Synthesis and Characterization of Silica-Coated Nanoparticles for Dye-Sensitized Solar Cells

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College of William and Mary

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Synthesis and Characterization of Silica-Coated Nanoparticles for Dye-Sensitized Solar Cells

A thesis submitted in partial fulfillment of the requirement for the degree of Bachelors of Science in Chemistry from The College of William and Mary

by

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Abstract

The majority of photovoltaics are expensive silicon-based devices. Dye-sensitized solar cells (DSSCs) have emerged as cheaper alternatives to silicon solar cells, but they have relatively low energy conversion efficiency. One proposed method to increase DSSC efficiency is through plasmon enhancement. Plasmon-enhanced DSSCs (PEDSSCs) are thought to show greater efficiencies since the enhanced electromagnetic (EM) field around a metal nanoparticle can increase dye absorption. However, the EM field decays rapidly with distance. The greatest enhancement is predicted to occur at small distances (~10 nm) from the nanoparticle’s surface, but extensive studies to quantify this value in the context of PEDSSCs have not occurred. In order to study the distance dependence of plasmon enhancement in PEDSSCs, we probed the enhancement in model PEDSSCs composed of silver nanoparticles that have been encapsulated in silica layers of various thicknesses (8.6 ± 3.2 nm, 9.1 ± 2.5 nm, 50.9 ± 4.3 nm, and 75.4 ± 4.8 nm). The fluorescence of rhodamine B (RB) dye molecules is measured as a probe of the distance dependence of plasmon enhancement, with preliminary measurements showing quenching at the surface of the nanoparticle and enhancement ratios of 1.99, 1.90, 1.41 on particles of 8.6 ± 3.2 nm, 50.9 ± 4.3 nm, and 75.4 ± 4.8 nm shell thicknesses, respectively. Future work will include covalent attachment of fluorophores and structural characterization with transmission electron microscopy (TEM).
**Introduction**

**The Energy Crisis and Solar Energy**

The majority of world energy is currently produced through the burning of fossil fuels. As they are nonrenewable resources, the supply of fossil fuels is limited. With total world energy usage continuing to increase each year, the use of alternative energy sources—such as wind, solar, and water—will soon become imperative. Therefore, the development of renewable energy sources is imperative to slow the depletion of fossil fuel reserves and to ensure the security of the world’s energy future. However, renewable energy sources have several disadvantages; at present, they are expensive and may have geographical restrictions due to their reliance on wind, water, volcanic activity, etc. Due to the abundance of renewable energy in the form of sunlight, much of the world has begun to turn to photovoltaics as alternative energy sources.

Photovoltaics (commonly known as solar cells) harness energy from sunlight and convert it to electricity. A majority of photovoltaic cells produced and sold are based on silicon. However, recent research has led to the development of similar technologies composed of a wide range of materials, such as CdS/CdTe, Cu(In, Ga)Se$_2$, or organic polymers. In comparison to silicon, these next-generation photovoltaic cells are relatively low-cost, more flexible and durable. In particular, dye-sensitized solar cells (DSSCs) are a class of organic-based photovoltaics that have shown tremendous potential as alternatives to silicon-based solar cells. Nevertheless, DSSCs have not yet been commercially marketed because they cannot match the energy conversion efficiency of silicon-based devices, which is ~25%. The original DSSC efficiency was reported at 7% in 1991 and since then has plateaued at ~11%. An understanding of the fundamental
mechanisms of DSSCs and identification of the processes that hinder their efficiency would lead to the development of better DSSCs and a commercially viable product.

The chemical and physical processes that take place during solar energy conversion in DSSCs are widely studied. DSSCs are composed of arrays of semiconductor nanoparticles—often of titanium dioxide (TiO$_2$)—that have been outfitted with dye molecules that act as sensitizers to absorb solar radiation (see Figure 1). Dye molecules are excited by incoming photons of sunlight and then transfer an electron adjacent TiO$_2$ particles through the process teemed forward electron transfer (FET). The electrons then move to the electrode to produce a current. The dye returns to its ground state through one of two processes: (1) reduction by an electrolyte solution, or (2) the process of back electron transfer (BET), in which an electron from the semiconductor recombines with the dye molecule, as shown in Figure 1. It is thought that BET can severely hinder overall DSSC efficiency. Although it has been established that the rate of FET ($k_{\text{FET}}$) is much faster than the rate of BET ($k_{\text{BET}}$), this complex process of electron transfer is not yet fully understood in the context of the heterogeneous environment within DSSCs. It is believed that ET kinetics are dependent on the dye sensitizer, the surface of the semiconductor, and the geometry of the device. Due to the complexity of the interactions among these components, a complete model for the electron transfer (ET) kinetics within DSSCs has not yet been developed. A better understanding of ET kinetics could help in the production of a more-efficient DSSC, but other potential strategies may succeed as well.

An alternative strategy for increasing DSSC efficiency is based on plasmon enhancement, which involves the increase of dye absorption through the introduction of
Figure 1. Depiction of the electron transfer processes that occur in DSSCs. Sunlight excites a Rhodamine B dye molecule ($k_{exc}$) which can undergo FET or BET. On the left, electron transfer within the DSSC is depicted. On the right, electron transfer among the energy levels of the dye and TiO$_2$ is shown.

metallic nanoparticles into the system. However, the effect of plasmonic particles in DSSCs is not well-understood, and thorough studies of the molecular interactions of dye and nanoparticle must be performed before a sufficient device is designed. In order to study the efficacy of plasmon-enhanced dye-sensitized solar cells (PEDSSCs), a basic understanding of the complex physical processes that occur during plasmon enhancement is required. The subsequent section will discuss the theory behind plasmon enhancement in order to provide the necessary background for the experiments described later in this thesis.

**Plasmonics for Dye-Sensitized Solar Cells**

A plasmon is a collective movement of charges about the surface of a metal, where the frequency of this oscillation occurs at the plasmon resonance.$^{17}$ Plasmons arise from the interaction of electromagnetic (EM) radiation with certain metals (e.g. silver and
Metals are composed of positive ion cores surrounded by clouds of freely-moving, negatively-charged electrons. A plasmon resonance occurs when the incident EM wave interacts with the electric and magnetic fields of the metal and causes a displacement of the electrons with respect to the position of the metal core. Furthermore, when the wavelength of incident radiation is much larger than the size of the plasmonic particle (i.e. a nanoparticle), the collective and coherent oscillation of electrons is the “plasmon,” and the frequency at which it occurs about a nanoparticle is called the localized surface plasmon resonance (LSPR). The LSPR occurs when excitation by EM radiation forces the electron cloud to move coherently away from the positive core. However, electron-electron repulsion and Coulombic attractions to the positively-charged center produce a strong restoring force that pushes the electrons back toward their original positions. This repeated excitation and restoring force action causes a back-and-forth sloshing of the electrons shown in Figure 2.

Figure 2. Depiction of electron oscillation associated with the LSPR when metal nanoparticles are excited by light (hv).
The LSPR of metal nanoparticles has two important characteristics. First, the LSPR of an excited plasmon can be measured as an extinction spectrum representing the combined scattering and absorbance properties of the nanoparticle, where the peak maximum corresponds to the LSPR frequency. An example of an extinction spectrum for colloidal silver nanoparticles can be seen in Figure 3. The extinction spectrum changes with variations in nanoparticle shape, size, composition, and local environment. Each of these characteristics (described in further detail below) can be modeled using Mie’s solution to Maxwell’s equations, which describes the scattering and absorption (i.e. extinction) of light by isolated nanoparticles.

In general, as nanoparticles deviate from perfect symmetry (i.e. spherical shapes), they tend to exhibit additional peaks in their extinction spectra; the peaks occur because

\[ \lambda_{\text{max}} = 405 \text{ nm} \]

Figure 3. Extinction spectrum of colloidal silver nanoparticles showing a \( \lambda_{\text{max}} \) at 405 nm.
of the additional resonance modes they can exhibit along different symmetry axes. Increases in nanoparticle size produce red-shifts and broadening of the extinction spectrum; the extinction cross-section increases exponentially as nanoparticle radius increases, as seen in the relationship described in Mie’s solution to the Maxwell equations: \( E(\lambda) \propto R^3 \), or the extinction cross-section is proportional to the radius of the nanoparticle cubed.\(^{18-19}\) Finally, the composition and local environment of the nanoparticle have a substantial effect on its LSPR frequency.\(^{18}\) The LSPR extinction maximum occurs when the dielectric constant is equal to negative two times the dielectric constant of the surrounding environment (i.e. when \( \epsilon_{out} = -2\epsilon \)). Therefore, changing the composition of the nanoparticle will cause a shift in its extinction spectrum maximum \( (\lambda_{\text{max}}) \). Additionally, this condition requires that changes in the local environment of the nanoparticle will cause its extinction spectrum to change.\(^{18}\) Local environmental changes can be mathematically related to the shift in extinction spectrum \( \lambda_{\text{max}} \) using Equation 1:

\[
\Delta \lambda_{\text{max}} = m \Delta n \left[ 1 - \exp \left( -\frac{2d}{l_d} \right) \right]
\]

where \( \Delta \lambda_{\text{max}} \) represents the shift in LSPR extinction wavelength maximum, \( m \) is the bulk refractive index response of the nanoparticle, \( \Delta n \) is the change in refractive index of the environment, \( d \) is the thickness of the environmental “layer” around the nanoparticle, and \( l_d \) is the decay length of an EM field around the nanoparticle in that specific environment. Therefore, a change in the nanoparticle’s local environment can be measured by observing changes in its extinction spectrum.
Due to the many factors that influence LSPR and the ability to make nanoparticles of different shapes, sizes, and compositions, a great variety of LSPR-exhibiting nanoparticles can be synthesized.\textsuperscript{17-21} For applications to PEDSSCs, nanoparticles with compositions that give extinction spectra maxima within the solar spectrum are needed. The noble metals (silver and gold) display extinction maxima within this range, making them viable materials for performing PEDSSC studies; for this reason (among others to be discussed later), silver is the metal used in the studies described later in this thesis.

The second important characteristic of the LSPR is the locally-enhanced EM field produced upon photoexcitation of the nanoparticle. Incoming EM radiation triggers an acceleration of the metal’s electrons, causing the inherent electric and magnetic fields of the metal to interact with each other. The changing magnetic field produced by the moving electrons induces an electric field that is different from the metal’s intrinsic field (Faraday’s Law of induction).\textsuperscript{22} The result is the generation of a new EM field: a set of oscillating electric and magnetic fields that travel away from the nanoparticle’s core. The greatest field enhancement occurs at the surface of the plasmonic nanoparticle, and the enhancement quickly tapers off with increasing distance from the nanoparticle surface.\textsuperscript{4}

The enhanced EM field generated upon optical excitation of a metal nanoparticle has the potential to change the behavior of nearby molecules. For example, it can change the absorption and emission (see Figure 4) properties of chromophores (molecules that can absorb light in the visible range) and fluorophores (molecules that can emit energy in the form of light).\textsuperscript{23} This phenomenon, termed plasmon enhancement, is the reason why PEDSSCs are thought to be more efficient.
Figure 4. Jablonski Diagram depicting the processes of absorbance (red), fluorescence (green), and vibrational relaxation (blue). Straight lines represent radiative (light-requiring) processes, while dashed lines represent non-radiative processes. $S_0$, $S_1$, and $S_2$ represent the electronic energy levels of a given molecule, with $S_0$ being the ground state, $S_1$ the first excited state, and $S_2$ the second excited state. The thinner lines within the electronic energy levels represent vibrational energy levels.

Plasmon enhancement of absorption or fluorescence can occur through various mechanisms: plasmonic nanoparticles can act as nanoantennae or “hot spots” where increased absorption and/or emission rates occur in chromophores because of a concentrated electric field. The quantum yield and fluorescence lifetime of chromophores can be altered through changes in their radiative and non-radiative decay rates.\cite{24,25} Both mechanisms are dependent on the spectral overlap between the nanoparticle LSPR and chromophore/fluorophore absorption peaks, scattering intensity of the nanoparticle LSPR, nanoparticle morphology, proximity to other nanoparticles, wavelength of incident radiation, and distance between the nanoparticle and the chromophore.\cite{25,26}

In the context of PEDSSCS, this second important characteristic of the LSPR is the focus because of the absorption enhancement due to the concentrated field around a nanoparticle. Ideally, a study involving the effects of nanoparticles in PEDSSCs would
focus solely on the absorption enhancement in chromophores located near plasmonic nanoparticles. However, single-particle absorption properties are difficult to probe. Instead, this thesis will focus on the fluorescence properties of dyes located near plasmonic nanoparticles because single-particle fluorescence is relatively easy to measure and because fluorescence intensity can be related to the absorbance rate using Equations 2 and 3, describing the intensity of fluorescence ($I_f$) and the fluorescence quantum yield ($\Phi_f$).\(^{23}\)

\[
I_f = k_a[S_0]k_f\tau_f = k_a[S_0]\Phi_f
\]

\[
\Phi_f = \frac{k_f}{k_f + k_{nr}}
\]

In these equations, $k_a$ represents the rate of absorbance, $S_0$ the initial concentration of dye molecules, $k_f$ the rate of fluorescence, $\tau_f$ the fluorescence lifetime, and $k_{nr}$ the rate of non-radiative decay. Because the fluorescence intensity is relatable to the absorbance rate, the remaining theory and studies discussed in this thesis will focus solely on emission/fluorescence enhancement.

In order for plasmonic emission enhancement to occur, the nanoparticle and the molecule must have similar extinction spectra. In general, overlap between the extinction spectrum of the plasmonic nanoparticle and the absorption spectrum fluorophore produces the greatest enhancement factors. An example of peak overlap can be seen in Figure 5.

More specifically, in the case of fluorescence enhancement, it has been found that the optimal nanoparticle LSPR peak position should overlap with and be blue-shifted
(of a lower wavelength) relative to the emission spectrum of the affected molecule. However, variations in fluorescence intensity can occur among nanoparticles with identical LSPR peak wavelengths. It has been found that when considering nanoparticles with the same LSPR $\lambda_{\text{max}}$, enhancement is greatest near particles that have larger LSPR scattering intensities. Both the radiative and nonradiative decay rates of the chromophore are enhanced with increasing LSPR intensity, but the radiative rate increases more rapidly, leading to a higher overall emission rate.

Logically, then, plasmonic enhancement will vary with changes in the shape and size of the plasmonic nanoparticle as the LSPR spectrum itself changes with morphological changes.\textsuperscript{27,28} In general, an increase in nanoparticle size leads to an
increase in enhancement. Trends associated with shape changes are more difficult to observe, as there are numerous possible forms a nanoparticle can take. Additionally, the spacing between nanoparticles can tremendously affect the local field enhancement.\textsuperscript{27,29} Two nanoparticles in close proximity produce a greater electric field than that of a single nanoparticle. In fact, the electric field can be amplified by almost ten times in the vicinity of two nanoparticles due to the complexities of their interacting fields. The wavelength of the incident radiation can also determine the strength of plasmonic enhancement.\textsuperscript{30-32} Electric field enhancement peaks when the plasmonic nanoparticle is excited by EM radiation of a wavelength slightly red-shifted from its LSPR $\lambda_{max}$, leading to the greatest absorption and emission enhancements in that region.

Finally, plasmonic enhancement of chromophore emission is distance-dependent.\textsuperscript{28,29,33} As previously discussed, the EM field produced around a plasmonic nanoparticle decays as the distance from the core of the nanoparticle increases. A chromophore oriented closer to the surface of a plasmonic nanoparticle will therefore experience a greater EM field. However, chromophores located too close (e.g. touching the surface) to a plasmonic nanoparticle will experience quenching of fluorescence.

The numerous factors contributing to plasmon enhancement make it an extremely complex process. Therefore, the introduction of plasmonic nanoparticles into DSSCs would require a fundamental understanding of the plasmonic effect as it would apply to their heterogeneous environment and the heterogeneity of the nanoparticles themselves. There have already been successful attempts to incorporate plasmonic nanoparticles into DSSCs, showing an increased absorption coefficient (which is correlated to amount of absorption) of the dye sensitizers and a greater amount of electron transfer to the
Although promising, these studies only serve as a proof of concept: plasmon enhancement can increase the overall efficiency of DSSCs. In order to fully maximize the efficiency of PEDSSCs, however, a thorough bottom-up investigation of plasmon enhancement, considering its effects on all processes within a DSSC, must be performed. The complexities of the interactions among dyes, plasmonic nanoparticles, and semiconductors in this context are not well understood. Furthermore, the disadvantages of introducing plasmonic structures into DSSCs must also be examined. For example, introduction of a metal nanoparticle can increase the rate of non-radiative decay processes that prevent the circulation of electrons required to produce a current. Consequently, an investigation of the fundamental dynamics occurring between dyes and nanoparticles at the single-particle level is necessary. The work presented in this thesis is aimed at understanding the dye-nanoparticle interactions in model PEDSSCs through transmission electron microscopy (TEM), LSPR measurements, and single-particle fluorescence spectroscopy.

The remaining sections of this thesis will describe studies of the distance-dependence of fluorescence enhancement near Ag nanoparticles that are currently underway. Silver colloids are easy to prepare and roughly spherical, ensuring that the field around each nanoparticle is uniform at all points a certain distance from the particle’s center. Nanoparticles are encapsulated of silica shells of various thicknesses; the silica shells act as a uniform spacer from the surface of the nanoparticle, ensuring equal distance between the nanoparticle and a layer of fluorophores (which are subsequently spin-coated on top of the nanoparticles).
Figure 6. Depiction of the model system used to study the distance-dependence of plasmon enhancement of fluorescence. A rhodamine B molecule near silver nanoparticles (grey) with a silica coat (light blue) of varying distances (in this case, ~10 nm) will be probed.

Single particle fluorescence spectroscopy is then performed. Fluorescence intensity measurements of dye molecules on individual nanoparticles are acquired. Then, a ratio of fluorescence on each nanoparticle is compared to the background to measure enhancement. Figure 6 is a depiction of the model system used to understand fluorescence enhancement at different distances from the surface of a silver nanoparticle.
Experimental Section

Materials

Deionized water was used for all experiments; water was filtered through a Barnstead Easypure II System (Thermoscientific) to a resistance of 18.2 MΩ/cm. Concentrated sulfuric acid (H$_2$SO$_4$), concentrated hydrochloric acid (HCl), concentrated nitric acid (HNO$_3$), sodium citrate dehydrate, and ethanol (200 Proof) were purchased from Fischer Scientific. All acids were Certified ACS Plus Grade. Silver nitrate (AgNO$_3$) and 16-mercaptohexadecanoic acid (16-MHA) were obtained from Aldrich. A 40 wt.% aqueous solution of dimethylamine (DMA) and Rhodamine B (99+% pure) were purchased from Acros Organics. Tetraethoxysilane (TEOS, 99.9%) was purchased from Alfa Aesar.

Synthesis of Colloidal Silver Nanoparticles

All glassware was cleaned with aqua regia (3:1 ratio of HCl:HNO$_3$) and rinsed thoroughly with deionized water. To 500 mL deionized water, 90 mg AgNO$_3$ was added while heating and stirring. Once the solution came to a rapid boil, 10 mL of a 1% sodium citrate solution was added. The resulting solution was allowed to boil for 30 minutes; within 5 minutes, a color change to a muddy greenish brown was observed. Then, the solution of silver colloids was removed from heat and allowed to cool. Silver colloids were diluted with deionized water to a final volume of approximately 1 L and stored in the dark. All colloids used for subsequent characterization and silica-coating procedures were used within three weeks of their original synthesis.

Silica-Encapsulation of Silver Nanoparticles

Citrate-reduced silver colloids were sonicated for 30 minutes. Then, specific amounts of colloid solution (1.334, 1.303, or 1.327 mL) were transferred to 1.5 mL graduated, flat-
cap microcentrifuge tubes (Fischer Scientific). An ethanolic solution of 16-MHA of a specific concentration (180, 153, or 173 µM, respectively) was added to each tube (180, 197, or 173 µL, respectively) to a final concentration of 20 µM. Solutions were allowed to sit overnight, then centrifuged for 10 minutes at a relative centrifugal force of ~2000 to concentrate nanoparticles. The supernatants were removed using a micropipetter and nanoparticles were resuspended in 13.857 mL ethanol and sonicated for 30 minutes. Solutions were transferred to stir plates and stirring at ~750 rpm was initiated (enough stirring to ensure complete mixing without splashing). Next, various amounts (3.35, 2.51, 0.95, or 0.84 µL) of an ethanolic solution of TEOS was added to the stirring colloid solution to final TEOS concentrations of 1.00, 0.75, 0.28, or 0.25 mM, respectively. A 1.139 mL aliquot of aqueous DMA was then rapidly injected into the colloid solution (for a final DMA concentration of 0.6 M), and the solution was allowed to stir for approximately 3 hours. The solution was removed from the stir plate, sonicated for 30 minutes, and subsequently centrifuged for 10 minutes at a relative centrifugal for of ~2000 to collect nanoparticles. Supernatants were removed and silica-coated nanoparticles were redispersed in deionized water.

**Transmission Electron Microscopy**

Nanoparticle solutions were sonicated for 30 minutes then drop-coated onto TEM grids (Ted Pella, Copper Formvar 300-mesh, Carbon Type B). Grids were allowed to dry overnight. TEM images were obtained on a Zeiss EM109 TEM microscope operating at 80 kV. Images were analyzed using Adobe Illustrator.
Sample Preparation for Optical Microscopy

Glass cover slips (Fischer Scientific, 25x25mm) were allowed to soak in H$_2$SO$_4$ for 24 hours then rinsed thoroughly with deionized water. Samples were sonicated for 30 minutes before being drop-coated onto cover slips. Cover slips were allowed to dry overnight. Rhodamine B dye was prepared for spin-coating through a series of serial dilutions in deionized water. Dye at a concentration of 10$^{-4}$ M was spin-coated onto the sample cover slips using a spin-coating program: 10 s at 500 rpm, 30 s at 3000 rpm (WS-400-6NPP-LITE, Laurell Technologies). Cover slips were allowed to dry overnight.

Localized Surface Plasmon Resonance (LSPR) Measurements

Bulk solution LSPR (absorption) measurements were taken using a Perkin-Elmer Lambda 35 UV/VIS spectrophotometer.

Fluorescence Measurements

Glass coverslips were placed atop a nano-positioning stage (Queensgate, NPS-XY-100B) on an inverted microscope (Nikon Eclipse Ti-U) equipped with a dark-field condenser (Nikon, Dry NA = 0.95-0.80) and a variable NA 100x oil-immersion objective (Nikon Plan Fluor, NA = 0.5–1.3) set to NA = 0.7. A color camera (Edmund Optics, EO-0413C) was used to record images of the samples. Fluorescence images were acquired using a 532 nm laser at a power of 0.01 μW. Emission from the sample was sent through an emission filter (Semrock, LP03-532RS-2S) and then collected using an avalanche photodiode detector (MPD) with a 50 μm aperture to provide confocal resolution. All data were acquired using a custom LabView code.
Results and Discussion

Silica-Coating of Colloidal Silver Nanoparticles

In order to study the distance dependence of the plasmon enhancement effect in PEDSSCs, silica-coated silver nanoparticles (SCNPs) of various shell thicknesses were synthesized. First, colloidal silver nanoparticles were produced through a citrate reduction of silver nitrate. The resulting nanoparticles are stabilized in solution by the citrate capping ligand. Solutions were characterized using TEM and shown to contain particles of various shapes and sizes (as seen in Figure 7); however, the majority of nanoparticles are spherical and have diameters ranging from 35-65 nm. The colloidal suspension demonstrated an extinction maximum ($\lambda_{\text{max}}$) at 405 nm as shown in Figure 9 which was reproducible within 1 nm for each synthesis.

Nanoparticles were subsequently coated in a layer of silica (see Figure 7). Silica-encapsulation has several advantages: (1) silica replaces the electrostatically-bound citrate capping ligand with a more stable covalently-attached shell (2) SCNPs are chemically inert in most common solvents, and (3) the silica shell acts as a uniform spacer that is easily quantified using TEM, providing a consistent and controllable distance between particle and dye for subsequent fluorescence measurements. Nevertheless, the process of silica-coating of noble metal nanoparticles can be complicated and hard to reproduce; the harsh reagents used in typical procedures can damage or destroy the nanoparticles, and extremely thin silica shells have been difficult to synthesize.

In order to combat these obstacles, the silica-coating of colloidal silver nanoparticles was performed using a modified Stöber method. A traditional Stöber
process is performed in ethanol, using an ammonia (NH$_3$) catalyst to perform the hydrolysis and condensation of tetraethoxysilane (TEOS).\textsuperscript{37,39} This type of procedure cannot be utilized when working with colloidal silver nanoparticles, as NH$_3$ can oxidize the metal, which leads to etching or complete dissolution of the particles. Previous methods have used polymers as capping agents in order to protect the particles from NH$_3$ degradation, but these procedures still run the risk of nanoparticle dissolution if the particles are not completely coated with ligand.\textsuperscript{40} Other groups have studied the use of alternative amine catalysts and produced uniform shells in sol-gel type procedures; however, these studies could not produce silica shells of a thickness less than ~30 nm.\textsuperscript{38} Xue et al. crafted a similar procedure for triangular nanoprisms, in which the thickness of shells was controllable solely by changing the concentration of TEOS in the reaction mixture. They employed a milder amine catalyst and an organic linker molecule (16-mercaptophexadecanoic acid, or MHA) as a substrate for the initiation of silica shell
growth, but again, this synthesis was limited to a minimum silica coating of ~15 nm as attempts to achieve thinner shells produced incomplete coatings.\textsuperscript{37} In order to produce the thinner shells required to observe plasmonic enhancement, we adapted the Xue procedure, which had so far produced the thinnest shells, for use with citrate-stabilized colloidal silver nanoparticle solutions.

To prime the nanoparticles for silica-encapsulation, the electrostatically-attached citrate cap was removed and replaced with a covalently-attached linker molecule: MHA. Upon addition of MHA to the citrate-reduce colloids, a covalent Ag-S bond is formed, causing citrate ions to be displaced from the surface of the metal. Figure 8 depicts the MHA-attachment step as well as the following steps involved in silica-encapsulation.
The possibility for electrostatic interaction of the silver surface with the carboxylic acid end of MHA is repressed by the covalent bond that silver forms with sulfur. The colloidal nanoparticle solution was treated with MHA overnight. The presence of covalently-attached MHA was verified by a measured change in optical properties of the bulk nanoparticle solution using UV-Visible spectroscopy after overnight treatment and removal of excess MHA solution, results of which are depicted in Figure 9.

A shift in the absorbance $\lambda_{\text{max}}$ of approximately 10 nm was consistently observed after MHA treatment, a figure that is close to the ~15 nm shift expected from previous
The observed shift in LSPR is consistent with the addition of MHA, since the LSPR spectrum is sensitive to the refractive index of the nanoparticle’s local environment. The silica shell was then grown through the DMA-catalyzed hydrolysis and condensation of TEOS onto the carboxylic acid moiety of MHA. Figure 8 shows a summary of all synthetic steps. Different amounts of TEOS were added to try to vary shell thickness.

The structural properties of the silica-coated silver nanoparticles (SCNPs) were characterized using TEM. Uniformly-coated nanoparticles with little clumping were observed. Although small amounts of uncoated nanoparticles were seen, a majority of

![Figure 10](image_url)

**Figure 10.** Variation in silica shell thickness with concentration of TEOS added. Average shell thicknesses are plotted with standard deviations for each data set show as error bars.
particles were encapsulated in silica shells of consistent thicknesses. Greater variations in shell thickness occurred at lower TEOS concentrations. As expected, the thickness of the silica coat could be controlled by varying the amount of TEOS added to the reaction mixture.\textsuperscript{37} Shell thickness was found to vary linearly with concentration of TEOS in the reaction solution as shown in Figure 10.

In particular, TEOS concentrations of 0.25 mM, 0.28 mM, 0.75 mM, and 1.00 mM produced average shell thicknesses of $8.6 \pm 3.2$ nm, $9.1 \pm 2.5$ nm, $50.9 \pm 4.3$ nm, and $75.4 \pm 4.8$ nm, respectively (as determined by TEM measurements). Average shell thicknesses, which are shown in Table 1, are based on sample sizes of $N = 64$, $37$, $14$, and $50$, respectively. Images of SCNPs of each shell thickness are shown in Figure 11.

<table>
<thead>
<tr>
<th>Amount TEOS Added (μL)</th>
<th>Concentration TEOS (mM)</th>
<th>Average Shell Thickness (nm)</th>
<th>Standard Deviation</th>
<th>Number of Particles Measured (N)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.35</td>
<td>1</td>
<td>75.4</td>
<td>4.8</td>
<td>50</td>
</tr>
<tr>
<td>2.51</td>
<td>0.75</td>
<td>50.9</td>
<td>4.3</td>
<td>14</td>
</tr>
<tr>
<td>0.95</td>
<td>0.28</td>
<td>9.1</td>
<td>2.5</td>
<td>37</td>
</tr>
<tr>
<td>0.84</td>
<td>0.25</td>
<td>8.6</td>
<td>3.2</td>
<td>64</td>
</tr>
</tbody>
</table>

Again, the change in optical properties of the nanoparticles produced by the silica coating was monitored using UV-Visible spectroscopy of the bulk solution. A further shift in the $\lambda_{\text{max}}$ of $\sim 10$ nm, displayed in Figure 9, was observed after the synthesis was completed, which is again close to the expected shift of $\sim 15$ nm. However, unlike previous studies,\textsuperscript{37} a broad, red-shifted absorbance peak was also observed. This peak is likely due to the variety of nanoparticle geometries and aggregation states in the synthesized SCNPs. Therefore, bulk LSPR spectroscopy of the nanoparticle solution is
used as a qualitative tool to verify that a change in nanoparticle environment has occurred.

![TEM Images of silica-coated nanoparticles with shell thicknesses](image)

**Figure 11.** TEM Images of silica-coated nanoparticles with shell thicknesses of (a) 8.6 ± 3.2 nm, (b) 9.1 ± 2.5 nm, (c) 50.9 ± 4.3 nm, and (d) 75.4 ± 4.8 nm.

**Fluorescence Enhancement of RB near SCNPs**

The SCNPs described in the previous section were used to investigate the distance dependence of fluorescence enhancement of rhodamine B (RB) dye molecules. RB was chosen as the fluorophore for these studies for several reasons: (1) its absorbance spectrum overlaps with the LSPR spectrum of the colloidal Ag nanoparticles as shown in Figure 12, (2) its absorbance $\lambda_{\text{max}}$ is at 557 nm (see Figure 14), which is close to the excitation wavelength used in these experiments (532 nm), and (3) it has previously been used as a dye sensitizer in DSSCs.
Solutions of RB at a concentration of $10^{-4}$ M were spin coated onto glass cover slips containing SCNPs. Images of single particle scattering intensities (LSPR images) were taken of each sample area in order to correlate particle position with fluorescence intensity. Then, single particle fluorescence spectroscopy was subsequently performed on the same sample area. Fluorescence measurements were obtained using laser excitation at 532 nm and intensity counts were detected every 0.01 µm$^2$. Fluorescence images were then analyzed to determine fluorescence intensity of dyes located on each particle compared to the background. A depiction of the correlation of LSPR images to fluorescence intensity images can be seen for each silica shell thickness in Figures 13, 14, 15, and 16. Figure 13 shows the fluorescence quenching of RB dye molecules on seven

![Figure 12](image-url)
bare nanoparticles. The dark spots seen on the fluorescence image that correspond to nanoparticles (bright spots) on the LSPR image show that less fluorescence intensity is measured in those locations (quenching).

Figure 14 shows the correlated LSPR-fluorescence images of RB on Ag nanoparticles with shells of 8.6 ± 3.2 nm thickness. The fluorescence image shows bright spots that correspond to the locations of nanoparticles on the LSPR image, indicating
enhancement. Figures 15 and 16 (LSPR and fluorescence on silver nanoparticles with silica shell thicknesses of: 50.9 ± 4.3 nm and 75.4 ± 4.8 nm) also show enhancement.

The quenching and enhancement of fluorescence of RB seen on bare nanoparticles and silica-coated nanoparticles of various shell thicknesses, respectively, is consistent with what has been reported in the literature.\textsuperscript{33} Fluorescence is predicted to be maximally enhanced at a distance of ~7 nm from the nanoparticle surface, with the enhancement factor decaying slowly as that distance is increased. However, dye molecules positioned closer than ~7 nm from the nanoparticle surface experience fluorescence quenching, and

\textbf{Figure 15.} Correlated 5x5 µm LSPR (left) and false-colored fluorescence intensity (right) images of RB molecules on Ag nanoparticles with silica coats of 50.9 ± 4.3 nm, with particles circled. Counts per 10 ms range from

\textbf{Figure 16.} Correlated 10x10 µm LSPR (left) and false-colored fluorescence intensity (right) images of RB molecules on Ag nanoparticles with silica coats of 75.4 ± 4.8 nm, with particles circled. Counts per 10 ms range from 1034 to 2979.
the greatest quenching is seen at the immediate surface of the nanoparticle.

The fluorescence intensities on each particle were measured and subsequently compared to the intensity of the entire background. The ratio of intensities “on particle” to “off particle (or background)” was used to calculate the enhancement factor of each particle as seen in equation 4:

\[
\text{Enhancement Factor (EF)} = \frac{I_{\text{on particle}}}{I_{\text{off particle}}} \tag{4}
\]

These values were averaged to produce the average enhancement factors seen in Table 2.

<table>
<thead>
<tr>
<th>Shell Thickness (nm)</th>
<th>Average Enhancement Factor</th>
<th>Standard Deviation</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>75.4 ± 4.8</td>
<td>1.41</td>
<td>0.25</td>
<td>55</td>
</tr>
<tr>
<td>50.9 ± 4.3</td>
<td>1.90</td>
<td>0.71</td>
<td>19</td>
</tr>
<tr>
<td>8.6 ± 3.2</td>
<td>1.99</td>
<td>0.96</td>
<td>29</td>
</tr>
<tr>
<td>0 (Bare Nanoparticles)</td>
<td>0.84</td>
<td>0.15</td>
<td>45</td>
</tr>
</tbody>
</table>

At this point, the fluorescence enhancement seen on SCNPs with thick and thin shells, 75.4 ± 4.8 nm and 8.6 ± 3.2 nm respectively, and on uncoated particles has been well measured and quantified. Fluorescence enhancement ratios of 1.99 ± 0.96, 1.90 ± 0.71, and 1.41 ± 0.25 were observed on particles of 8.6 ± 3.2 nm, 50.9 ± 4.3 nm, and 75 ± 5 nm shell thicknesses. On bare nanoparticles, quenching occurred, producing an average fluorescence enhancement ratio of 0.84 ± 0.15. Further data collection is in progress for medium and thin shells (50.9 ± 4.3 nm and 8.6 ± 3.2 nm, respectively); preliminary results are shown in Table 2.

Although the process of data collection is not yet complete, the distance dependence of fluorescence enhancement is consistent with the literature values discussed above. The greatest enhancement is seen on shells of ~8.6 nm, which is
consistent with the literature prediction that enhancement peaks at ~ 7 nm from the surface of the nanoparticle. \(^{33}\)

**Conclusions and Future Work**

Silica-coated nanoparticles of various shell thicknesses have been synthesized and characterized. Shell thicknesses of \(8.6 \pm 3.2\) nm, \(9.1 \pm 2.5\) nm, \(50.9 \pm 4.3\) nm, and \(75.4 \pm 4.8\) nm were reproducibly produced and quantified using TEM. Changes in optical properties of the bulk SCNP solutions were measured with UV/Visible spectroscopy.

Fluorescence of RB dye molecules has been studied and quantified on SCNPs of three different shell thicknesses and on bare nanoparticles. Ratios of fluorescence on the particles compared to the background were calculated. Particles with silica shells of \(0\) nm (bare nanoparticles), \(8.6 \pm 3.2\) nm, \(50.9 \pm 4.3\) nm, and \(75.4 \pm 4.8\) nm produced fluorescence ratios of \(0.84 \pm 0.15\) (quenching), \(1.99 \pm 0.96\), \(1.90 \pm 0.71\), and \(1.41 \pm 0.25\), respectively. We have concluded that nanoparticles with thin shells (\(8.6 \pm 3.2\) nm) produced the greatest fluorescence enhancement.

Although these measurements are reliable, some inconsistencies in the data have occurred. Uneven dye coatings due to the random nature of spin-coating can produce “clumpy” fluorescence measurements or inconsistent background measurements. Additionally, dye orientation cannot be controlled, which can have an effect on enhancement factors. Future work will involve covalent attachment of dyes to the silica shell of SCNPs in order to control both the concentration of dyes around each nanoparticle and the orientation of the dyes.

Other discrepancies in the data can occur due to the presence of silica-coated dimers or multimers and nanoparticles of various sizes. Although most SCNPs are single nanoparticles encapsulated in silica, some aggregation of particles within a single silica
shell has occurred. Correlated single particle LSPR/fluorescence spectroscopy does not allow the characterization of structural characteristics such as the number or size of SCNPs, only the size of the silica coat around the nanoparticles. Additionally, silica shells within each batch have some small variations in shell thickness, and greater variation occurs with thinner shells. Therefore, future studies will involve structural characterization of each individual particle’s size and shape, the exact thickness of the silica shell, and the multiplicity of nanoparticles within each shell using TEM. Further studies involving the nature of plasmonic fluorescence enhancement in the context of TiO₂ will take place to better model the actual environment within PEDSSCs.
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References


