ABSTRACT

ROWE, LAUREL RENE. Morphologically Controlled Overcoating of Gold Nanorods with Silica. (Under the direction of Dr. Joseph B. Tracy).

Gold nanorods (GNRs) are of interest for many applications, most notably for theranostics and biomedical sensing. Encapsulating GNRs in silica (SiO$_2$) via a modified Stöber method enhances their thermal and chemical stability, provides a framework for molecular loading, and introduces a surface that can be readily functionalized. Herein, the synthesis, characterization and reaction mechanism for forming SiO$_2$-overcoated GNRs (SiO$_2$-GNRs) with select morphologies are discussed. Specifically, fully encapsulated SiO$_2$-GNRs, as well as those with distinct SiO$_2$ lobes at the tips of the GNR, are generated. The morphology of the structures is modulated by adjusting the alcohol concentration in the reaction solution. Higher alcohol concentrations are thought to drive reverse condensation mechanisms, whereby condensed SiO$_2$ becomes soluble and is redeposited onto the GNRs, which assist formation of thermodynamically favored arrangements of SiO$_2$ (spheres/lobes). The ability to tailor the morphology of SiO$_2$ on GNRs introduces a framework for site-specific functionalization and self-assembly applications.
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Morphologically Controlled Overcoating of Gold Nanorods with Silica

by
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DEDICATION

I dedicate this thesis to my dad for his never-ending support and love, without whom I would not be the person I am today. Thank you for teaching me to be an independent thinker, to work diligently towards my goals and most importantly to find joy in all that surrounds me.
BIOGRAPHY

Laurel Rene Rowe was born in Charlotte, North Carolina on October 20th, 1991. She was raised in Mooresville, NC where she attended Lake Norman High School and found a new interest for chemistry. She went on to study chemistry at North Carolina State University receiving her bachelor’s degree in 2014. Shortly following, she joined the Department of Materials Science & Engineering at North Carolina State University to pursue her graduate studies.
ACKNOWLEDGMENTS

I would like to thank my adviser Joseph Tracy for his mentorship throughout my time in graduate school; he’s truly dedicated to his students and their success. I would also like to thank my colleagues and other graduate students with whom I’ve had the pleasure of working with over the past year and a half. My family and friends have also been an enormous source of love and support for which I am forever grateful.
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Chapter 1: History and Properties of Colloidal Gold Nanorod Solutions

1.1 History of Colloidal Gold

Gold has been a valuable element for centuries due to its lustrous and tarnish-resistant nature, often symbolizing wealth and power in many societies. Gold doesn’t always exist in a shiny, yellow form, however. Colloidal gold, or dispersions of gold particles on the micrometer or sub-micrometer scale, also exist. Colloidal dispersions of gold exhibit colors ranging from red to blue due to the interaction of light with the particles in solution, and were used as colorants for glass and ceramics dating as far back as the 5th century B.C.\(^1\) The color of such solutions is due largely to the shape and size of the particles that make up the solution.\(^1\) Henceforth, solutions of gold nanorods (GNRs), or anisotropic particles of gold with defined aspect ratios, will be discussed.

1.2 Synthesis of Gold Nanorods

Researchers developed electrochemical techniques to synthesize nanometer-sized clusters of transition metals in the early 1990s.\(^2\) The experimental method for doing such consisted of a standard electrochemical cell, in which application of a current drove oxidation of the bulk metal anode and reduction into small metallic clusters, of oxidation state zero, at the cathode.\(^2\) It was noted that added “ammonium stabilizers” prevented agglomeration of the metallic clusters.\(^2\) This electrochemical method for synthesizing colloidal transition metal solutions was first performed using palladium but was shortly adapted to generate colloidal
gold solutions.\textsuperscript{2,3} Using a gold anode, platinum cathode, and electrolytic solution containing cetyltrimethylammonium bromide (CTAB), a cationic surfactant, researches demonstrated the ability to generate gold nanorods of different aspect ratios (Figure 1).\textsuperscript{3} The specific rod shape was attributed to the use of CTAB.

\textbf{Figure 1.} Transmission electron micrograph of gold nanorods synthesized via electrochemical techniques.\textsuperscript{3}

Shortly following, a seed-mediated growth technique was shown to be successful and became a preferred synthetic method over the electrochemical approach.\textsuperscript{4} Jana et al. demonstrated that GNRs could be made via the addition of gold “seeds” to a “growth” solution.\textsuperscript{4} The aqueous seed solution consisted of gold particles approximately 3.5 nm in size and was made by reducing chloroauric acid (HAuCl\textsubscript{4}) with sodium borohydride.\textsuperscript{4} The prepared seed solution was then added to a growth solution, which led to the deposition of gold onto the
seeds to generate rods. The growth solution was tailored depending on the desired GNR aspect ratio but always contained HAuCl₄, CTAB and ascorbic acid. Ascorbic acid is used in the growth solution because it is a milder reducing agent, reducing gold ions onto preexisting seeds and causing growth into larger particles, as opposed to nucleation of new seeds in solution, as is observed with the stronger reducing agent, sodium borohydride. Some researchers further modified this seed-mediated synthesis by introducing a secondary surfactant to increase yield and homogeneity.

Use of ammonium containing compounds and most commonly, CTAB, is critical in the reaction processes of GNR syntheses. At first, it was believed that cylindrical CTAB micelles in water templated the deposition of gold and was responsible for the ultimate growth into rod-like structures. However, it was found that CTAB micelles do not serve as scaffolds but rather their head groups bind to specific crystallographic faces of gold thereby directing GNR growth. The ammonium head groups of CTAB molecules were observed to preferentially bind to crystallographic faces along the length of a GNR seed, and avoid binding to those faces at the ends or tips of the seeds. This binding specificity promotes gold deposition on the vacant seed tips, those unoccupied by CTAB, and growth along the length of the structure into a rod. It was observed that the CTAB molecules bound to the sides of the GNR form bilayers with one set of ammonium head groups facing inward toward the GNR and the other set facing outward towards the aqueous environment. The alkyl chains of the surfactant molecules, interacting via van der Waals forces, form the innermost part of this bilayer and were found to affect the aspect ratio of resultant GNRs; larger aspect-ratio GNRs can be made from surfactant molecules with longer alkyl chains and vice versa. Techniques
for synthesizing gold nanorods are well established; today’s research aims to further increase the homogeneity and yield of GNR syntheses.

1.3 Optical Properties of Gold Nanorods

One of the most attractive properties of colloidal gold solutions is their color. The range of colors observable among GNR solutions originates from their localized surface plasmon resonances. The surface plasmon effect emanates from the fact that colloidal solutions have particles smaller than the micron scale. Due to their small size, incident electromagnetic radiation can cause the conduction band electrons of gold particles to oscillate. This coherent oscillation of electrons reaches a resonance condition and thus causes light absorption at specific wavelengths. This phenomenon is illustrated in Figure 2.

![Surface plasmon resonance effect](image)

**Figure 2.** Surface plasmon resonance effect.
The localized surface plasmon resonance of GNRs actually causes absorption of light at two distinct wavelengths due to the anisotropic structure of GNRs, and induces electron oscillations both along the length of the rod (longitudinal mode) and across the width or diameter of the rod (transverse mode). These optical phenomena can be visualized by examining the optical absorbance spectrum of a GNR solution (Figure 3). As shown in Figure 3, there are two peaks; the smaller peak at shorter wavelength corresponds to the transverse surface plasmon mode and the larger peak corresponds to the longitudinal surface plasmon mode.

**Figure 3.** Optical absorbance spectrum of a GNR solution illustrating both the transverse and longitudinal surface plasmon modes.

The peak at longer wavelengths corresponds to the longitudinal surface plasmon mode, and is determined by the aspect ratio of the GNR. GNRs with higher aspect ratios absorb at longer wavelengths, while GNRs with lower aspect ratio rods absorb at shorter wavelengths (Figure
The transverse surface plasmon mode generally remains fixed near 530 nm. It is also evident from Figure 4a that changing the aspect ratio of the rod changes the wavelength of light it absorbs, thereby changing the color of the dispersion (Figure 4b).¹

![Figure 4.](image)

**Figure 4.** (a) Optical absorbance spectra of GNRs with different aspect ratios. (b) Solutions of GNRs with different length to diameter dimensions (L/d, aspect ratio).¹

### 1.4 Stabilization of Gold Nanorods

The innate characteristic allowing colloidal solutions to remain well dispersed and resistant to sedimentation is Brownian or thermal motion.¹ A particle’s ability to exhibit thermal motion is dependent upon its size and temperature. Sharma *et al.* estimate that gold nanoparticles above 0.5 μm in diameter cannot be stabilized in a solvent with a density comparable to that of water, because the particles no longer experience Brownian motion due to their high density, which causes them to sink and undergo sedimentation in the earth’s
It should also be noted that both the length scale and the time scale are critical factors to consider when examining the Brownian motion of colloidal systems. A key attribute of a colloid is its ability to quickly move distances on the order of, or larger than, its size due to Brownian motion. To give an analogy, for a brick to move a distance comparable to its size by means of Brownian motion it would take time on the order of millions of years, whereas a colloid can do this in fractions of a second. For GNRs specifically, they have been observed to grow no larger than 600 nm in length and 20-30 nm in diameter, likely due to the loss of Brownian motion at and above this size.

The stabilization of colloidal solutions due to Brownian motion can be disrupted or overpowered, however. Electrostatic, van der Waals and viscous forces must also be considered for colloidal systems. Van der Waals attractive forces are typically quantified using the Hamaker constant, which describes the attractive interaction between particles. This constant is specific to each material and also depends on the medium within which the particles are dispersed. The electrostatic interaction between two particles can be described by Coulomb’s law at a first approximation, but is also more specifically dependent on the size and shape of the particles. It should be noted that the electrostatic forces between two bodies are actually “moderated by ions in the intervening fluid,” or in other words, moderated by the interaction of counter-ionic atmospheres. Lastly, the viscous forces experienced by particles in solution can be estimated using Stoke’s law, taking into account the particle size, the effective gravitational force and the difference in density between the particle and the medium in which it is dispersed. Sharma et al. described the magnitude of these characteristic forces
on the colloidal scale relative to one another, shown in Table 1. These quantities describe spherical particles but are qualitatively similar for rods.

**Table 1.** Relative interactive forces on the colloidal scale where \( a \) is the diameter of the particle, \( U \) is the velocity of the particle, \( \rho \) is the density of the medium/solvent, \( \Delta \rho \) represents the difference in density between the particle and the medium in which it is dispersed, \( g \) is the acceleration due to gravity, \( A_{\text{eff}} \) is the Hamaker constant, \( \zeta \) is the electrostatic potential, and \( \varepsilon \) is the dielectric constant.

<table>
<thead>
<tr>
<th>Force Type</th>
<th>Formula</th>
</tr>
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<tbody>
<tr>
<td>Electric</td>
<td>( \frac{a \varepsilon_0 \zeta^2}{kT} \approx 10 )</td>
</tr>
<tr>
<td>Brownian</td>
<td>( \frac{A_{\text{eff}}}{kT} \approx 10 )</td>
</tr>
<tr>
<td>Attractive</td>
<td>( \frac{\Delta \rho g}{kT} \approx 0.01 )</td>
</tr>
<tr>
<td>Viscous</td>
<td>( \frac{\eta U a^2}{kT} \approx 0.01 )</td>
</tr>
<tr>
<td>Brownian</td>
<td>( \frac{\eta U a^2}{kT} \approx 0.01 )</td>
</tr>
<tr>
<td>Gravitational</td>
<td>( \frac{\eta U a^2}{kT} \approx 0.01 )</td>
</tr>
<tr>
<td>Viscous</td>
<td>( \frac{\rho a^2 U^2}{kT} \approx 10^{-4} )</td>
</tr>
</tbody>
</table>

The stability of colloidal solutions of GNRs results from a fine balance of Van der Waals attractive, electrostatic repulsive, Brownian, viscous, and gravitational forces; all forces synergistically interact to keep colloidal solutions suspended. The aforementioned forces can be manipulated by adding salts, surfactants, different solvents, among other means.
REFERENCES


Chapter 2: Characterization of Gold Nanorods

2.1 Optical Absorbance Spectroscopy

Light can induce electronic transitions in materials. The amount of energy needed to change the electronic arrangement within a molecule is on the order of a few electronvolts (1 eV ≈ 8000 cm⁻¹), more precisely depending on the type of molecule and its classification as an insulator, conductor, or semiconductor.¹ Therefore, photons accompanying electronic transitions are of energies typically found in the visible or ultraviolet regions of the electromagnetic spectrum.¹ An optical absorbance spectrophotometer measures the absorption or transmittance properties of a material as a function of wavelength.

The Beer-Lambert law is commonly applied to quantitatively relate the absorption of a sample measured in a spectrophotometer with its chemical properties. The Beer-Lambert law (Beer’s Law) relates the concentration of a species to its absorbance (Equation 1).

\[ A = \varepsilon b C = \log \left( \frac{I_0}{I} \right) \]  

(Equation 1)

In Equation 1, \( A \) represents the absorbance of the sample (no units), \( \varepsilon \) is the molar absorptivity or extinction coefficient (L/mol⁻¹cm⁻¹), \( b \) is the path length (cm), \( C \) is the concentration of the sample (mol/L), \( I \) is the incident light intensity and \( I_0 \) is the transmitted light intensity.² From Equation 1, it is evident that as the sample concentration increases, the absorption of the species increases. It is important to note that samples measured using optical absorbance spectroscopy should be fairly dilute and not too concentrated. Measuring highly concentrated samples will cause significant absorption and oversaturation of the detector. Furthermore, Beer’s law is only valid for dilute solutions because this law assumes a linear relationship between absorbance

¹ Beer’s Law is a linear relationship between absorbance and concentration. It is a fundamental principle in spectroscopy, used in industries like medicine, food science, and environmental analysis. It is particularly useful in analyzing the concentration of substances in solutions, as it allows for the quantification of the amount of a substance based on its absorbance at a specific wavelength. The Beer-Lambert law is expressed as \( A = \varepsilon b C \), where \( A \) is absorbance, \( \varepsilon \) is the molar absorptivity, \( b \) is the path length, and \( C \) is the concentration. The law is applicable in dilute solutions where the path length is short, and the Beer-Lambert law holds true.
and concentration (Equation 1). At high absorbance values, this relationship becomes significantly non-linear, and Beer’s law becomes invalid.

2.2 Transmission Electron Microscopy

Optical absorbance spectroscopy is coupled with transmission electron microscopy to characterize GNR samples. A transmission electron microscope (TEM) gives researchers visual representations of their samples via the scattering of electrons. In a TEM, a condensed beam of electrons, typically less than 5 nm in diameter, is directed at a thin slice of a sample. Incident electrons from the beam can be scattered by the sample due to Coulombic repulsion as negatively charged electrons closely approach atoms’ electron clouds. Ultimately, all of the electrons are transmitted through the specimen; however, some are scattered, which leaves an uneven distribution of emergent electron intensity, compared to the homogenous beam to which the material was initially exposed. This uneven scattering distribution is plotted as a contrast image, which gives a visual representation of examined samples. The thickness of the specimen as well as the atomic number (Z) of the component elements affect their scattering ability and thus the resultant TEM image. Thicker specimens will scatter more because they have more mass from which to scatter. Likewise, materials of greater atomic number (high Z) scatter more because their electron clouds are larger. Ultimately, thicker and higher Z materials provide more contrast and typically yield better TEM images than their thin, low Z counterparts. Gold, a high Z material, provides excellent contrast in TEM (Figure 1). For this reason gold nanoparticles have been used to stain biological specimens (low Z) for imaging by TEM.
Figure 1. TEM Image of gold nanorods.\textsuperscript{5}
REFERENCES


Chapter 3: Silica Overcoating of Gold Nanorods

3.1 Introduction

Silicon dioxide (SiO$_2$), also known as silica, can be classified into three broad categories: crystalline, vitreous, and amorphous.$^{1,2}$ The structure of crystalline SiO$_2$ depends on the temperature and pressure to which the material is exposed.$^1$ Each subclass of SiO$_2$ has unique chemical properties. Quartz, which forms at high temperatures and pressures, is an enormously abundant and recognizable mineral on Earth found as rocks or as finely ground sand.$^1$ Vitreous SiO$_2$, most commonly referred to as silica glass, is not entirely crystalline nor amorphous; it possesses some long-range structural order but not to the point at which it has a defined crystal structure.$^{2,3}$ Amorphous silica can exist in the form of colloids, gels, or those materials lacking structural periodicity or atomic order.$^4$ In liquids, colloidal particles, or “sols,” can aggregate due to van der Waals attractive forces to form extended, solid structures called gels.$^4$ Removing the liquid phase after gel formation via drying yields structures that are referred to as xerogels, if the gel experiences volume shrinkage and aerogels, if the volume of the structure is conserved upon drying.$^4$ Henceforth, silica colloids and gels exclusively will be discussed.
3.2 Hydrolysis and Condensation of Silicates

Silica gels are generated by hydrolysis and condensation events commonly referred to as sol-gel reactions (Figure 1).

![Figure 1. Sol-gel reactions.](image)

Metal alkoxides are the most common sol-gel precursors because they are easily hydrolyzed in the presence of water (Figure 1a). In the case of silica gel formation, silicon alkoxides (alkoxysilanes) possessing methoxy, ethoxy, \( n \)-propoxy, or iso-propoxy, etc. ligands are used as silicon precursors. The alkoxy silanes then undergo bimolecular nucleophilic substitution (SN2) reactions, whereby silicon atoms are attacked by hydronium ions, if the synthesis is acid catalyzed, or hydroxyl ions if base catalyzed, to form silanols, which react and link together to form siloxane bonds (Figure 2).
3.3 The Stöber Method

The development of the Stöber method in the 1960s spurred a great deal of research in the area of silica nanoparticle synthesis, modification and application, which continues today. Stöber developed techniques to synthesize monodisperse silica spheres of varying sizes (0.05-2.0 μm) using water-alcohol mixtures, ammonia (NH₃), and alkyl silicate precursors under basic conditions (pH > 11).⁶ Using tetraethyl orthosilicate and ethanol as the solvating alcohol, Stöber was able to make monodisperse silica spheres less than 1 μm in size (Figure 3).
The effect of various reaction parameters on the particular synthesis was examined. NH$_3$, which was used as the catalyst, was found to greatly influence the morphology of the resultant silica structures; without NH$_3$ non-spherical, or irregularly shaped particles were observed. The alcohol and alkyl silicate used were found to affect the reaction rate and the final particle size. Shorter-chained alcohols increased the rate of the reaction while longer-chained alcohols slowed the rate at which hydrolysis and condensation events occurred. Furthermore, syntheses using shorter-chained alcohols yielded smaller, monodisperse particles while longer-chained alcohols had the opposite effect. Silicates with shorter alkyl groups proceeded at faster rates and generated smaller particles compared to their longer-chained counterparts. The water
content was also found to be an important parameter in the synthesis by changing the condensation rate and final particle size. Stöber reported the quick and robust technique for synthesizing monodisperse silica particles on the micrometer, or sub-micrometer, scale and also demonstrated the system’s sensitivity to changing reaction parameters. Even today, experimentalists further study, modify and integrate the Stöber method into different systems.

3.4 Sol-Gel Syntheses: Reaction Parameters and their Effects

Sol-gel reactions are intricate systems with interdependent variables. A few of the most important parameters which affect the reactions and their products will be discussed.

3.4.1 Catalyst

Sol-gel reactions may be carried out under acidic or basic conditions. It was found that the strength and concentration of the catalyst, regardless of whether acidic or basic, are critical factors that affect sol-gel reactions. High catalyst concentrations and strengths are important for realizing the products of sol-gel syntheses. When weaker catalysts are used, the hydrolysis and condensation reactions proceed, but at slower rates. As discussed earlier, the Stöber method is carried out at high pH (≥11) to yield colloidal monodisperse silica spheres. It should be noted that “base” catalysis in sol-gel syntheses is considered to apply to any system at or above pH 2. This practice is used because the isoelectric point of silica is near pH 2. Silanols are deprotonated above pH 2 and are protonated below it.
3.4.2 Water Concentration

The water content in sol-gel reactions significantly impacts the structures that result. Generally, the water content of a reaction solution is quantified relative to the silicon content and is given as a molar ratio, $r (r = \text{H}_2\text{O}/\text{Si})$. Solutions with high $r$ values, near 50 or greater, generate dense, colloidal silica structures like those observed in Stöber syntheses. Reducing the water content to give $r = 10$ yields films, while further reduction to give ratios near $r = 1$ generates fibrous silica structures.

3.4.3 Alkoxy silane Precursor

The type of precursor used can affect the reaction kinetics. Alkoxy silanes possessing longer, and especially bulkier, alkyl groups retard the rate at which hydrolysis and condensation occur. Furthermore, compounding or complicating the alkyl chains with electron donating or withdrawing groups can affect the acidity or basicity of silanols and consequently influence the pH at which condensation takes place in solution. Therefore, tetramethyl orthosilicate (TMOS) and tetraethyl orthosilicate (TEOS) with their short, linear alkyl chains are the most widely used precursors in sol-gel syntheses.
3.5 Silica Shells on Gold Nanorods: Synthesis and Properties

CTAB stabilized gold nanorods (GNRs) can be synthesized using different approaches. It was once believed that the stabilizing, CTAB bilayer on GNRs did not promote SiO$_2$ growth, and the deposition of an intermediate layer on top of the CTAB capped GNRs was needed before SiO$_2$ overcoating.$^7$ However, it has been shown that SiO$_2$ can be directly deposited on CTAB stabilized GNRs without an intervening layer. The synthetic pathways and properties of deposited SiO$_2$ shells on GNRs are discussed.

3.5.1 Synthesis

Some materials such as magnetite, titania and zirconia have natural affinities for SiO$_2$, but most others do not.$^8$ Therefore, polymers or silane linking reagents such as poly(vinylpyrrolidone) (PVP) or aminopropyltrimethoxysilane (APS) were often added to syntheses involving the SiO$_2$-overcoating of materials such as GNRs.$^7,8$ However, it was shown that mediating materials which promoted SiO$_2$ deposition were not required and that CTAB capped GNRs could be directly and easily coated with SiO$_2$ using a single-step technique.$^7$ Gorelikov and Matsuura showed that SiO$_2$ shells can be formed on GNRs (Figure 4) by removing excess CTAB from aqueous GNR solutions via centrifugation, adjusting the solution’s pH to values between 10-11, injecting TEOS until a concentration of ~8 mM is obtained, and allowing the reaction solution to stir for several days; this has been the most widely adopted and adapted synthetic technique for overcoating GNRs with SiO$_2$.$^7$ Removing excess CTAB is necessary so as to direct SiO$_2$ deposition on the GNR surface because without doing such, TEOS would condense on free floating CTAB micelles in solution and form
spherical SiO$_2$ particles.$^7$ By removing CTAB, the GNRs are forced to serve as nucleation sites for TEOS condensation. It should be noted that the high pH (~10-11) and water content regimes are very similar to the reaction conditions set forth in the Stöber method, and the resultant SiO$_2$ structures are consequently similar in nature.

Figure 4. (a) TEM image of SiO$_2$-GNRs synthesized by Gorelikov and Matsuura,

(b) SEM image of SiO$_2$-GNRs synthesized by Gorelikov and Matsuura.$^7$
3.5.2 Properties

Tailoring the thickness of SiO$_2$ shells on GNRs has been achieved using multiple approaches. Perhaps most simply, the SiO$_2$ shell thickness can be modulated by adjusting the volume of TEOS that is added to reaction solutions. GNR solutions with more TEOS will have thicker SiO$_2$ shells and conversely, thinner shells will result from solutions with less injected TEOS (Figure 5).

Figure 5. TEM images of GNRs with varying SiO$_2$ shell thicknesses synthesized by injecting different volumes of a TEOS solution: (a) no TEOS, bare GNRs (b) 31.3 μL TEOS solution, 3.3 nm shells, (c) 62.5 μL TEOS solution, 7.7 nm shells, (d) 125 μL TEOS solution, 10.3 nm shells, (e) 250 μL TEOS solution, 16.0 nm shells, (f) 500 μL TEOS solution, 17.3 nm shells.
Polyethylene glycol silane (PEG-silane) is also commonly added to reaction solutions to terminate SiO$_2$ shell growth.$^9$ PEG-silane initially adsorbs to the surface of existing silica followed by covalent attachment to form molecular networks that block subsequent silica deposition.$^{10}$ The use of PEG-silane as a quenching agent in SiO$_2$-GNR solutions allows for precise control over shell thickness (Figure 6).

**Figure 6.** TEM images of SiO$_2$-GNRs resulting from the injection of PEG-silane at different times: (a) termination after 30 minutes of shell growth, (b) termination after 45 minutes of shell growth, (c) Termination after 60 minutes of shell growth, (d) termination after 120 minutes of shell growth.$^9$
It has also been shown that the silica shell thickness can be tailored by adjusting the CTAB concentration in the reaction solution.\textsuperscript{11} When excess CTAB is present in GNR reaction solutions, TEOS will condense on free floating CTAB micelles, instead of the GNRs, thereby reducing the amount of SiO\textsubscript{2} that is deposited on the GNRs.\textsuperscript{11} If the CTAB concentration is reduced, there are fewer micellar nucleation sites in solution, and TEOS is forced to condense on the GNRs, yielding thicker shells (Figure 7).

\textbf{Figure 7.} Dependence of silica shell thickness on CTAB concentration.\textsuperscript{11}

The silica shells deposited using the outlined synthetic conditions are all mesoporous in nature with pore sizes near ~4 nm and having pore walls approximately 2 nm thick.\textsuperscript{7} SiO\textsubscript{2} serves as to protect GNRs from harsh thermal environments, stabilizing GNRs at temperatures
exceeding 700 °C. Upon thermal heating, bare GNRs reshape into spheres within 1 hour at temperatures greater than 250 °C, so SiO₂ provides an enormous amount of thermal protection. It is evident that SiO₂ preserves the GNR structure at high temperatures, and it has also been found to minimally affect the optical properties.

3.6 Effects of Silica Shells on Optical Properties of Gold Nanorods

Mesoporous SiO₂ shells protect GNRs in environments in which they would normally be unstable. They do so without significantly affecting the optical properties of the GNRs; the overall spectral shape is preserved, but minor spectral shifting may occur. Upon SiO₂ overcoating, GNRs experience red-shifting in their optical absorbance spectra proportionate to the thickness of the silica shell. Red-shifting is observed because SiO₂ is a medium of higher refractive index compared to the water within which the GNRs are dispersed. The refractive index of water is 1.33, while that of SiO₂ ranges between 1.28-1.46, depending on the type of SiO₂. In this case, mesoporous SiO₂ encapsulates the GNRs, suggesting an SiO₂ index of refraction higher than water (1.33), but less than quartz (1.46).
REFERENCES


Chapter 4: Applications of Gold Nanorods

4.1 Applications of Bare Gold Nanorods

Gold nanorods (GNRs) have several potential applications in multiple fields, but most notably biomedical applications, for which selected applications are presented.

4.1.1 Photothermal Therapy

GNRs have the ability to absorb light and convert it to heat, which if collected at specific sites in the body, can be used to the eradicate, or essentially burn away, cancer cells, bacteria and viruses.\(^1\) The wavelength of light typically used in photothermal therapies is in the near infrared (NIR) region of the electromagnetic spectrum because GNRs are optically responsive, and biological tissues and fluids are permeable to light of this energy.\(^1\) Researchers have used photothermal therapy to target and destroy cancerous tumors representative of colon cancer and squamous cell carcinoma in mice.\(^1\)

4.1.2 Biomedical Imaging

GNRs intensely scatter light at their LSPR wavelength (NIR), often generating $10^5$-$10^6$ times more light than a fluorescent dye would emit.\(^1\) Therefore, they can be directly visualized using dark field microscopy and are often conjugated with receptors for detecting specific biomolecules inherent to cancerous tumors for diagnostic purposes.\(^1\) Irradiating functionalized GNRs which have attached to biomarkers on diseased surfaces allows not only for detection but for site-specific imaging and observation of disease.
The strong absorption of GNRs is an advantage for photothermal and photoacoustic imaging techniques. Samples generate heat from the light they absorb. Detecting the specific locations of evolved heat is the means by which samples are viewed with photothermal imaging.\textsuperscript{1} Similarly, for photoacoustic imaging, materials are observed via the detection of acoustic waves after light absorption causes thermal expansion of air surrounding the sample.\textsuperscript{1} As mentioned previously, functionalizing GNRs with specific receptors helps for targeting the GNRs to sites of interest where the receptor may find its conjugate and form a complex for selective imaging.

### 4.1.3 Sensing

GNRs can be used in sensing applications because of their distinct and sensitive longitudinal surface plasmon resonances (LSPR). Shifts in the LSPR caused by refractive index variations are indicative of changes in the local environment of the GNR and can be used to probe and detect molecules near the nanoparticle.\textsuperscript{1} When placed in a higher refractive index medium, or due to the adsorption of molecules, a nanoparticle’s LSPR will redshift.\textsuperscript{1-4} Similarly, if placed in a medium of lower refractive index, or because of molecular desorption, the LSPR will blueshift.\textsuperscript{1-4} Some researchers have used LSPR shifts to detect the association and disassociation of antibodies with antigens in solution.\textsuperscript{1}

### 4.1.4 Surface-Enhanced Raman Scattering

Raman scattering uses inelastically scattered light to acquire information about the vibrational and molecular structure of materials, approaching single molecule sensitivity.\textsuperscript{5} The
frequency of elastically versus in- elastically scattered light is closely monitored, and the
difference is given as a Raman signal. Placing analytes on roughened, metal surfaces enhances
their Raman signal because the substrate material has a greater surface area from which the
molecules can scatter, and incident light can excite surface plasmons (Chapter 1) in the metal;
this technique is called surface-enhanced Raman scattering (SERS). The intensity of the
electromagnetic field at the surface of a particle is known to be augmented at its plasmon
resonance. An analyte’s Raman signal is significantly enhanced if the surface plasmons are
excited in the material on which the analyte is adsorbed.

Aggregated GNRs were found to enhance SERS signals. Specifically, aggregated
GNRs are of interest for SERS because in the aggregated form, particles are in close proximity
to one another and their combined effects become significant. For example, the enhanced
electromagnetic field at the surface of an aggregate is much stronger than at the surface of a
discrete particle. At some regions in the GNR aggregate, “hot spots,” or zones that concentrate
the energy of the excitation source, are generated. The characterization ability of SERS has
allowed for the study of small molecules such as hormones, nucleic acids and proteins, which
can be used to understand and develop treatments and/or cures for diseases.
4.2 Applications of Silica-Overcoated Gold Nanorods

In addition to being used in photothermal therapeutic, imaging and sensing applications as mentioned previously for bare GNRs, silica overcoated GNRs (SiO₂-GNRs) have unique properties which give them added applications.

4.2.1 Drug Delivery

The porous shells of SiO₂-GNRs can be loaded with drugs and serve as carriers for delivery to afflicted sites in the body. GNRs are coupled specifically with mesoporous silica (SiO₂) because SiO₂ has been shown to be biocompatible and easily taken up by cells in the body.⁷ In addition to drugs, SiO₂ pore channels can accommodate nucleic acids, fluorescent dyes, and MRI contrast agents, among other species for in vivo delivery.⁷ Another property that makes SiO₂-GNRs particularly appealing for drug delivery is the ability of the SiO₂ surface to be functionalized.⁷ Typically, conjugated molecules on the surface of the SiO₂ serve as modulating agents for drug release.⁷ Molecules sensitive to pH, or light can be used to trigger the release of the contents loaded in SiO₂-GNRs.⁸⁻¹⁰

4.2.2 Catalysis

Metal nanoparticles have extremely high surface to volume ratios, which allows them to serve as catalysts, with greater efficiencies than their bulk metal counterpart catalysts, not only due to their small sizes but also because of their altered electronic structures.¹¹ Gold nanoparticles specifically have been sought for catalyzing various oxidation and reduction reactions, such as the reduction of 4-nitrophenol, which is a model target for measuring
catalytic efficiency\textsuperscript{11} Due to the excellent thermal and chemical stabilization imparted by SiO\textsubscript{2} shells, SiO\textsubscript{2}-GNRs serve as durable and reusable catalysts in many chemical reactions.\textsuperscript{11,12}
REFERENCES


Chapter 5: Understanding and Controlling the Morphology of Silica Shells on Gold Nanorods

5.1 Introduction

This chapter will be submitted for publication with Rowe as first author and is coauthored by Brian S. Chapman and Joseph B. Tracy. Rowe’s contribution to the research included all aspects of surveying the literature, synthesizing and characterizing nanoparticles (with the exception of a few TEM images), and writing the manuscript.

5.2 Copy of Manuscript

Understanding and Controlling the Morphology of Silica Shells on Gold Nanorods
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Gold nanorods, site selective, silica, CTAB, TEOS, spatial control, asymmetric functionalization

ABSTRACT

Subtle variations in the conditions for addition of a tetraethyl orthosilicate (TEOS) / methanol (MeOH) solution to gold nanorods (GNRs) stabilized by cetyltrimethylammonium bromide (CTAB) allow for morphological control of the silica (SiO₂) shells deposited onto the GNRs. Specifically, the concentration of TEOS in the TEOS/alcohol mixture determines
whether the SiO$_2$ shell uniformly coats the whole GNR or is deposited only in lobes on the ends of the GNRs. Changes in the optical absorbance of SiO$_2$-coated GNRs (SiO$_2$-GNRs) after purification with MeOH suggest that CTAB can be dissolved through the porous SiO$_2$ shells. The size of the lobes can be controlled, but there is a minimum lobe size, below which full encapsulation is favored. The following mechanism of lobe formation is proposed: Initially, a SiO$_2$ shell fully encapsulates the CTAB-stabilized GNR core. Under certain reaction conditions, the SiO$_2$ shell can reshape into lobes, which are more thermodynamically stable because they reduce the surface energy. In addition to use of a minimum amount of TEOS per GNR, a MeOH concentration near 9 v% is also necessary for lobing. Formation of lobed structures may be attributed to the protic nature of MeOH, which allows it to participate in reverse sol-gel reactions. Lobed SiO$_2$ coatings can be obtained when MeOH facilitates repeated depolymerization and polymerization reactions that drive deposition of SiO$_2$ into the thermodynamically favored lobed structures. Patchy nanoparticles, such as lobed SiO$_2$-GNRs, are of interest for applications in self-assembly and spatially controlled functionalization. The mechanistic insights gained through this study may be applicable to related core materials and the deposition of other kinds of oxides.

**INTRODUCTION**

Janus and patchy nanoparticles (NPs) have regions with distinct surface chemistry and are of interest for spatially controlled functionalization and for directing self-assembly. The patches can be functionalized with different chemistry from the underlying core material to impart anisotropic properties.$^1$ For example, such dual functionalization can allow NPs to
behave as surfactants, if they have hydrophobic and hydrophilic regions. Similarly, if the patches are oppositely charged, application of an electric field can drive assembly or alignment of patchy NPs. This concept can be further extended to complex NPs with patches that respond locally to different kinds of physical and chemical stimuli (e.g., optical, magnetic, or catalytic).

Silica (SiO$_2$) is of special interest for deposition in patches on inorganic NPs because silane chemistry for depositing SiO$_2$ and for subsequent surface functionalization is well established, and SiO$_2$ is biocompatible. Preceding interest in patchy NPs, the development of the Stöber method in 1968 has inspired nearly half a century of research on the synthesis, manipulation, and applications of silica (SiO$_2$) NPs. Addition of cationic surfactants is a common modification of the Stöber method for synthesizing sub-µm, mesoporous SiO$_2$ structures with variable pore sizes. The porosity and surface area of such structures allow for their application in catalysis, biosensing, and theranostics. Porous SiO$_2$ can be loaded with molecular cargo and can be functionalized for different kinds of surface chemistry, including click chemistry reactions.

There is significant interest in overcoating functional NPs with SiO$_2$, and methods have already been established for overcoating noble metal, semiconductor, and magnetic NPs. SiO$_2$ shells can improve the stability of NPs and protect them from degradation in harsh thermal and chemical environments, such as high or low pH and high electrolyte concentration. SiO$_2$ shells also improve the biocompatibility of some kinds of NPs stabilized by cationic surfactants, such as gold nanorods (GNRs), by trapping or providing a barrier between the cationic surfactant and the environment.
Anisotropically shaped core NPs have presented both challenges and opportunities for morphological control of SiO$_2$ overcoatings. SiO$_2$ deposited from tetraethyl orthosilicate (TEOS) onto GNRs stabilized by cetyltrimethylammonium bromide (CTAB) has been reported as both uniform shells$^{11,19}$ and as lobes on the ends of the GNRs.$^{37,38}$ In this process, CTAB templates deposition of TEOS. CTAB has been used to template and guide deposition of SiO$_2$ shells on many kinds of NPs and also serves as a template for mesoporous SiO$_2$. Another common approach for NPs with hydrophobic coatings uses nonionic surfactants to form reverse microemulsions, which serve as nanoreactors for SiO$_2$ deposition. For example, morphological control of SiO$_2$ shells on CdSe/CdS quantum dot nanorods and tetrapods has been reported.$^{27,39-41}$

Here, we report a method for controlling the morphology of SiO$_2$-overcoated GNRs (SiO$_2$-GNRs). The concentration of alcohol in the reaction mixture determines whether the SiO$_2$ shell fully encapsulates the CTAB-stabilized GNR (CTAB-GNR) core or if patchy lobes of SiO$_2$ form on the ends of the CTAB-GNRs, leaving the Au core exposed on the sides. Lobed SiO$_2$-GNRs are of interest for spatially controlled functionalization with silanes on the SiO$_2$ lobes and with thiols on the exposed Au. Intermediate structures are also reported, and the size of the lobes can be adjusted. Similar methods have been reported for depositing SiO$_2$ and TiO$_2$ lobes on CTAB-GNRs, but insights into morphological control and the underlying mechanism were limited.$^{26,37,38,42}$ This report addresses a significant need to comprehensively understand the levers that control the morphology of SiO$_2$ deposition and the underlying mechanism.

Many variables affect deposition of SiO$_2$ using sol-gel techniques. For example, temperature, pH, and water and alcohol content all affect the hydrolysis and condensation of
alkoxysilanes. Varying the concentrations of methanol (MeOH), tetraethyl orthosilicate (TEOS), and GNRs yields significant insights about the mechanism by which the morphology of the SiO₂ is determined. Additional experiments also highlight the role of MeOH. We identify the MeOH concentration as the key lever for controlling the morphology of SiO₂-GNRs, which allows or hinders reshaping of uniform SiO₂ shells into lobed structures at early stages in the reaction.

**EXPERIMENTAL SECTION**

**Chemicals.** CTAB (Sigma-Aldrich, 99%, H6269 and VWR Amresco, high purity), KBr (Alfa Aesar, ACS, 99% min), AgNO₃ (Alfa Aesar, 99.9995%), HAuCl₄·xH₂O (Alfa Aesar, 99.999%, where x was estimated as 3), deionized water (Ricca, ACS Reagent grade, ASTM Type I, ASTM Type II), ascorbic acid (AA, J.T. Baker, 99.5%), and NaBH₄ (Sigma-Aldrich, 99%, 213462) were used in GNR syntheses. TEOS (Alfa Aesar, 99.9%), NaOH (Sigma-Aldrich 98%), 2-[methoxy(polyethyleneoxy)₉₋₁₂propyl]trimethoxysilane (PEG-silane, Gelest, 90%), and anhydrous MeOH (EMD, DriSolv) were used for the SiO₂ overcoating. MeOH (Macron, ChromAR) was used for purification of SiO₂-GNRs and PEG-functionalized SiO₂-GNRs (PEG-SiO₂-GNRs). Tetrahydrofuran (THF, EMD, OmniSolv, Non-UV) was used instead of MeOH for synthesizing selected samples.

**Synthesis and Purification of GNRs.** CTAB-stabilized GNRs (CTAB-GNRs) were synthesized using a previously reported method that yields 1 L of solution containing approximately 190 mg of GNRs of aspect ratio ~4 (~80 nm × ~20 nm) and longitudinal surface plasmon resonances (LSPRs) of ~800-830 nm. For each SiO₂-GNR synthesis, 100 mL of this
stock solution was concentrated to 10 mL via a two-step centrifugation process (IEC Centra-MP4 with IEC 854 rotor) to bring the final CTAB concentration within a certain range. In the first centrifugation step, the CTAB-GNR stock solution was divided into aliquots of 40 mL per centrifuge tube (Nalgene Oak Ridge 3119) and centrifuged at 14,000 g for 20 minutes. After centrifugation, the nearly colorless, aqueous CTAB supernatant was removed by pipetting, reducing the volume remaining in each tube to 1.5-2.0 mL. Deionized H₂O was then added to bring the volume in each tube back to the initial volume before removing the supernatant, yielding a 20-30 fold dilution of the CTAB, while maintaining the same mass of CTAB-GNRs. Adjusting the CTAB concentration in this manner is important for avoiding agglomeration, which occurs if too much CTAB is removed. Centrifugation was repeated at 14000 g for 20 minutes, and the colorless supernatant was again removed, leaving a volume of 1.5-2.0 mL in each tube. Deionized water was added to bring the final volume in each tube to 4 mL, effectively increasing the GNR concentration by a factor of 10 and giving a CTAB concentration of 1.3-2.4 mM. This is slightly above the critical micelle concentration of CTAB, which has been reported as 0.90-0.98 mM in water. Purification of 100 mL of CTAB-GNR stock solution yielded 10 mL of concentrated CTAB-GNRs.

**Synthesis and Purification of SiO₂-GNRs.** Each SiO₂ overcoating reaction was conducted using 10 mL of concentrated CTAB-GNRs, which was kept in a water bath at 29 °C to avoid CTAB crystallization and stirred at 150 rpm. The pH was adjusted to 10.4-10.5 by adding 0.1 M NaOH dropwise. TEOS and anhydrous MeOH were quickly and thoroughly mixed to form solutions of different TEOS concentration by volume (specified in Table 1) for injection into the CTAB-GNR reaction mixture. In many instances, a larger volume of the
injection solution was prepared to reduce measurement errors when working with small volumes. The TEOS-MeOH solution was immediately injected at a constant rate into the stirring CTAB-GNR solution via syringe pump over a period of 5 minutes. In most of the reactions, the amount of TEOS-MeOH injection solution added corresponded to 50 µL of neat TEOS. Upon completing the injection, stirring was continued at a reduced rate of 70 rpm for 30 minutes and then turned off, while the mixture was left unperturbed in the water bath at 29 °C for an additional 20 hours.

For selected samples, the effects of modifications (specified in Table 1) to this general method were investigated, including varying the CTAB-GNR concentration and amount of TEOS, adding PEG-silane to terminate the reaction early, preadding the MeOH to the CTAB-GNR solution before adding TEOS, and substituting THF in place of MeOH. For one sample, SiO₂ shell growth was terminated early by injecting 40 µL of neat PEG-silane 30 minutes after completing injection of the TEOS-MeOH solution, followed by stirring at 70 rpm for an additional 30 minutes, and then allowing the reaction solution to sit unperturbed in the water bath at 29 °C for 20 hours. In one experiment, MeOH was preadded to the concentrated CTAB-GNR solution and allowed to stir for 5 minutes, followed by manual injection of 50 µL of neat TEOS over a period of 5 minutes (one 10 µL aliquot per minute).
Table 1. Reaction Conditions for Synthesizing SiO$_2$-GNRs

<table>
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<tr>
<th>Figure</th>
<th>Synthetic Conditions$^a$</th>
<th>V% TEOS</th>
<th>V% MeOH</th>
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<td>$V_{\text{TEOS}}/V_{\text{MeOH}}$ (μL)</td>
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<td>0.5</td>
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<td>50/950$^b$</td>
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$^a$All syntheses included 10 mL H$_2$O.

$^b$THF used in place of MeOH.

After the 20-hour reaction period, the SiO$_2$-GNRs were removed from the water bath, placed in a centrifuge tube and washed 4 times with MeOH (Macron, ChromAR) by filling the remaining volume with MeOH and centrifuging at 8400 g for 10 minutes. Between centrifugation cycles, the supernatant was removed as completely as possible by pipette without breaking up the pellet of SiO$_2$-GNRs before adding more MeOH and then briefly sonicating to redisperse the SiO$_2$-GNRs. While each sample presented here was washed and centrifuged 4 times, in some similar samples not reported, agglomeration occurred prior to 4 purification cycles. For such samples, monitoring by optical absorbance spectroscopy between
cycles is helpful for distinguishing the onset of agglomeration. Samples terminated using PEG-silane were generally less likely to agglomerate during multiple cycles of centrifugation. After the last centrifugation cycle, the SiO$_2$-GNRs were redispersed for storage by sonication in approximately 1 mL of the supernatant left in the centrifuge tube.

**Characterization.** The SiO$_2$-GNR products were imaged by transmission electron microscopy (TEM) using a JEOL 2000FX microscope operated at an accelerating voltage of 200 kV. Optical absorbance spectra were acquired using an Ocean Optics CHEM-USB4-VIS-NIR spectrometer and a glass cuvette with a 1 cm path length. All optical absorbance spectra were normalized at 400 nm to the CTAB-stabilized GNRs.

**RESULTS AND DISCUSSION**

**Morphological Control of SiO$_2$ Shells.** Adjusting the ratio of TEOS to anhydrous MeOH in the injection solution (Table 1) yields SiO$_2$-GNRs with different SiO$_2$ shell morphologies (Figure 1). Completely omitting MeOH from the injection solution, giving neat TEOS, yields fully encapsulated SiO$_2$-GNRs (Figure 1a). Dissolving TEOS in alcohols is a common practice in the aqueous synthesis of SiO$_2$ because TEOS is not soluble in water, causing phase separation at the beginning of the reaction. The alcohol produced from the initial stages of hydrolysis of alkoxysilanes, however, is adequate to fully dissolve the TEOS.$^{45}$ Therefore, fully encapsulated SiO$_2$-GNRs can be obtained without dissolving TEOS in MeOH. Injection solutions having concentrations of 50, 20, and 10 v% TEOS in MeOH also yield uniform SiO$_2$ shells (Figure 1b-d). When the concentration of the injection solution is reduced to 7 v% TEOS, non-uniform SiO$_2$ shells form, resembling peanuts (Figure 1e). Further dilution
to 5 v% TEOS causes formation of distinct SiO$_2$ lobes at both ends of the GNRs (Figure 1f). When the TEOS concentration is further reduced to 3 and 1 v%, the lobed morphology is lost, and a reversion back to full encapsulation is observed, albeit with less uniform SiO$_2$ surfaces (Figure 1g,h).

**Figure 1.** TEM images of SiO$_2$-GNRs prepared using different concentrations of 50 µL of TEOS prediluted in anhydrous MeOH. The scale bar in (a) applies to all panels except the inset in (f), showing a lobed SiO$_2$-GNR at higher magnification.
**Optical Absorbance Spectra.** The optical properties of the GNRs were preserved during SiO$_2$ overcoating. Optical absorbance spectra were acquired before and after SiO$_2$ overcoating, and before and after purification (Figure 2 and Supporting Information, Figures S1-S4). All SiO$_2$-GNRs, irrespective of the morphology, experience a redshift upon overcoating. This redshift, which is already known for uniformly coated SiO$_2$-GNRs, is attributed to the higher refractive index of SiO$_2$ than water (1.33).$^{13,18,46}$ The refractive index of porous SiO$_2$ has been reported to range from 1.28 to 1.45 and scales with its density.$^{45,47,48}$ Therefore, redshifts after depositing mesoporous SiO$_2$ shells suggest the refractive index of the SiO$_2$ shells is between 1.33 and 1.45. The LSPR of GNRs is highly sensitive to the local dielectric environment.$^{49-51}$ Increasing or decreasing the refractive index of the solvent for GNRs causes a redshift or blueshift, respectively, in the LSPR.$^{50,52}$ The magnitude of the shift scales with the change in refractive index.$^{50,52}$

While redshifts were consistently observed after depositing the SiO$_2$ shells or lobes, purifying the SiO$_2$-GNRs in MeOH caused a blueshift in the LSPR, bringing the LSPR near to that of bare CTAB-GNRs (Figure 2 and Supporting Information, Table S1, where the maximum absorbance wavelengths are tabulated for CTAB-GNRs and SiO$_2$-GNRs both before and after purification). Water and MeOH have nearly identical refractive indices, resulting in a negligible shift in the LSPR when varying the proportions of water and MeOH.$^{53}$ The blueshift observed during purification therefore suggests additional chemical modification of SiO$_2$-GNRs occurs during purification. We attribute this blueshift to dissolution of the CTAB coating on the GNRs that templates deposition of SiO$_2$ and remains between the Au core and the SiO$_2$ shell. CTAB readily dissolves in MeOH, and the porous SiO$_2$ structure is expected to allow
MeOH to access and dissolve the CTAB coating, which is transported through the porous structure and into solution. Molecular transport through mesoporous SiO$_2$ is well established,$^{54,55}$ and the porous SiO$_2$ shells of SiO$_2$-GNRs have been loaded with other molecules, which is of interest for drug delivery.$^{56-60}$

**Figure 2.** Optical absorbance spectra for CTAB-GNRs and SiO$_2$-GNRs before and after purification for samples prepared using (a) 5 v% TEOS and (b) 20 v% TEOS.
These observations are consistent both with our previous results of a redshift for unpurified SiO$_2$-GNRs$^{26}$ and with a report by Murphy and coworkers of a minimal redshift for SiO$_2$-GNRs relative to CTAB-GNRs after purification with alcohols.$^{11}$ CTAB removal during purification of SiO$_2$-GNRs is expected to cause a blueshift because organic coatings or adsorbates on GNRs generally cause a redshift due to their higher refractive index than that of water and MeOH.$^{51}$ While we have not quantified the extent of CTAB removal, the magnitude of the blueshift suggests substantial CTAB removal. Future work will include quantifying CTAB removal, which is important for biomedical applications because of its toxicity.$^{61}$

**Adjusting the SiO$_2$ Lobe Size.** SiO$_2$ lobes of different sizes would offer SiO$_2$ and Au patches of different sizes for functionalization with silanes and thiols, respectively. The SiO$_2$ lobe size can be controlled by adjusting the concentration of CTAB-GNRs in the reaction solution, thereby varying the amount of TEOS per GNR, if the amount of TEOS ($5\,$v%) is held fixed (Figure 3). Halving the GNR concentration should result in deposition of twice as much SiO$_2$ per GNR, as compared with the standard reaction procedure (Figure 1f), yielding larger SiO$_2$ lobes. Indeed, upon halving the concentration of CTAB-GNRs, the SiO$_2$ lobes grew and appear to have merged into each other (Figure 3a). Increasing the GNR concentration by a factor of 1.5 similarly yielded smaller SiO$_2$ lobes due to the reduced amount of TEOS per GNR (Figure 3b). Further increasing the GNR concentration to twice the initial concentration, however, resulted in fully encapsulated SiO$_2$-GNRs (Figure 3c) rather than even smaller lobes. This result suggests SiO$_2$ lobes below a certain size are not stable because thin shells that fully encapsulate the CTAB-GNRs are favored, when depositing smaller amounts of SiO$_2$. 

Figure 3. TEM images of SiO$_2$-GNRs prepared using the same volume of 5 v% TEOS and different concentrations of CTAB-GNRs, where 1× corresponds to the standard concentration of 1.9 mg/mL. The scale bar in (a) applies to all panels.

Additional experiments were conducted to investigate the transition between small lobes and uniform shells by reducing the amount of TEOS (from 50 μL to 10 μL or 25 μL) added in two different ways. In one case, the injection solution concentration was held at 5 v% TEOS, which is the standard protocol, and different volumes were injected (Table 1, Figure 4a,b). Consequently, the amount of MeOH added scaled with the amount of TEOS added. In the second case, the total MeOH concentration in the reaction mixture after adding the TEOS solution was held constant by adding 10 μL of TEOS at 1 v% and 25 μL of TEOS at 2.5 v%, which both yielded final MeOH concentrations near 9 v%. Approximately 9 v% MeOH was chosen because injecting 1000 μL of a 5 v% TEOS solution in the standard procedure for synthesizing lobed SiO$_2$-GNRs (Figure 1f) gives a final MeOH concentration of 9 v% (Table 1). All of these experiments yielded fully encapsulated SiO$_2$-GNRs, which suggests a minimum amount of TEOS exceeding 25 μL is required for forming lobes.
Additional Experiments to Investigate Lobing. The results reported and discussed thus far, have suggested that having ~9 v% MeOH in the reaction mixture after injection of the TEOS solution and a sufficiently large amount of TEOS are necessary conditions for obtaining deposition of SiO$_2$ in lobes (Figures 1f, 3a,b). Before proposing a mechanism in the next section, three experiments are presented to answer three specific questions about how the deposited SiO$_2$ evolves over time and the role of the solvent:

(1) Does the deposited SiO$_2$ nucleate as lobes, or does it first completely encapsulate the GNR, followed by reshaping into lobes? To answer this question, PEG-silane was used to terminate SiO$_2$ shell growth, as described previously.$^{26}$ After terminating the shell growth at
30 minutes, rough surfaces on tapered SiO\textsubscript{2} shells were observed, where the shells were thicker on the ends of the GNRs (Figure 5a). This result suggests SiO\textsubscript{2} does not nucleate only on the ends of the GNRs; rather SiO\textsubscript{2} is initially deposited everywhere and reshapes into lobes.

(2) Is simultaneous addition of TEOS and MeOH by diluting the TEOS required for lobe formation? Do SiO\textsubscript{2} lobes still result, if the MeOH is added to the CTAB-GNRs before adding TEOS? Preadding the same amount of MeOH (950 µL) to the GNRs as in the 5 v\% TEOS injection solution that gives lobes and then adding 50 µL of neat TEOS yields fully encapsulated SiO\textsubscript{2}-GNRs (Figure 5b). Therefore, premixing and simultaneously injecting TEOS and MeOH are required for lobe formation.

(3) Does the protic nature of MeOH affect lobing? 950 µL of THF was used as a substitute for MeOH, giving a 5 v\% TEOS injection solution that would otherwise result in SiO\textsubscript{2} lobes. This substitution gave fully encapsulated SiO\textsubscript{2}-GNRs. As discussed in the next section, the protic nature of MeOH is likely critical for forming lobes rather than fully encapsulating the GNRs.
Figure 5. TEM images of SiO$_2$-GNRs prepared using 5 v% TEOS under different reaction conditions (a) injection of PEG-silane after 30 min to terminate the reaction, (b) preadding the MeOH to the CTAB-GNRs before adding neat TEOS, (c) substituting THF for MeOH with predilution of TEOS in THF. The scale bar in (a) applies to all panels except the inset in (a), showing a SiO$_2$-GNR at higher magnification.

Proposed Mechanism of Lobing. Sol-gel synthesis of mesoporous SiO$_2$ from alkoxyisilane precursors under acidic or basic conditions involves hydrolysis and condensation reactions. The forward reactions are most commonly discussed, but the reverse reactions can also have important effects. As mentioned earlier, MeOH and other alcohols are often used to dissolve alkoxyisilanes for sol-gel syntheses. The protic nature of MeOH allows it to also modulate the extent to which reverse hydrolysis (esterification) and reverse alcohol condensation (alcoholysis) reactions occur (Scheme 1). Alcoholysis and hydrolysis reactions allow for siloxane bond cleavage, or depolymerization of condensed SiO$_2$, whereby it dissolves back into solution and can be preferentially redeposited through condensation reactions to form different morphologies.
Scheme 1. Sol-gel reactions for deposition of SiO$_2$ from TEOS, adapted from Brinker.$^{45}$

Alcoholysis and hydrolysis(2) reactions are believed to occur via bimolecular nucleophilic substitution (S$_{N}$2) mechanisms, where alcohols or water become deprotonated and serve as nucleophiles to cleave siloxane bonds.$^{45}$ The extent of the occurrence of these reverse reactions depends on the nature of the solvent and any co-solvents. Here, MeOH and water can be deprotonated at high pH and form strong nucleophiles to drive alcoholysis and hydrolysis(2). Aprotic species, such as THF, cannot participate in reverse reactions and are comparatively inert in sol-gel reactions.$^{45}$

Water was present in a large excess for all of the reactions; the rate of hydrolysis of siloxane bonds (Scheme 1c) is assumed to be the same for all samples. The rates of alcoholysis and esterification (Scheme 1a,b) depend on the amount of MeOH added, which was varied and determined the SiO$_2$ morphology. In the absence of MeOH, fully encapsulated SiO$_2$-GNRs were obtained. We propose that at low MeOH concentrations, there is not enough MeOH present to significantly drive alcoholysis and esterification, leaving the morphology
unchanged. At higher MeOH concentrations, alcoholysis becomes more favorable, causing deposited SiO$_2$ to dissolve and then be redeposited through the forward reactions. Such a dissolution and redeposition process would drive the SiO$_2$-GNRs toward the most thermodynamically stable, equilibrium morphology.

This proposed mechanism for reshaping of SiO$_2$ is consistent with other results. At the early stage of SiO$_2$ deposition, before complete condensation, SiO$_2$ is a highly pliant gel capable of reshaping.$^{62}$ Base catalysis of SiO$_2$ deposition (pH 10) also increases the rate of dissolution.$^{63}$ Gas chromatographic and $^{29}$Si NMR studies have shown that unhydrolyzed monomers exist past the gel-point for base-catalyzed silicate reactions, even in solutions of excess water, which proves reverse reactions occur.$^{45,64,65}$

Adding MeOH can drive alcoholysis and esterification but becomes self-limiting, because increasing the concentration of MeOH in water-MeOH-silicate solutions slowly causes a decrease in the solubility of SiO$_2$. $^{63,66}$ Therefore, at high MeOH concentrations, the low solubility of SiO$_2$ hinders its redistribution. We propose, there is an optimal, intermediate MeOH concentration at which alcoholysis occurs and drives reshaping of fully encapsulated SiO$_2$-GNRs into more stable lobed SiO$_2$-GNRs (Scheme 2). Below this optimal MeOH concentration, there is insufficient MeOH to drive alcoholysis, and SiO$_2$ reshaping is inhibited. Above the optimal MeOH concentration, SiO$_2$ solubility is limited.
Scheme 2. Cartoon depicting proposed mechanism of lobe generation facilitated by MeOH.

Which morphology (fully encapsulated vs. lobed) is more thermodynamically stable can be understood by considering the surface energies of the exposed CTAB coating and of the SiO₂ network. For small amounts of SiO₂, full encapsulation is always favored. Forming small lobes would leave a large exterior surface area of the CTAB coating exposed, which is avoided with full encapsulation. As the amount of SiO₂ is increased, however, the -Si-O-Si- network in the SiO₂ has a greater overall contribution to the energy. Forming lobes can reduce the exterior surface area of SiO₂, compared with uniform shells containing the same volume of SiO₂. The energetic stabilization in the SiO₂ from forming lobes comes at a cost of exposing part of the CTAB-GNR core, but the total free energy is apparently lower than for a uniform SiO₂ shell.

An alternative mechanism is formation of SiO₂ lobes driven by nucleation directly onto the ends of the CTAB-GNRs because the CTAB coatings are less stable on the ends, resulting in higher surface energy on the ends of the CTAB-GNRs. In our proposed mechanism, optimization of the MeOH concentration is the key lever for obtaining lobes, which are obtained only for sufficiently high amounts of TEOS and at ~9 v% MeOH in the reaction.
mixture. It is not clear, how this observation could be explained using a direct nucleation model. Our results further support reshaping of SiO$_2$ shells that initially fully encapsulate CTAB-GNRs rather than direct nucleation of SiO$_2$ lobes.

Terminating deposition of SiO$_2$ by adding PEG-silane (Figure 5a) shows that reshaping begins quickly, since tapered, lobed SiO$_2$-GNRs were observed 30 minutes after starting the reaction. Such restructuring of thin SiO$_2$ shells into spheres has also been observed for CdSe/CdS core/shell tetrapods.$^{39}$ Preadding MeOH to the GNR solution (Figure 5b) inhibits lobe formation, even though 50 µL of TEOS was added and there was 8.6 v% of MeOH in the reaction mixture. We attribute this result to the higher starting concentration of MeOH, which may potentially alter or damage the CTAB coating prior to deposition of SiO$_2$ in a manner than inhibits reshaping of the SiO$_2$ shell into lobes, than when it is injected along with the TEOS. The lack of lobing when using THF in place of MeOH (Figure 5c) highlights the role of the protic solvent in facilitating reshaping of the SiO$_2$; without reshaping, fully encapsulated SiO$_2$-GNRs are obtained. There are, however, some minor indentations in the shells on the sides of the SiO$_2$-GNRs. This suggests some SiO$_2$ was pulled toward the ends, as in the lobing process, but this process did not significantly proceed toward forming distinct lobes. Indeed, many of the fully encapsulated SiO$_2$-GNRs that we report show similar small indentations. Therefore, we believe MeOH concentration is the primary lever for controlling lobe formation, but removing MeOH does not completely inhibit SiO$_2$ rearrangement.

In some of the SiO$_2$-GNRs synthesized using 5 v% TEOS in MeOH, large lobes were achieved by reducing the concentration of CTAB-GNRs used in the reaction (Figure 3a). The
lobes joined as they grew into each other but did not reshape into uniform SiO$_2$ shells despite the optimal MeOH concentration for reshaping. For this case of lobes that entirely encapsulate the CTAB-GNR, a uniform shell with a lower exterior surface area would reduce the surface energy. This result suggests reshaping into a thick, uniform shell was not possible and that reshaping into lobes occurs at an early stage in the reaction to form a template on which more SiO$_2$ is deposited. When the lobes grow into each other later in the reaction, a greater extent of condensation of the SiO$_2$ shell and a lower concentration of unreacted monomers might inhibit reshaping.

CONCLUSIONS

Lobed SiO$_2$-GNRs with control over the lobe size have been obtained using a simple modification of an existing method for synthesizing fully encapsulated SiO$_2$-GNRs. A mechanism is proposed for lobe formation. Initially, SiO$_2$ shells are deposited that fully encapsulate CTAB-GNRs. If an adequate amount of TEOS is dissolved in MeOH and added, such that the final MeOH concentration is near 9 v%, then the SiO$_2$ shells may reshape into lobes, which are more thermodynamically stable. Alcohols specifically drive reshaping because of their protic nature and their ability to drive alcoholysis reactions. A blueshift in the optical absorbance spectrum after purification with MeOH suggests MeOH dissolves CTAB away through the pores in the SiO$_2$ shells of both lobed and fully encapsulated SiO$_2$-GNRs. Lobed SiO$_2$-GNRs are of interest as patchy NPs for applications in self-assembly and spatially controlled functionalization. The synthetic methodology and approach reported here may be applicable to related core materials and the deposition of other kinds of oxides.
ASSOCIATED CONTENT

Supporting Information. Optical absorbance spectra for samples presented in Figures 1, 3-5 and measurements of the maximum absorbance wavelength. This material is available free of charge via the Internet at http://pubs.acs.org.

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Figure S1. Optical absorbance spectra for the samples presented in Figure 1, prepared using different concentrations of 50 µL of TEOS prediluted in anhydrous MeOH.
**Figure S2.** Optical absorbance spectra for the samples presented in Figure 3, prepared using the same volume of 5 v% TEOS and different concentrations of CTAB-GNRs, where 1× corresponds to the standard concentration of 1.9 mg/mL.
Figure S3. Optical absorbance spectra for the samples presented in Figure 4, prepared using reduced amounts of TEOS and different concentrations of TEOS in the injection solution.
Figure S4. Optical absorbance spectra for the samples presented in Figure 5 prepared using 5 v% TEOS under different reaction conditions (a) injection of PEG-silane after 30 min to terminate the reaction, (b) preadding the MeOH to the CTAB-GNRs before adding neat TEOS addition, (c) substituting THF for MeOH with predilution of TEOS in THF.
Table S1. Optical Absorbance Maxima and Shifts for CTAB-GNRs and SiO$_2$-GNRs Before and After Purification with MeOH

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<th>2. Before Purification (nm)</th>
<th>3. After Purification (nm)</th>
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Chapter 6: Outlook & Conclusions

6.1 Summary

Gold nanorods (GNRs) are extremely versatile nanoparticles with unique properties that allow for their application in theranostics, surface-enhanced Raman scattering (SERS), and catalysis, among others. Herein, the synthesis and characterization of silica-encapsulated GNRs (SiO$_2$-GNRs) were examined. The SiO$_2$-GNRs presented had morphologies that ranged from uniform to lobed, and were selectively synthesized by modulating the alcohol concentration in the sol-gel reaction solution.

6.2 Future Work

The ability to locally deposit SiO$_2$ on GNRs provides a framework for site-specific functionalization of GNRs for potential sensing, imaging, delivery, and assembly applications. Furthermore, the work presented herein, specifically the ability to generate lobes on the tips of GNRs, can be extended and studied in other anisotropic nanoparticle systems, such as gold nanostars. The mechanism by which SiO$_2$ shells form on GNRs was extensively probed, and could be further studied by more closely monitoring reaction parameters such as the cetyltrimethylammonium bromide (CTAB) concentration. More extensive time dependent studies with polyethylene glycol silane (PEG-silane) could also be completed. Ultimately, SiO$_2$ shells were selectively deposited on GNRs to yield structures with distinct morphologies, such as SiO$_2$ lobes, which have been sparsely reported in the literature, to date. Additionally, the mechanism underlying asymmetric, or non-uniform, SiO$_2$ shell formation on GNRs was
investigated, and a deeper understanding than what has been previously reported in the literature was demonstrated.