaterials would be beyond the scope of this dissertation, so discussion will center on a few important categories of nanomaterials relevant to the work presented here.

1.2.1 Plasmonic Nanomaterials

Plasmonic nanomaterials derive their unique properties from surface plasmon resonance (SPR), a phenomenon in which plasma oscillations along the interface of a metal and a dielectric interact with incident light such that the frequency of these oscillations matches that of the wave. SPR is described by Equation 1.2 as:

\[ \beta = k \sqrt{\varepsilon_\text{m} n_s^2 / (\varepsilon_\text{m} + n_s^2)} \]

Where \( \beta \) is the propagation constant for the plasma wave along the interface of the metal and its surroundings, \( k \) is the free space wave number, \( \varepsilon_\text{m} \) is the dielectric constant of the metal (\( \varepsilon_\text{m} = \varepsilon_\text{mr} + i\varepsilon_\text{mi} \)), and \( n_s \) is the refractive index of the surrounding medium. SPR can occur if \( \varepsilon_\text{mr} < -n_s^2 \). As shown in this equation, SPR is sensitive to both the material comprising the nanoparticle as well as the material surrounding the particle. Generally, this process is exclusive to metals, although more recently it has also been observed to occur in semiconductors in the NIR region. The most commonly utilized materials in this field are Au, Ag, and Cu, which exhibit strong plasmonic responses in the visible region of the electromagnetic spectrum. Although these SPRs can be observed in bulk metals, they simply manifest as the well-known metallic “shine” to an observer, due to the many possible plasma oscillations which may occur to scatter light throughout the visible spectrum. However, at the nanoscale, SPR is strongly affected by the particle size and shape, and the extinction band (or bands) becomes much narrower and controllable.
Due to their unique color properties, which can be shifted by various environmental perturbations, plasmonic materials are currently being investigated for a wide range of applications, particularly for biological sensing applications.

1.2.2 Silver Nanoplates

Among plasmonic nanomaterials, silver nanoplates are presently the focus of intensive study due to their excellent and highly tunable plasmonic properties. While gold has traditionally been a more popular plasmonic material, largely due to its greater chemical stability, silver has several inherent advantages. Besides its significantly lower materials cost, silver also has an SPR which is orders of magnitude greater than that of gold. Also importantly, silver is much easier to synthesize in a controlled manner, and thus a larger array of precise nanoparticle morphologies can be obtained.

Typically, silver nanoplates are synthesized by a reduction method in the presence of a growth directing surfactant, usually trisodium citrate (TSC), resulting in a colorful solution with two significant SPR peaks, as shown in Fig. 1.1a. The major peak is due to the resonance of the in plane dipole, while the minor peak is caused by the in plane quadrupole. When the conditions for this synthesis are varied, a wide variety of sizes and aspect ratios can be obtained, creating nanoplates with a plethora of colors, as demonstrated in Fig. 1.1b. In order to produce silver nanoplates with a specific plasmon band for an application, it is thus of great importance to have a high degree of control over the size and shape of the particles.

Recently, a method was developed for growing silver nanoplates with a wide range of aspect ratios, ranging from < 10 to > 300. Instead of relying solely on a direct synthesis,
Figure 1.1 Typical UV-vis spectrum of silver nanoplates a). Silver nanoplate samples featuring a wide array of colors due to varied SPR properties derived from their morphology.
this method utilized small silver nanoplates as seeds, with TSC added as a growth
directing reagent. When Ag\(^+\) was slowly added to the seed solution, the plates gradually
grew to progressively larger diameters. Due to the presence of TSC, which selectively
adsorbed to the (111) surfaces on the faces of the nanoplates, silver deposition was
restricted to the plate edges. The result was silver plate growth that occurred almost
exclusively in the lateral directions, producing plates with extremely high aspect ratios
that would be impossible to obtain via direct synthesis. However, an unexplained
reversible shape change occurred during the seeded growth, in which the plates would
transition from their original triangular shape to a rounded or hexagonal morphology,
after which they would revert back to a triangular shape. This morphology change is
depicted in Fig. 1.2. Although this phenomenon was initially ignored, it was highly
relevant to understanding the mechanism behind the plate growth. As discussed later in
this chapter, this shape change was investigated thoroughly and some intriguing results
were obtained.

1.2.3 Magnetic Nanoparticles

Magnetic nanoparticles have attracted major attention in recent years due to their
ability to be physically manipulated with an applied magnetic field. When a magnetic
field is applied to a magnetic nanoparticle, it develops a magnetic dipole parallel to the
applied field.\(^{25}\) The dipoles of adjacent particles will then interact, and the force exerted
on one particle by another is described as:

\[
F = [3(1 - 3\cos^2\alpha)m^2/d^4] \cdot r
\]

Figure 1.2 Silver nanoplates exhibiting reversible shape transition during seeded growth. The amount of growth solution added increases from a) to c).
Where \( \alpha \) is the angle of the applied field, \( m \) is the magnetic moment, \( d \) is the center-center distance, and \( r \) is the unit vector parallel to the line connecting the two particle centers. As can be seen in the equation, the dipole-dipole force is strongly dependent on the angle of the applied magnetic field, such that the force is attractive when \( \alpha < 54.09^\circ \) and repulsive when \( \alpha > 54.09^\circ \). Therefore, if the magnetic field is sufficiently strong to overcome thermal fluctuations, the magnetic nanoparticles will be driven to align with the applied magnetic field into 1D structures. This feature makes them useful for a variety of applications; they are particularly effective when harnessed to manipulate objects, such as in the case of the magnetic separation of a colloid or microbiological sample from a solution. Magnetic field is a convenient stimulus, because it requires no direct contact with the solution and magnetic particles respond rapidly to the applied field.

Of particular importance are superparamagnetic nanoparticles, which exhibit strong magnetic moments when under the influence of an applied field and no net moment when the field is removed. For a single magnetic nanoparticle, this property is described in Equation 1.4 as:

\[
\tau_n = \tau_0 \exp \left( \frac{KV}{k_bT} \right)
\]

Where \( \tau_n \) (the Néel relaxation time) is the average time required for a particle’s magnetization to flip due to thermal fluctuations, \( \tau_0 \) is a length of time characteristic of the material called the attempt time, \( K \) is the magnetic anisotropy of the particle, \( V \) is the particle volume, \( k_b \) is Boltzmann’s constant, and \( T \) is the temperature. As can be seen
from the equation, for an extremely large (bulk) particle volume, $\tau_n$ becomes very large, such that a solution of these particles will retain a net magnetic moment in a given direction indefinitely, and remain permanently magnetized as a ferromagnetic solution. However, at very small particle volumes, typically < 50 nm, $\tau_n$ becomes very small, and as a result a solution of these particles will rapidly revert to having no net magnetic moment once a magnetic stimulus is removed. Thus, magnetic nanoparticles can exhibit superparamagnetic behavior, which makes it possible to effectively turn the magnetic behavior “on” and “off.”

1.2.4 Manipulation of Magnetic and Nonmagnetic Particles

As stated previously, when a magnetic field is applied to a solution of superparamagnetic nanoparticles, they will align into 1D structures parallel to the magnetic field. This property can be used to great effect to align magnetic structures in a controlled manner. For instance, if the size of the magnetic particles is within the range of 100-200 nm, they can be assembled into tunable photonic chains, such that incident light of a precise wavelength can be reflected via Bragg reflection. Additionally, magnetic nanoparticles can also be harnessed to manipulate non magnetic materials as well. One method for accomplishing such assembly is to disperse the nonmagnetic material in a ferrofluid, which is a concentrated solution of superparamagnetic nanoparticles. When a magnetic field is applied to the system, the nonmagnetic material acts as a series of “nonmagnetic holes,” around which the ferrofluid becomes aligned. As a result, they require a nonmagnetic moment in the reverse direction of the field, which is given by:

\[
m_v = -V\chi_{\text{eff}} H
\]
Where $m_n$ is the nonmagnetic moment, $V$ is the nonmagnetic particle volume, $\chi_{\text{eff}}$ is the magnetic susceptibility of the ferrofluid, and $H$ is the strength of the applied magnetic field. Due to this acquired nonmagnetic moment, nonmagnetic particles can also be aligned in a magnetic field. When the use of a ferrofluid is undesirable, however, a simpler method for magnetic alignment of a nonmagnetic material is to affix it to magnetic nanoparticles, mimicking the same process. This technique is used later in this work to great effect.

1.2.5 Photocatalytic Nanoparticles

Another major class of functional nanomaterial is that of nanocatalysts.\(^4\) By virtue of their small size, ready dispersibility, and extremely high surface to volume ratio, nanoparticles make ideal heterogeneous catalysts for many important reactions. Such materials have been known for a long time and are in widespread use in industry. As nanocatalysts represent too broad of a topic to discuss in this space, the focus here will be on photocatalytic nanomaterials.

Since photoinduced water splitting was first discovered using crystalline TiO\(_2\),\(^{29}\) photocatalysis has been an area of strong interest due to its promise as a means to harness solar energy to produce unlimited supplies of renewable fuels. In a typical catalyst design, depicted in Fig 1.3, a semiconducting material with a band gap in the UV, visible, or NIR region is dispersed in an aqueous or alcohol-based solution and irradiated with sunlight. The incident light is absorbed by the semiconductor to produce electrons and holes, which subsequently diffuse to the surface of the material to induce oxidation and reduction reactions to produce fuel.\(^{30}\) Typically, a noble metal co-catalyst is also
Figure 1.3 Schematic for the operation of a typical Au/TiO$_2$ nanoscale photocatalytic system in which ethanol is reformed via incident irradiation to produce hydrogen and acetaldehyde.
incorporated into the design in order to lower the overpotential for hydrogen reduction and improve the separation of charge carriers to enhance photocatalytic efficiency. By virtue of their small size and high surface area, nanomaterials are highly suitable for this application, as they can be made highly dispersible in reaction solutions and have numerous exposed catalytic sites.

Although TiO$_2$ has a large band gap (~3.2 eV), rendering it unable absorb light outside of the UV portion of the solar spectrum, it is by far the most popular photocatalyst material.\textsuperscript{31} Despite its narrow absorption range, TiO$_2$ is low cost, non-toxic and is extremely stable even under the harsh conditions common during electrochemical reactions. Its limited solar absorption range, its major weakness, can be rectified via doping to narrow its effective band gap, or by the incorporation of a plasmonic metal nanoparticle, which not only serve as a cocatalyst for hydrogen reduction but can also absorb visible light through its SPR band.\textsuperscript{32} For this reason, gold is commonly seen in this system, as it is chemically stable and has a strong SPR in the visible region of the electromagnetic spectrum.

One issue with this system, however, is the tendency of the Au component to aggregate during processing steps. Typically, a gold titania photocatalyst is produced by depositing Au on the TiO$_2$ particle surface, which allows it to diffuse freely and sinter,\textsuperscript{33} especially at high temperatures. In later sections of this work, a method is described for producing a new structural configuration for this photocatalyst system, which can protect the gold component against sintering, even at high processing temperatures.
1.3 Use of Composite Nanomaterials in This Work

1.3.1 Composite Nanomaterials

Composite nanomaterials comprise a class of nanomaterials in which two or more distinct components are combined into one. Such materials can be prepared through a number of methods, including simple conjugation, impregnation, or coatings. The primary benefit of preparing composite nanomaterials is the potential to produce a new material with multiple functionalities which might otherwise be hard to obtain. A classic example is magnetic fluorescent nanoparticles. While it is extremely difficult to prepare a nanomaterial that exhibits both bright visible fluorescence and superparamagnetism, by combining a fluorescent material with a magnetic material, followed by a coating to hold them together, it is possible to produce a new nanomaterial with both properties.

Composites can be utilized in other capacities as well. For instance, a binary composite can be prepared as an intermediate step in a complex synthesis. An example of this would be sacrificial templating to produce hollow nanostructures. In this scheme, a one material is coated onto another, after which the original material in the core of the composite is selectively removed, leaving behind a hollow structure of the second material. This technique can prove very useful, as it is often difficult to produce a hollow nanomaterial directly. Another use for producing a composite is to provide contrast against a different component. Due to the fact that a transmission electron microscope (TEM) micrograph will show different levels of darkness depending on the Z of the atoms of the material being studied, two materials within a composite which contains different elements will appear differently when observed. This system can be useful in determining the
The fundamental properties of a nanomaterial, as the progress of physical or chemical changes to the material can be observed directly.

1.3.2 Utilization of Composite Nanomaterials

In Chapter 2 of this dissertation, a composite particle is produced for the purpose of studying the growth mechanism of a nanomaterial.\(^37\) As previously discussed at the end of Section 1.2.2, the seeded growth of silver nanoplates is known to exhibit an unusual phenomenon, in which the shape of the plate changes from triangular, to hexagonal/rounded, and back during the course of the reaction. *Prima facie*, this reversible shape change is difficult to explain, as typically a nanomaterial undergoes a shape to produce a more thermodynamically stable structure, which is not conducive to reversal under steadily maintained conditions. The challenge in this case is the fact that it is difficult to see where new silver deposition occurs relative to the original structure of the plate, making it hard to pinpoint the mechanism.

In this work, a solution is found by creating a composite and utilizing it in a marker experiment. By depositing a thin layer of gold on the edges of the nanoplate seeds, it was possible to demarcate the boundaries of the seed particle. It was then discovered that the deposited ring of gold did not interfere with normal seeded growth of the plates. When plates grown from the gold-rimmed seeds were observed via TEM, the large difference in Z between gold and silver provided substantial contrast between the two materials, making it possible to compare the original dimensions and orientation of the plate with the subsequent silver growth. As a result of this new ability to compare the original plate structure with the new morphology, it was possible to determine a mechanism for the
seeded growth of the nanoplates. Thus, creating a composite nanomaterial was an effective means to study the underlying principles of silver nanoplate growth.

In Chapter 3, a composite is demonstrated which combines the functionalities of two separate nano- and microscale components, gold microplates and superparamagnetic iron oxide nanoparticles. Gold microplates feature a high aspect ratio (~ 100) and are extremely reflective due to their broad, flat metallic planar surfaces, while Fe$_2$O$_3$ nanoparticles are superparamagnetic. By themselves both particles make poor dynamic optical components, as gold microplates cannot be easily actuated and iron oxide nanoparticles are isotropic, such that little difference in the optical properties of the solution are evident regardless of the applied magnetic field angle.

In this work, a method was developed to functionalize iron oxide nanoparticles with amine groups. When the amine-terminated particles were mixed with gold microplates, a strong coordinating bond was formed between the amine moieties and the microplate surface, resulting in a strong attachment. The composite material is both strongly magnetic and highly reflective, and can be aligned in a magnetic field such that the major axis of the structure is oriented parallel to the magnetic field. Due to the highly anisotropic nature of the microplates, when the composite microstructure is rotated with a magnetic field, the result is a strong contrast between different orientations in the form of “on” and “off” states. By creating a composite from an optical and a magnetic material, a new material with readily tunable optical properties is formed.

In Chapter 4, an Au@TiO$_2$ core-shell composite is utilized for the photocatalytic production of hydrogen.$^{38}$ Although gold and titania are often seen in the form of
composite photocatalysts, one potential issue is the sintering of Au during processing of the material. Because small Au nanoparticles readily fuse together at elevated temperatures,\textsuperscript{33} it is often difficult to produce a gold-titania heterostructure that contains small, uniformly sized gold nanoparticles. This issue not only affects the performance of the photocatalyst in actual applications, but makes it difficult to perform systematic studies of this system due to the variance in gold particle size depending on the Au loading percent and processing conditions.

This problem is resolved, however, by producing a core-shell composite, in which the Au nanoparticle component is coated with a layer of titania. Unlike a traditional Au-TiO\textsubscript{2} composite photocatalyst, in which the Au is deposited on the TiO\textsubscript{2} surface and is free to sinter, the core-shell system creates a physical barrier around the Au nanoparticle, effectively preventing sintering of the metal even under high-temperature processing conditions. Thus, a core-shell photocatalyst design was able to solve the stability issues of the Au-TiO\textsubscript{2} photocatalyst system and allow for a more controlled photocatalysis study.

In this dissertation, a wide variety of nanomaterials is explored, touching on a number of applications. However, the common thread behind all of this work lies in the development and utilization of nanoscale composites to solve materials science problems. Synthesizing composite nanomaterials combines the useful attributes of multiple constituents, allowing the development of materials with completely new features and applications. Through the continued development of such materials, new classes of functional materials can be developed and previously difficult challenges solved.
1.4 References


Chapter 2

Monitoring the Shape Evolution of Silver Nanoplates:
A Marker Study

2.1 Introduction

In the past two decades, substantial efforts have been made to control the shape of nanostructured materials because of their strong shape dependent chemical and physical properties. Classic examples include semiconductor nanorods that exhibit linearly polarized emission\(^1\) and metal nanoplates that show tunable surface plasmon resonance.\(^2\)

To study the mechanism of shape evolution during nanostructure growth, aliquots are often removed from a reacting solution and the particles are analyzed using imaging techniques such as transmission electron microscopy (TEM). However, as it is impossible to continuously monitor the growth of one particular particle, this catch-and-see method may not be able to unambiguously reveal the exact growth mechanism. One example is an interesting triangle-round-hexagon-triangle shape transition that we have recently observed during the seeded growth of silver nanoplates.\(^3\) This transition has been very difficult to explain based on the simple observation of the shape change. In this work we demonstrate that the marker technique, which was widely used in studying atomic diffusion phenomena,\(^4\) can be successfully adopted to help outline the original boundaries of the silver nanoplate, provide a clear picture of plate growth, and give insight into possible structures for the original seed and final product.
Since the seminal paper by Mirkin and coworkers, colloidal silver nanoplates have been intensively studied due to their exceptional plasmonic properties, which lend them to numerous applications including surface enhanced Raman scattering (SERS). Silver nanoplates can be synthesized using either photoinduced or chemical reduction of Ag⁺ in the presence or absence of seeds, each of which produces uniform samples of triangular nanoplates with relatively high yield. Further research has investigated ways to alter the morphology of nanoplates using either chemical or photomediated etching, which enables precise control over the optical properties. We and other groups have also explored seeded growth processes for synthesizing larger nanoplates with very high aspect ratios. In addition to the development of various syntheses for silver nanoplates, the study of their structure and the mechanism which induces this structure has also received much attention. It is generally understood that the plates are fcc crystals containing single {111} facets on their two planar surfaces. The facet composition of the nanoplate sides is less clear, although recent high-resolution TEM experiments indicate a mixture of {100} and {111} facets. Forbidden reflections of 1/3{422} are observed, which are attributed to internal stacking faults which are parallel to the nanoplate surface. While the effects of surfactants and other synthetic conditions are significant, these defects are believed to be the driving factor behind the 2-dimensional anisotropic structure of the nanoplates.
2.2 Experimental

2.2.1 Seeded Growth of Ag Nanoplates.

Nanoplate seeds are first synthesized using a modified chemical reduction method based on previous reports.\textsuperscript{10a} Seeded growth is then performed using a technique developed precedently in our group.\textsuperscript{3} First, the as-synthesized seeds are collected by centrifugation for 14 minutes at 15,000 rpm and then re-suspended in a solution comprising DI H\textsubscript{2}O (20 mL), TSC (75 mM, 250 \textmu L), and L-ascorbic acid (AA, 0.1 M, 750 \textmu L). The nanoplate solution is stirred rapidly, after which growth is initiated by using a syringe pump to slowly add (0.2 mL/minute) silver growth solution, containing silver nitrate (1 mM, 40 mL), citric acid (0.1 M, 250 \textmu L), and TSC (1.5 mM, 200 \textmu L). At various points, the injection is stopped and aliquots are removed to enable observation of the shape changes during growth.

2.2.2 Nanoplate Growth Using Au Frames as Seeds

Nanoplate seeds are washed in a manner to that described above, except they are suspended in a solution containing H\textsubscript{2}O (25 mL), TSC (30 mM, 1.5 mL) and PVP (29,000 MW, 0.7 mM, 1.5 mL). The solution is then stirred rapidly and heated to 60 °C, after which HAuCl\textsubscript{4} (1 mM, 800 \textmu L) is slowly added. The frames are collected by centrifugation for 14 minutes at 15,000 rpm, and then re-suspended in a solution containing H\textsubscript{2}O (20 mL), TSC (75 mM, 250 \textmu L) and AA (0.1 M, 750 \textmu L). Backfilling and growth is initiated by adding the same silver growth solution at the same rate used in the case of silver plate seeds via syringe pump, and ceases upon stopping the injection.
2.2.3 Nanoplate Growth in the Presence of PVP

For the PVP-directed growth of silver nanoplates, only one half of a typical nanoplate seed synthesis is used (all reagent volumes decreased by 50%). The seed nanoplates are collected by centrifuging the mixture of the seed solution and additional PVP (55,000 MW, 0.25 g) for 12 minutes at 11,000 rpm, re-suspended in a PVP solution (55,000 MW, 10 mM, 10 mL), centrifuged again to remove the supernatant, and re-suspended in a solution of DI water (18.9 mL), PVP (10 mM, 1.1 mL) and AA (0.1 M, 375 μL). The extra washing step is critical for removing residual TSC. Growth is induced by adding silver nitrate growth solution (1 mM, containing no citrate, unlike previous cases) using a syringe pump at a rate of 0.2 mL/minute, and can be stopped by terminating the injection. At intervals of 10 mL of growth solution addition, 20 mL of the solution is removed and DI water (8.9 mL), PVP (10 mM, 1.1 mL), and AA (0.1 M, 375 μL) are added to enable continued silver reduction and hasten the growth process.

2.3 Results and Discussion

2.3.1 Seeded Growth

Recently, we reported a procedure for the synthesis of large Ag nanoplates using previously synthesized smaller plates as seeds. When Ag⁺ was added to silver nanoplate seeds in the presence of reducing agent and citrate ion, the citrate selectively hindered growth on the {111} planar surface, allowing growth to occur only at the edges to produce high aspect ratio nanoplates. We observed in the early stages of Ag addition that the plates became largely circular, which was attributed to instability of the original seeds resulting from the removal of the stabilizing ligand PVP. However, when this synthesis
Figure 2.1  Step by step growth of large silver nanoplates using small plates as seeds. Images show a) the original sample and the sample after the addition of b) 0.3 μmol, c) 2 μmol, d) 3 μmol, e) 4.5 μmol, and f) 9.5 μmol of silver nitrate.
Figure 2.2 Normalized UV-Vis extinction spectra of samples after the addition of increasing amounts of Ag nitrate: a) Blueshift and b) subsequent redshift of Ag nanoplate-seeded sample during growth; c) blueshift and d) redshift of nanoframe-seeded sample during growth.
is performed using more uniform triangular plates as seeds, for which washing is unnecessary due to modification of the seed synthesis to exclude PVP, a notable shape transition from triangular to circular can still be observed, depicted in representative TEM images in Fig. 2.1. Initially, the nanoplate seeds are mostly triangular (Fig. 2.1a), but after only a small amount of silver precursor is added to the solution the plates become noticeably more rounded (Fig. 2.1b). With further Ag addition, the nanoplates become roughly hexagonal (Fig. 2.1c), and finally return to their original triangular shape, albeit larger (Fig. 2.1f). The shape transition is confirmed by plasmonic shifts in the corresponding extinction spectra (Fig. 2.2). In the early stages of growth, the plasmon band blueshifts (Fig. 2.2a), which is indicative of the plates becoming more rounded as has been noted in previous literature.\cite{18} Later, the spectrum begins to redshift as a result of the plates growing laterally and is consistent with our prior observations concerning seeded nanoplate growth.

2.3.2 Marker Experiment

Although cursory examination of the step by step growth of the plates confirms that a shape change occurs, similar to those observed in recent publications from other groups,\cite{13, 19} more in-depth study is necessary to fully comprehend its underlying causes and mechanism. To acquire a better understanding of this system, we have performed a straightforward but informative marker experiment using galvanic replacement by gold,\cite{20} followed by seeded growth using the resulting nanoframe structure as a seed. Due to the significant difference in atomic number between silver and gold and their small lattice mismatch, gold has suitable contrast with silver and can also readily seed the growth of
silver, making it a suitable choice of marker. By partially replacing the silver in the nanoplate with gold, we can outline the original boundaries of the silver nanoplate, clarifying observations of subsequent seeded growth.

Interestingly, frames can act as seeds for large silver plate growth in a nearly identical manner to that of normal small silver plates, depicted in TEM images in Fig. 2.3. Upon the addition of silver growth solution, the gold nanoframes are initially backfilled with silver (Figs. 2.3b and 2.3c) and then undergo normal growth into large nanoplates (Figs. 2.3d-2.3f). Backfilling occurs first due to deposition at high-energy facets in the frame interior, after which lateral outward growth proceeds. This assertion is supported by corresponding extinction spectra, which depict the initial blueshift (Fig. 2.2c) and ensuing redshift (Fig. 2.2d) of the in-plane dipole of the nanoframes, which are indicative of silver deposition and increasing aspect ratio, respectively.

Crucially, the presence of gold frames as markers enables significant insights to be obtained from TEM observations during growth. After the initial backfilling step, the frame/plates grow outward in the same manner as silver nanoplates, undergoing a similar shape transition and ultimately returning to a triangular morphology (Figs. 2.3d-2.3f). Notably, throughout the various stages of outward growth, there is a preference for deposition on the edges of the frame/plates with little to none occurring at the corners, causing the triangular to circular/hexagonal transition. As more silver is deposited, the shape returns to triangular due to new corners being formed at the deposition sites (Fig. 2.3e), resulting in a sample of frame/plates in which the majority contain an embedded frame pointed 180° relative to the orientation of the silver plate. Further silver addition
Figure 2.3 Step by step growth of silver nanoplates using Au nanoframes as seeds. Images depict a) Au nanoframe seeds and frame/plates after the addition of b) 0.3 μmol, c) 3 μmol, d) 4.1 μmol, e) 7.5 μmol, and f) 10.75 μmol of silver nitrate.
results in the plate growing larger but does not induce additional shape changes (Fig. 2.3f), which is consistent with our previous work. These results indicate that the cause of the observed shape transition is the almost exclusive deposition of silver on the nanoplate edges.

### 2.3.3 Model for Shape Transition

Clarification of the means of shape transition leads to the additional question of why the transition occurs in this manner. The fact that deposition occurs selectively and only one shape change takes place during growth implies that the original nanoplate seed structure changes to a more stable morphology over the course of the growth process. To explain the selective edge deposition, we employ a structural model proposed recently by Kelly and coworkers.\(^{16}\) Based on HRTEM experiments, they ascertained that Ag nanoplates are comprised of two \textit{fcc} regions of different thicknesses sandwiching an \textit{hcp} layer originating from a series of internal stacking faults. To explain this observation, they devised a model in which each nanoplate edge consists of a \{111\} facet and a \{100\} facet of different sizes, which is possible due to the twinning in the center of the plate. Thus, a truncated triangular nanoplate should comprise six edges, half containing a larger \{111\} facet and half with a dominant \{100\} facet (Fig. 2.4, center structure). This model suggests that the familiar shape of silver nanoplates is due to preferential deposition on the less thermodynamically stable \{100\} dominated edges, producing a triangular structure bounded by \{111\} dominated edges.

Using this model, the mechanism behind our observations can readily be explained, illustrated in Fig. 2.4. Initially, the sample consists of triangular nanoplates with \{100\}
Figure 2.4 Schematic illustration of the structural change of Ag nanoplates during seeded growth. Preferential silver deposition on the \{100\} dominated edges of the seeds leads to a rounded or hexagonal intermediate with a mix of \{100\} and \{111\} dominated edges, after which further silver deposition produces a larger triangular plate with \{111\} dominated edges.
dominated edges. Although this is less thermodynamically stable than a \{111\} dominated configuration, it occurs because borohydride is used as the reducing agent during the seed synthesis, causing a rapid reaction. As a result, the plate structure is controlled by kinetic conditions, which favor \{100\} dominated edges. This assumption can also explain why other groups have had difficulty obtaining stable nanoplates without PVP or another \{100\} specific ligand.\textsuperscript{10a} During subsequent seeded growth, ascorbic acid is used as the reducing agent and the Ag\textsuperscript{+} concentration is deliberately kept low, leading to a slower reaction rate, creating conditions in which thermodynamic considerations are of primary importance. As a result, a structure with the highest percentage of \{111\} surfaces is the most stable configuration, leading to selective deposition on \{100\} dominated sides and causing the observed shape transition to a structure with \{111\} dominated edges.

2.3.4 PVP Control Experiment

In order to further support this assertion, we performed an additional experiment in which seeded growth was performed in the presence of PVP and absence of citrate. While citrate primarily adheres to \{111\} surfaces, PVP selectively blocks growth on \{100\} surfaces and as such, should interfere with the lateral growth of the plates as well as the accompanying shape transition. Fig. 5 depicts the step by step seeded growth of silver nanoplates in the presence of PVP. Because of the lack of citrate in the system, growth on the planar surfaces of the nanoplates is more favorable and they become substantially thicker during the course of the reaction, evidenced by the greater contrast compared with citrate grown plates. Additionally, a triangular to hexagonal to triangular
Figure 2.5 Stepwise growth of silver nanoplates with PVP present. Images portray the sample after the addition of a) 2.5 μmol, b) 10 μmol, c) 20 μmol, d) 30 μmol, e) 40 μmol, and f) 50 μmol of silver nitrate.
shape transition is still evident and the plates also grow laterally, indicating that in spite of the different surfactant system some deposition still occurs on the plate edges and the overall mechanism of growth is the same. These results are consistent with those obtained by Xia et al from a similar synthesis.\textsuperscript{13} Most significantly, however, is the fact that the shape transition is “delayed” in the sense that the PVP grown plates are much larger (~ 530 nm edge length) than their citrate grown counterparts (~ 90 nm edge length) at the point at which the growth transition is nearly complete. This observation implies the seeds have \{100\} dominated edges, because while a shape transition still occurs, it is effectively retarded by the selective \{100\} adhesion of PVP, which decreases the energy difference between \{111\} and \{100\} surfaces on the seed. The smaller energy difference enables substantial deposition at both the \{100\} and \{111\} surfaces on the plate edges, resulting in a “slower” shape transition due to the decreased preference for \{100\} deposition. These results further support that the shape transition is motivated by the thermodynamically induced switch from a nanoprism with \{100\} dominated sides to a structure with \{111\} dominated edges.

2.4 Conclusion

In summary, we have presented a new marker technique which uses embedded Au frames as markers to define the original boundaries of small silver nanoplates utilized in a seeded growth reaction, clarifying the nature of an observed reversible shape change which takes place during growth. Based on the opposing orientations of the inner frame and surrounding plate, it is apparent that the shape transition is caused by the nanoplates morphing from structures with primarily \{100\} facets on their edges into more
thermodynamically stable structures with \{111\} dominated edges via selective silver deposition on \{100\} facets. This study is significant because unlike previous works, it gives an unambiguous picture of the manner in which plate growth occurs as well as insight into possible structures for the original seeds and final products. Using this approach, we have determined that the plate does not grow evenly in two dimensions as was previously believed, but in fact grows exclusively in certain directions, inducing a transformation into a larger plate with a similar appearance but a substantially different surface structure. This transition would be very difficult to observe with conventional methods but with the addition of a gold marker it becomes readily apparent. We believe the marker technique might have the potential to become a general tool to help determine the mechanism of shape evolution of nanostructures.
2.5 References


Chapter 3

Magnetically Tunable Colloidal Micromirrors

3.1 Introduction

Over the past decade, research in nanomaterials synthesis has grown to produce innovative materials with a broad array of functional properties, including superparamagnetism,\(^1\) plasmonic properties,\(^2\) and fluorescence,\(^3\) as well as an assortment of anisotropic structures, such as rods,\(^4\) cubes,\(^5\) octahedra,\(^6\) and plates.\(^7\) By taking advantage of this expanding library of nanomaterials, subsequent research efforts have focused on producing nanostructures with a combination of properties by incorporating two or more materials with different properties into a single composite. In this vein, there is much recent work involving the pairing of magnetic particles with anisotropic nano- and micromaterials via chemical bonding through surface moieties; this imbues the resultant hybrid material with both anisotropic and magnetic properties, effectively creating a magnetically anisotropic nanostructure which also possesses the properties of the original base material. Examples include magnetically actuated Au nanorods,\(^8\) which by virtue of the anisotropic nature of the Au rods and the magnetic property of the adjacent magnetic nanoparticles represent a tunable plasmonic system which holds promise for novel optical devices.

A class of magnetic-anisotropic composites of particular interest is that of magnetically functionalized microplates, which comprise a highly anisotropic 2D sheet or microplate with chemically adhered magnetic nanoparticles. Such a system has been explored by Studart and coworkers,\(^9\) who were able to use an applied magnetic field to adjust the plate
orientation prior to curing in a ceramic-polymer composite film, allowing control of the
toughness of the material based on the plate orientation relative to the film surface. The
one potential disadvantage of this system, however, is that it uses the electrostatic
attraction of highly oppositely charged microplates and magnetic particles to render the
plates magnetic, which may limit the possibility for this method to be extended to other
materials.

Similar 2D systems have been developed for magnetically tunable optical mirror
applications, utilizing reflective metal microplates suspended in a ferrofluid as
anisotropic optical valves,\textsuperscript{11,12} the orientation of which could be adjusted by changing the
direction of the applied magnetic field to alter the transparency and reflectivity of the
system. While the optical properties of these systems could be tuned, they unfortunately
suffered from the fact that the ferrofluid component is highly anisotropic at the
concentration necessary to control the plate orientation, and as a result the system permits
only limited light transmittance, which is less than optimal for an optical material.

In this work, we present a solution to the issues suffered from previous magnetically
tunable optical microplate systems, in which high aspect ratio (~ 97) Au microplates are
rendered magnetically functional via conjugation to amine terminated superparamagnetic
Fe\textsubscript{3}O\textsubscript{3}@SiO\textsubscript{2} nanoparticles, which strongly adhere to the Au surface due to the lone pair
of the amine attacking dangling metallic Au bonds. Since only a thin layer of magnetic
material is necessary to render the plates magnetic, they retain their high reflectivity and
their surrounding solution remains transparent, while their optical properties can be
readily and rapidly tuned by applying a magnetic field oriented in varying directions. We
expect this new material to be useful for both smart window technologies as well as novel microscale optical systems.

3.2 Experimental

3.2.1 Reagents

Methanol, denatured ethanol, isopropanol, cyclohexane, and acetone were purchased from Fisher. Poly(diallyldimethylammonium) chloride (PDDA, MW = 400,000-500,000, 20 wt % in H₂O), oleic acid, iron pentacarbonyl, and tetramethylammonium hydroxide (TMAH, 25 wt % in H₂O) were purchased from Sigma-Aldrich. HAuCl₄ trihydrate, octadecene (ODE), tetraethylorthosilicate (TEOS), NH₃ (~ 29 wt % in H₂O), and (3-aminopropyl)triethoxysilane (APTES) were purchased from Acros. Salicylic acid was purchased from MP Biomedicals, and agarose was purchased from Biorad. All reagents were used as received without additional purification.

3.2.2 Au Plate Synthesis

Au microplates were synthesized using an acid-mediated reduction method modified from a previous publication.¹² In a typical synthesis, DI water (70.2 mL), PDDA (1.8 mL, diluted to 2 wt % in H₂O), and salicylic acid (8 mL, 18.1 mM) were heated to 80 °C in an Erlenmeyer flask under stirring. The reaction was then initiated by adding HAuCl₄ (3.2 mL, 48.6 mM), after which the solution was stirred for 10 min to yield a turbid, golden solution. The solution was then cooled and centrifuged in six 15 mL centrifuge tubes at 4000 rpm for 4 min, after which the supernatant was removed with a pipette. The remaining contents of the six tubes were then combined into a single 50 mL centrifuge tube, and were washed in water 8 times for 5 minutes at 11000 rpm. Finally,
the Au microplates were dispersed in 2 mL of DI H₂O to produce a suspension with a final concentration of 55 mg/1 mL. The resulting microplates had an average diameter of 7.28 ± 2.61 µm and a thickness of ~ 75 nm.

3.2.3 Ferrofluid Synthesis

Fe₂O₃ ferrofluid was synthesized using a previously published high-temperature oil-phase protocol. First, 100 mL of ODE was mixed with 9 mL of oleic acid and degassed with N₂ for 1 hr at 100 °C. Next, 2 mL of iron pentacarbonyl was injected into the solution, which was then heated to 295 °C, leading to a color change in the solution from orange to black. After the solution became black and completely opaque, the solution was further heated for 1 hr at the same temperature. Afterwards, the solution was cooled to 200 °C and air was gently bubbled in for 2 hrs. Finally, the solution was cooled to room temperature, yielding a ferrofluid consisting of 16.5 nm Fe₂O₃ nanocrystals. The particles were then processed by dividing the solution into ten 50 mL centrifuge tubes, and then 20 mL of acetone to each. The samples were then centrifuged for 6 min at 10000 rpm, after which the supernatant was removed and the samples were combined into two tubes, to which 10 mL of cyclohexane was added (to each) to disperse the pellets, followed by 20 mL of acetone. The samples were then centrifuged for 5 min at 9000 rpm, and were washed one more time. Finally, the samples were combined and dispersed in 10 mL of cyclohexane.

3.2.4 Ferrofluid Phase Transfer

The ferrofluid was subsequently transferred to the aqueous phase using a published method. Briefly, 1 mL (10 %) of the ferrofluid in cyclohexane was added to 3 mL of
acetone and placed in two 2 mL centrifuge tubes. The sample was sonicated for 1 min, then centrifuged for 5 min at 15000 rpm, after which the acetone was removed and the sample was allowed to sit uncapped for 10 min to evaporate residual acetone. The samples were then dispersed in 10 mL of TMAH (diluted to 10 wt % in H₂O), sonicated for 15 min, and aged for 1 hr, after which the sample was separated out with a magnet and the solution was decanted. 5 mL of TMAH was then added to the sample, which was sonicated for 15 min and aged for 1 hr; the sample was again separated out with a magnet and the TMAH was poured off. This process was repeated one more time, after which the sample was finally dispersed in 5 mL of DI H₂O.

3.2.5 Amine Functionalization of Ferrofluid

The Fe₂O₃ particles were coated with SiO₂ using a modified Stöber process.¹⁵ Typically, 1 mL (20%) of the ferrofluid sample dispersed in H₂O was added to 20 mL of denatured ethanol, to which 2 mL of DI H₂O and 50 μL of TEOS was also added. The reaction was then initiated by adding NH₃ (1 mL, 29 wt % in H₂O), and the solution was covered and stirred for 20 minutes. Afterwards, the solution was centrifuged 4 times and washed with ethanol 3 times via centrifugation at 15000 rpm for 10 min. The sample was dispersed in 5 mL of isopropanol, then washed in methanol 4 times, isopropanol 2 times, and finally dispersed in 5 mL of isopropanol. Likewise, amine functionalization of the nanoparticles followed a previous recipe. The sample was then added to 15 mL of isopropanol in a 3-neck flask connected to a water-cooled jacketed condenser, to which 5 μL of APTES was added. The solution was then heated to reflux at 80 °C for 2 hrs, cooled, and washed 3 times in ethanol, until finally the sample was suspended in 5 mL of
DI H₂O to produce an aqueous, amine-functionalized ferrofluid with a concentration of 6 mg/1 mL.

### 3.2.6 Magnetic Functionalization of Au Microplates

To render the Au microplates magnetic, 25-500 μL of the aqueous ferrofluid solution was dispersed in 12 mL of DI H₂O; the solution was mixed and sonicated for 5 min. Next, 500 μL of the Au plate solution was added, and the solution was shaken and sonicated for 30 minutes to ensure the adsorption of the ferrofluid particles onto the Au surface. Afterwards, the solution was centrifuged and decanted, and the magnetized microplates were suspended in 1 mL of DI H₂O for use in performance studies.

### 3.2.7 Microscopy and Photography

Transmission electron microscopy (TEM) was performed using a Philips Technai 12 operated at 120 kV; all TEM samples were prepared via dropcasting. Scanning electron microscopy (SEM) was performed using a Philips XL30 FEG instrument; samples were dropcast on Si wafers. Optical microscopy was performed using a Zeiss Axio Imager A1m. Microplate samples for optical imaging were prepared by diluting a magnetized plate sample 15 times in DI H₂O, then mixing the 120 μL of the diluted sample with 5 μL of aqueous agarose solution (0.5 wt %, stored at 70 °C); the agarose served to reduce precipitation and aggregation of the microplates. The plate sample was then added into a 0.4 mm flat glass capillary (EMS); both ends were sealed using optical glue. The microplates were then rotated by placing a ~2300 G rare earth magnet near the sample and varying its orientation. For photographs of the plates in bulk, the microplate solution was injected into a 3 mm path length homemade cuvette; the cuvettes were made by
placing a rubber plumbing O-ring between two glass slides and gluing them together using epoxy. After the epoxy was cured, the sample could be conveniently injected into the cuvette by piercing the rubber O-ring with a hypodermic needle. Plates were rotated using a ~ 2900 G rare earth magnet at a center-center distance of ~ 5 cm.

3.2.8 Transmittance and Reflectance Measurements

Optical transmittance and reflectance measurements were taken using an Ocean Optics DH-2000-BAL UV-Vis spectrophotometer using the respective attachments. For transmittance measurements, the microplate solution was placed in a sealed 1 mm thick flat glass capillary (EMS). A ~ 2900 G magnet was placed ~ 8.5 cm (center-center distance) beneath the sample and rotated to change the microplate orientation relative to the beam path. For reflectance measurements, the conditions were similar except a 3 mm path length cuvette was used.

3.2.9 Optical Modulation Measurements

Optical modulation measurements were conducted by passing a 635 nm laser through a 3 mm cuvette containing microplate samples with varying magnetic loading. The microplate sample was manipulated using a standard magnetic stir plate operating at 240 rpm, or 4 Hz, which generated a ~20 mT rotating magnetic field to actuate the microplates in a circular fashion, causing the sample to “blink” rapidly. The transmitted intensity was measured via a photodetector connected to an oscilloscope, which recorded the optical modulation over a set time. For each rotation of the stir plate, the microplates underwent two cycles of oscillation.
3.3 Results and Discussion

3.3.1 Magnetic Microplate Synthesis

The Au microplates used in this system (Fig. 3.1a) were prepared using a modified version of a previously published synthesis. Briefly, an aqueous solution of salicylic acid (reducing agent) and high molecular weight PDDA (growth directing surfactant) was heated to 80 °C, after which a solution of HAuCl₄ was added to initiate the reaction. After 5 minutes, the solution was cooled and washed many times to remove residual surfactant covering the surface and the microplate solution was concentrated in DI H₂O for later use. Superparamagnetic Fe₂O₃ nanocrystals were synthesized using a high-temperature oil-phase synthesis. The nanocrystals were subsequently rendered water-soluble, after which they were coated via a modified Stöber process and amine functionalized by depositing APTES on the particle surface; the resultant material is shown in Fig. 3.1b.

In order to render the microplates magnetic, a small amount of amine-functionalized magnetic nanoparticles was dispersed in DI H₂O, after which the Au plates were added. After mixing for a few minutes, the plates became noticeably magnetic due to the strong coordination of the amine with the Au surface (Fig. 3.1c). The magnetic plates were then washed to remove any unattached magnetic particles, and were used for subsequent performance tests. Although there was significant aggregation of the magnetic particles during this process, evident in Figs. 3.1d and 3.1e, the high degree of anisotropy of the microplates and the large size of the plates relative to the magnetic particles effectively results in a conformal coating of magnetic particles on the plate surface. The addition of
Figure 3.1 Dark-field optical micrograph of Au microplates after synthesis and washing a). TEM micrograph of amine-functionalized Fe$_2$O$_3$@SiO$_2$ nanoparticles b). Scheme depicting bonding of magnetic nanoparticle to Au plate surface c). SEM images of Au nanoplates prior to d) and following e) magnetic nanoparticle deposition.
excessive magnetic material resulted in significant aggregation of the microplates and poor optical properties for the system, so only moderate amounts of Fe$_2$O$_3$ were used.

### 3.3.2 Actuation of Microplates

Following conjugation to the magnetic nanoparticles, the Au microplates could then be magnetically manipulated, leading to changes in the optical properties of the bulk system that could easily be observed with the naked eye, as depicted in Fig. 3.2. In the absence of a magnetic stimulus, the plate solution exhibited a shiny, golden color reminiscent of bulk Au. Upon the application of a magnetic field oriented parallel to the viewing direction, the plates rapidly aligned with the applied field and the solution became transparent due to the minimized cross section of the microplates, with a faint brown tint due to the native color of Fe$_2$O$_3$. As the applied magnetic field was rotated such that the angle between the magnetic field and the viewing direction ($\theta$) increased, the plate solution transitioned from being clear and transparent to opaque and reflective. This optical change was due to the plates in the solution becoming aligned perpendicular to the viewing angle ($\theta = 90^\circ$), which maximized the projected cross section of the plates to reduce transmitted light, as well as direct more reflected light back to the observer.

The driving force behind the rotation of the magnetic plates is the minimization of potential energy within the applied magnetic field. This potential energy can be described in an equation recently derived by Studart and coworkers$^{16}$ (Equation 3.1), in which a circular, disc-like ellipsoid is used to approximate a non magnetic plate coated with magnetic particles:
Figure 3.2 Photographs of a bulk magnetic microplate solution under an applied magnetic field with various orientations (θ) relative to the viewing direction.
\[
U_{\text{plate}} = \frac{2}{3} \pi \left[ (a + \Delta)(b + \Delta)^2 - ab^2 \right] \mu_0 \left[ \chi_p^2 / (\chi_p + 1) \right] H_0^2 \sin^2 \theta
\]

Where \( U_{\text{plate}} \) is the magnetic potential energy of the microplate, \( 2a \) is the plate thickness, \( 2b \) is the plate diameter, \( \Delta \) is the thickness of the magnetic nanoparticle coating, \( \mu_0 \) is the permeability of free space, \( \chi_p \) is the susceptibility of the Fe\(_2\)O\(_3\), \( H_0 \) is the strength of the applied magnetic field, and \( \theta \) is the angle between the major axis of the plate and the magnetic field direction. \( \Delta \) is determined by the number of Fe\(_2\)O\(_3\) monolayers attached to the plate surface, while \( \chi_p \) is dependent on the percentage of the plate surface which is coated, such that \( \chi_p = C_{ff} \chi_{ff} \), where \( \chi_{ff} \) is the bulk susceptibility of Fe\(_2\)O\(_3\) and \( C_{ff} \) ranges from 0 to 1. The magnetic potential energy of the system is minimized when \( \theta = 0 \), and maximized when \( \theta = 90 \), as summarized in Equation 2:

\[
U_{\text{plate}} \propto \theta
\]

Thus, the impetus behind the magnetic field-induced rotation is the minimization of the magnetic potential energy, which is accomplished when the plates rotate such that their major axis is aligned with the applied magnetic field.

For observation of plate actuation on the microscale, a solution of plates was mixed with a small amount of agarose to stabilize the plates in solution, and placed in a flat 0.4 mm glass capillary under an optical microscope. A magnetic field was applied using a handheld rare earth magnet, and the resulting rotation of the microplate sample could readily be observed in bright field mode, as shown in the optical microscopy images in Fig. 3.3. Confirming the observations of the bulk solution, the plates align parallel to the applied field, as shown in Figs. 3.3a and 3.3c, in which the field is oriented parallel and perpendicular to the viewing direction, respectively. Despite the adsorbed Fe\(_2\)O\(_3\), the
Figure 3.3 Optical microscopy images of magnetic microplates under an applied magnetic field with varying orientations relative to the viewing direction; 0° a), 45° b) and 90° c). Optical modulation of microplate samples with different volumes of magnetic particles loaded under a rotating magnetic field; 200 µL (blue), 125 µL (red), 75 µL (green), and 25 µL (purple).
plates retain their high reflectivity and are quite shiny when oriented perpendicular to the viewer. The reflectivity of the plates has a strong directional dependence, however, which can be seen in Fig. 3.3b, in which the plates are rotated at a $45^\circ$ angle. In this image, the plates appear nearly as dark as in Fig. 3.3a and scattered light can be seen to one side, indicating that light is being preferentially scattered away from the viewer.

3.3.3 Optical Modulation

The response of the plates to the applied magnetic field was quite rapid and could be quantitatively measured with a simple experimental setup. Briefly, a laser was shone through a cuvette containing plate sample into a photodetector, which produced an output on a connected oscilloscope. The plate sample was rotated at 4 Hz using a magnetic stir plate, and the resulting changes in transmittance were recorded over time. Microplate samples with varying degrees of magnetic loading were tested for comparison, as shown in Fig. 3.3d. As shown in the figure, the plate samples displayed excellent optical modulation properties, with values reaching up to 37%. The optical performance was strongly dependent on the extent of magnetic loading, with higher values leading to enhanced performance and low loadings producing little response. However, as stated previously, too much magnetic loading resulted in aggregation of the sample, leading to limited dispersibility and poor optical properties. Optical modulation could be detected at frequencies of up to ~20 Hz, the maximum speed of the stir plate, although this resulted in unwanted vibrations of the sample that made accurate measurements impossible.
3.3.4 Reflectance and Transmittance Measurements

In addition to the optical modulation, the absorbance and transmittance of the plate sample were measured at various applied magnetic field angles. As shown in Fig. 3.4a, the reflectance of the plate suspension was strongly dependent on the magnetic field angle, ranging from 1 % when $\theta = 0^\circ$ to 6 % when $\theta = 90^\circ$, which represents a six fold difference between the maximum and minimum reflectance states. Interestingly, the relationship between $\theta$ and reflectance, shown in Fig. 3.4c, is highly nonlinear, with almost no change when $\theta$ was increased from 0-60°, and a dramatic surge in reflectance as $\theta$ was increased from 60° to 90°. This nonlinear dependence was primarily due to the highly directional nature of the reflectance property of the microplates; because of the small size of the pinhole on the reflectometer used, when the plates were rotated such that they were only slightly out of perpendicular, they would reflect light away from the pinhole at a slight angle, resulting in minimal signal being detected. This result implies that the plates actually behave as true microscale mirrors that can reflect light with high precision.

The transmittance of the sample, shown in Fig. 3.4b, could be varied from 42 % to 72 % as $\theta$ was decreased from 90° to 0°, and was largely due to changes in the projected cross section of the plates, which was minimized when the major axis was aligned with the beam path and maximized when the plates were oriented perpendicular to the beam path. In contrast to the reflectance measurements, the relationship between $\theta$ and transmittance, shown in Fig. 3.4d, exhibited a reverse trend, in which there was a
Figure 3.4 Optical spectra of magnetic microplate solution exposed to a magnetic field oriented at various angles relative to the path of the incident light. Sample UV-Vis reflectance a) and transmittance b) at various magnetic field orientations. Percent reflectance c) and percent transmittance d) of the sample versus magnetic field orientation. Dashed line in d) is the geometrically predicted percent transmittance normalized to the maximum and minimum transmittance of the sample.
dramatic change in transmittance as $\theta$ was varied from 0-60° and almost no change from 60-90°. This nonlinear relationship can be explained by simple geometric calculations of the projected area of the microplates. Assuming a triangular plate, which is rotated along the axis of its height, its projected area is simply its geometric area. However, as the plate is rotated along its vertical axis, its projected area becomes dependent on the angle between the viewing direction and its horizontal axis, as shown in Equation 3:

$$A_{\text{projected}} = \frac{1}{2} b \sin(\theta) h$$

Where $A_{\text{projected}}$ is the projected plate area, $b$ and $h$ are the base and height length, respectively, and $\theta$ is the angle between the horizontal axis of the plate and the viewing direction. This equation dictates a nonlinear relationship between $\theta$ and plate cross section, which results in the observed change in transmittance versus $\theta$. The ratio of $A_{\text{projected}}/A$ was calculated for different values of $\theta$, normalized to the maximum value for percent transmittance obtained experimentally, and plotted in Fig. 3.4d. As can be seen, the geometrically calculated trend mirrors the experimental data, supporting the possibility the relationship between $\theta$ and transmittance is due to geometric factors.

3.4 Conclusion

In this study, we have developed a straightforward method for conjugating Au microplates with amine-terminated Fe$_2$O$_3$ nanoparticles. Due to the strong interactions between the Au surface and the amine groups on the Fe$_2$O$_3$, the magnetic particles become tightly bound to the Au surface when the two particles are mixed, producing a composite possessing both the magnetic property of the Fe$_2$O$_3$, as well as the high degree of anisotropy and reflectance of the Au microplates. The resulting material exhibits a
response on the order of Hz when a magnetic field is applied, and will rotate to align with the direction of the applied field in order to minimize the magnetic potential energy of the system. In spite of the adsorbed magnetic particles, the material remains highly reflective, allowing it to retain good contrast between the “on” and “off” states. By applying a magnetic field at various angles, the transmittance of the system can be varied by a factor of ~2, while the reflectance can be varied by a factor of 6. We believe that this system has the potential for integration into a number of current tunable optical applications, such as smart windows, as well as possible new types of tunable optical systems operating at the microscale.
3.5 References


4.1 Introduction

Since the seminal discovery of TiO\(_2\) photocatalyzed water splitting by Honda and Fujishima in 1972,\(^1\) tremendous research efforts have been devoted to studying and improving this reaction to develop a renewable source of hydrogen fuel. However, due to the large electrochemical potential necessary to produce O\(_2\) from water and the limited visible light absorption of titania, a practical water-splitting photocatalyst with suitable efficiency has yet to be developed. More recently, research has focused on lower hanging fruit, namely, the photocatalysis of short chain alcohols to produce their corresponding aldehydes as well as H\(_2\).\(^2\) Due to their relatively favorable oxidation potentials, short-chain alcohols have long been used as sacrificial reagents in water-splitting studies.\(^3\) While alcohols would not be preferable as fuel feedstocks over water, the potential to photochemically convert them into commercially useful aldehydes represents a potentially less energy-intensive means for chemical production. For instance, acetaldehyde, of which a million tons is produced annually,\(^4\) is produced by the oxidation of ethylene. If this process could be replaced by the photocatalysis of ethanol, the energy necessary to produce this commercial chemical could be greatly reduced. Thus, it is of great interest to develop such photochemistry to produce less energy-intensive industrial chemical manufacturing processes.
Typically, a TiO$_2$ photocatalyst comprises a nanoscale TiO$_2$ support with a deposited metal co-catalyst, which acts as an electron well and lowers the overpotential necessary for hydrogen reduction.$^5$ While such a catalyst design is quite effective, it is limited in that the deposited metal is vulnerable to sintering during high-temperature processing,$^2$ often reducing the catalyst efficiency and making it difficult to compare the efficiency of various catalyst designs after calcination, and limits the available techniques for catalyst preparation. In order to combat this problem, a variety of yolk-shell and core-shell catalysts have been developed,$^6$-$^8$ in which the metal catalyst particles are encapsulated in a solid or hollow shell of a metal oxide. This configuration provides a physical barrier against sintering, allowing much greater calcination temperatures to be utilized without the risk of sintering and in the case of a solid shell, greater contact area between the metal and titania. However, while there are a number of methods for coating metal nanoparticles with TiO$_2$,$^9$-$^{12}$ few are able to coat nanoparticles of a sufficiently small size or with a tunable shell thickness so as to be useable in designing an optimized catalyst configuration. There are even fewer studies in which the TiO$_2$ shells were rendered crystalline and the particles tested in a photocatalytic system,$^{13}$-$^{14}$ and to our knowledge there are no other studies which vary the shell thickness and crystallinity of a core-shell metal@TiO$_2$ system and test the resulting effect on its photocatalytic properties.

In this work, we have developed an effective method for producing small core-shell Au@TiO$_2$ photocatalysts with a wide range of shell thicknesses and corresponding Au loading percents. We compared the photocatalytic activity of each of the various samples for the UV-driven photocatalytic reforming of ethanol to produce H$_2$. Additionally, we
compared the efficiency of several Au@TiO₂ catalysts processed at various calcination temperatures, and examined their crystallinity and porosity to explain their relative efficiencies.

4.2 Experimental

4.2.1 Gold Core Preparation

The Au co-catalyst cores were prepared by a seeded growth reaction previously developed in our group. Briefly, 600 µL of a freshly prepared, iced, aqueous solution of 0.1 M NaBH₄ was added to a flask containing 19.8 mL of DI H₂O, 200 µL of 25 mM trisodium citrate (TSC), and 1.97 µL of a 1g/1mL stock of HAuCl₄·3H₂O under rapid stirring to produce small Au seeds (~3-5 nm). The resulting solution was aged for 2 hours prior to use. A growth solution was then prepared containing 20 mL of H₂O, 4 mL of 5 wt % polyvinylpyrrolidone (PVP, MW=3500), 1.5 mL of 0.2 M KI, 2 mL of 0.1 M ascorbic acid, and 60 µL of 1g/1mL HAuCl₄·3H₂O stock. 2 mL of the seed solution was then added to the growth solution under rapid stirring, producing large (~25 nm) Au particles within 10 minutes. The core solution was then centrifuged 3x for 10 min at 15000 rcf in 50 mL tubes and washed with water, and was ultimately suspended in 20 mL of water. 77 mg of high molecular weight PVP (MW=360,000) was then added, and the solution was stirred overnight and used as a stock. Prior to coating, 3.2 mL of Au cores was concentrated to 0.85 mL via centrifugation in 2 mL tubes at 22000 rcf, at which point the Au cores were ready for coating.
4.2.2 Thin TiO$_2$ Coatings

Au@TiO$_2$ photocatalyst particles were produced by utilizing a sol-gel synthesis, followed by a calcination process, as shown in Fig. 4.1. To coat thin shells of TiO$_2$ on the Au cores, a sol-gel process was used. A reaction solution containing 20 mL of 200 proof ethanol, 4 μL of 20 mM HCl, 95 mg of PVP (MW=360,000), and 0.85 mL of concentrated Au cores was prepared, to which a solution of 50 μL of titanium tetraisopropoxide (TTIP) dissolved in 2.5 mL of 200 proof ethanol was injected at a rate of 0.15 mL/min using a syringe pump. After the injection was completed, the solution was stirred overnight, after which it was washed 2x with 200 proof ethanol, and suspended in 16 mL of 200 proof ethanol.

Subsequent coatings were performed to further increase the thickness of the TiO$_2$ shell. The second coating was performed in a manner similar to the first, except the reaction solution contained 12 mL of 200 proof ethanol, 4 μL of 20 mM HCl, 105 mg of PVP (MW=360,000), 0.4 mL of H$_2$O, and 8 mL (1/2 of the total) of 1x coated Au@TiO$_2$. After injection and reaction in a manner identical to the first coating process, the sample was washed and suspended in 16 mL of 200 proof ethanol.

3x coated particles were produced similarly, using a reaction solution of 8 mL of 200 proof ethanol, 12 mL (75 % of the total) of 2x coated Au@TiO$_2$, 105 mg of PVP (MW=360,000), 4 μL of 20 mM HCl, and 0.2 mL of H$_2$O. After injection and reaction, the sample was washed and suspended in 16 mL of 200 proof ethanol.
Figure 4.1 Scheme for the synthesis and calcination processing of Au@TiO$_2$ core-shell nanoparticle photocatalysts.
4.2.3 Thick TiO₂ Coatings

After three rounds of coating, the Au@TiO₂ samples were large enough to allow utilization of a method for coating large particles with TiO₂ previously developed in our group. In short, two 3x coated Au@TiO₂ samples were concentrated to 20 mL in 200 proof ethanol, and added to a reaction solution of 120 μL of H₂O and 0.1 g of hydroxypropyl cellulose (HPC, MW=80,000). The solution was stirred until the HPC completely dissolved, after which a solution of 0.5 mL titanium tetrabutoxide (TBOT) in 5 mL of 200 proof ethanol was injected at a rate of 0.5 mL/min. After completion of the injection, the solution was briefly stirred, and refluxed for 100 min. After cooling, the solution was washed 3x with 200 proof ethanol, and suspended in 16 mL of 200 proof ethanol.

To produce the thickest coated sample, the previous recipe was followed exactly, except only one 3x coated Au@TiO₂ sample was suspended in 20 mL of 200 proof ethanol instead of two.

4.2.4 Calcination of Au@TiO₂ Samples

Prior to calcination, in order to prevent the fusion of particles, Au@TiO₂ samples were first coated with silica using a modified Stober method. In this procedure, a 16 mL sample of Au@TiO₂ particles was added to a solution of 8 mL of ethanol, 100 μL of 5 wt % PVP (MW=3500), 0.2 mL of tetraethylorthosilicate (TEOS), and 1 mL of H₂O. 4 mL of aqueous ammonium hydroxide solution (30 wt %) was added to initiate the reaction, which was allowed to progress for 1 hr. This process could be scaled up by 6x to produce larger quantities of sample. The resultant SiO₂-coated particles were then
washed 4x and dried under vacuum. Once dried, the Au@TiO$_2$@SiO$_2$ particles were placed in a crucible and calcined for 4 hrs in air at 800 °C.

After the first calcination step, the SiO$_2$ shell was removed by a base etching process. The calcined particles were suspended in a solution of 6 mL of H$_2$O and 4 mL of 0.1g/mL NaOH, which was set on a hotplate set to 90 °C and stirred overnight. This step could also be scaled up. Afterwards, the solution was washed 3x with H$_2$O. The sample was then suspended in 20 mL of 0.05 M HCl solution and agitated for 30 minutes, after which the sample was washed 3x in H$_2$O followed by 2x in ethanol, and then dried under vacuum. The resulting powder was then further calcined for 2 hours at a desired temperature (500-800 °C) to increase the TiO$_2$ crystallinity, and was then used for catalytic experiments and sample characterization.

### 4.2.5 Catalyst Characterization

The metal loading percent was measured using inductively coupled plasma optical emission spectroscopy (ICP) on a Perkin-Elmer Optima 2000 DV instrument. Samples were prepared by dissolving 5 mg of Au@TiO$_2$ catalyst particles in 4 mL of sulfuric acid, heated overnight on a hotplate set to 270 °C, to digest the TiO$_2$ shell. The Au core was subsequently removed by adding 1 mL of freshly prepared aqua regia to the cooled solution (Caution: extremely violent reaction will ensue) under stirring. The resulting solution was then diluted 20x and used in ICP measurements.

Transmission electron microscopy (TEM) micrographs were taken using a Tecnai T12 TEM. Powder X-ray diffraction (XRD) measurements were taken using a Bruker D8 Advance Diffractometer. Adsorption-desorption experiments were performed using a
Quantachrome NOVA 4200e instrument. Subsequent Barrett-Joyner-Halenda (BJH) and Brunauer-Emmett-Teller (BET) calculations utilized the adsorption branch of the isotherm.

4.2.6 Photocatalysis Testing

During the testing of each photocatalyst, 5 mg of Au@TiO$_2$ powder was placed in a cylindrical pyrex reactor and suspended in 50 mL of 200 proof ethanol. The reactor was put under stirring and was placed 5 cm beneath an 8 watt 365 nm UV lamp and put under a continuous N$_2$ flow feeding into an HP 5890 Series II gas chromatograph (GC) with a thermal conductivity detector, using Ar as the carrier gas. After the system was flushed for 1 hr, the UV lamp was turned on and the H$_2$ content of the exhaust stream was measured at 10 min intervals for 2 hours, which was sufficient time for the H$_2$ production rate to plateau at its maximum.

4.3 Results and Discussion

4.3.1 Catalyst Synthesis

In order to coat Au nanoparticles with an initial shell of TiO$_2$, a controlled sol-gel reaction was utilized. The Au particles were inoculated with PVP prior to coating to prevent their aggregation in the ethanol solution, and were made highly concentrated in order to precisely control the amount of water present as a reactant and provide sufficient Au cores for the coating reaction. Dilute HCl was added as a catalyst for TTIP hydrolysis, and the TTIP solution was injected slowly so as to control the reaction kinetics to avoid the self-nucleation of TiO$_2$ particles. Additional coatings were performed in a similar manner to increase the shell thickness and correspondingly
decrease the Au weight %, except with a lower core concentration in the solution and a lower water concentration. These two factors proved to be the most significant in this synthesis. Lowering the core concentration changed the ratio of TTIP precursor to cores, increasing the amount of deposited TiO$_2$. Decreasing the H$_2$O concentration, on the other hand, enhanced the condensation of the TiO$_2$ at the expense of the hydrolysis of TTIP, leading to fewer, larger deposits of TiO$_2$ and thicker coatings. Thus, by controlling these two parameters during subsequent coatings to deposit progressively increasing amounts of TiO$_2$, it was possible to obtain significantly thicker shells without the need for excessive repeated coating steps. After three rounds of coating using this system, the particles became large enough (~100 nm in diameter) to coat with a method previously developed in our group,$^{16}$ which was utilized to produce the thickest coatings.

After Au@TiO$_2$ particles with the desired shell thickness were synthesized, they were coated with SiO$_2$ using a modified Stober method to prevent them from agglomerating during the initial calcination at 800 °C, which converted the TiO$_2$ layer into anatase (Fig. 4.5). The SiO$_2$ shell, while preventing aggregation, has the drawback of limiting the anatase grain size,$^{17}$ so the sample was treated with base to remove the SiO$_2$ and subsequently treated with acid. The acid treatment was performed to enhance the resulting grain size of the TiO$_2$ during a second calcination step,$^{18}$ after which the powder was ready for use in photocatalysis experiments. As shown in Fig. 4.2, core-shell particles with porous, crystalline TiO$_2$ shells, with thicknesses ranging from ~10 nm to 100 nm, could be obtained by performing the desired number of coating steps prior to calcination. The majority of particles consist of one Au core surrounded by a TiO$_2$ shell,
Figure 4.2 TEM images of Au@TiO$_2$ samples of varying shell thicknesses and Au loading amounts. (a) Uncoated Au particles, (b) 72.3 wt% Au, (c) 6.26 wt% Au, (d) 0.731 wt% Au, (e) 0.241 wt% Au, and (f) 0.204 wt% Au. All scale bars are 50 nm.
although a substantial number of particles fused during the second calcination step. Furthermore, the presence of the TiO$_2$ shell appears to prevent aggregation of the Au cores during calcination, enabling a comparison of the catalytic rates of the various samples at a constant Au core size.

**4.3.2 Effect of Au Weight % on Photocatalysis**

In addition to determining the shell thickness, the amount of deposited TiO$_2$ also corresponds to the Au weight % of the sample. The metal loading amount is critical in photocatalysis- as the metal only serves as a co-catalyst, too much will reduce UV light absorption and inhibit the reaction, whereas no metal at all will lead to extremely limited hydrogen production. In order to obtain this value, each sample was digested in acid and the relative abundance of Au and Ti in each sample was measured using ICP, from which the Au weight % was calculated. The samples were then compared for their photocatalytic efficiency for the UV-driven production of H$_2$ from ethanol under a continuous N$_2$ flow feeding into a GC, with which sampling of the exhaust stream was performed every 10 min. The rate of H$_2$ production was plotted versus irradiation time and is shown in Fig. 4.3. As indicated in the graph, the 3x coated sample, with an Au weight % of 0.731 %, exhibited the highest rate of H$_2$ production at 2.170 mL min$^{-1}$. Its high efficiency is due to the fact that it has a low Au weight %, ensuring there is sufficient TiO$_2$ to utilize incident light, while at the same time it possesses a substantially thin shell such that the solution is able to diffuse inward to reach the Au core. As the 0.731 weight % sample appears to straddle the optimum balance between core access and loading %, it was used as the basis for additional studies of the calcination temperature and porosity.
Figure 4.3 Plot comparing $\text{H}_2$ production rate versus time of photocatalysts with different Au wt%.
4.3.3 Effect of Calcination Temperature on Photocatalysis

Typically, the grain size of anatase TiO\textsubscript{2} plays a major role in determining its catalytic properties.\textsuperscript{19} To investigate the effect of TiO\textsubscript{2} grain size, 0.731 weight % Au@TiO\textsubscript{2} samples were calcined at 600, 700, 750, and 800 °C to produce particles with varying degrees of crystallinity, depicted in Fig. 4.4. Even at elevated calcination temperatures, the TiO\textsubscript{2} shells still appear to prevent the Au cores from sintering. XRD spectra of each sample, shown in Fig. 4.5, indicate the presence of metallic Au and anatase TiO\textsubscript{2}, with a small fraction of rutile phase present in the 800 °C sample. The average anatase grain size of each sample was calculated using a full width at half maximum calculation, and is shown in Table 1. As expected, with increasing calcination temperature, the crystallinity of the samples increases.

This set of samples was also tested for photocatalytic activity for UV-driven H\textsubscript{2} production from ethanol, the results of which are shown in Fig. 4.6. Although increased crystallinity in TiO\textsubscript{2} photocatalysts tends to promote improved activity, in this case the opposite occurred. Although the increase in anatase grain size is likely beneficial, it also contributes to decreased core accessibility, which inhibits its use as an H\textsubscript{2} production site. In order to confirm this assumption, BET analysis was conducted to determine the surface area, pore size, and pore volume, displayed in Table 4.1. As the grain size increases, the BET surface area and BJH pore volume decrease by about 50 %, while the BJH pore radius is moderately increased. These results are indicative of decreased porosity, which leads to reduced accessibility of the Au core and thus decreased activity of the more crystalline photocatalyst samples.
Figure 4.4 TEM images of 0.731 Au wt% samples calcined at (a) 600 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C. Scale bar is 50 nm.
Figure 4.5 XRD spectra for 0.731 Au wt% samples calcined at (a) 600 °C, (b) 700 °C, (c) 750 °C, and (d) 800 °C.
<table>
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<th>Calcination Temp. (°C)</th>
<th>Grain Size (nm)</th>
<th>BET Surface Area (m² g⁻¹)</th>
<th>BJH Pore Radius (nm)</th>
<th>BJH Pore Vol. (cm³ g⁻¹)</th>
<th>Max H₂ Rate (mL min⁻¹)</th>
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<td>0.923</td>
</tr>
</tbody>
</table>

Table 4.1 Average grain size, BET surface area, BJH pore size, BJH pore volume, and H₂ production rate of samples calcined at various temperatures.
Figure 4.6 Plot comparing $\text{H}_2$ production rate versus time for photocatalysts with different calcination temperatures.
4.4 Conclusion

In summary, we have developed a convenient sol-gel synthesis and calcination process for producing well-defined crystalline Au@TiO₂ core-shell nanoparticles. The TiO₂ shell acts as a physical barrier during calcination to prevent the Au core from sintering, enabling the study of the properties of catalysts prepared under various conditions without altering the Au size. Core-shell catalysts prepared at various calcination temperatures were tested for their activity for the UV-driven photocatalysis of ethanol to produce H₂, and it was found that a catalyst with an Au weight percent of 0.731 % calcined at 600 °C was the most efficient. The relatively high activity of this photocatalyst was due to the fact that it had a low Au loading amount, as well as a shell that was thin and porous enough to enable diffusion of the solution to the Au core. Although higher calcination temperatures could produce TiO₂ shells with larger grain sizes, resulting diffusion issues decreased the catalyst activity. While we have demonstrated that a core-shell configuration can produce an effective photocatalyst which can resist metal sintering during processing, this architecture is limited by problems with mass transport to the core. We believe that this design can be made much more efficient if a radially oriented porous TiO₂ coating were to be applied to the Au core instead of a randomly oriented porous coating. Such a structure could still be calcined at very high temperatures to improve the shell crystallinity, but would not suffer from hindered diffusion of the solution to the metal core.
4.5 References


