

Video Article

Synthesis, Characterization, and Functionalization of Hybrid Au/CdS and Au/ZnS Core/Shell Nanoparticles

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Abstract

Plasmonic nanoparticles are an attractive material for light harvesting applications due to their easily modified surface, high surface area and large extinction coefficients which can be tuned across the visible spectrum. Research into the plasmonic enhancement of optical transitions has become popular, due to the possibility of altering and in some cases improving photo-absorption or emission properties of nearby chromophores such as molecular dyes or quantum dots. The electric field of the plasmon can couple with the excitation dipole of a chromophore, perturbing the electronic states involved in the transition and leading to increased absorption and emission rates. These enhancements can also be negated at close distances by energy transfer mechanism, making the spatial arrangement of the two species critical. Ultimately, enhancement of light harvesting efficiency in plasmonic solar cells could lead to thinner and, therefore, lower cost devices. The development of hybrid core/shell particles could offer a solution to this issue. The addition of a dielectric spacer between a gold nanoparticles and a chromophore is the proposed method to control the exciton plasmon coupling strength and thereby balance losses with the plasmonic gains. A detailed procedure for the coating of gold nanoparticles with CdS and ZnS semiconductor shells is presented. The nanoparticles show high uniformity with size control in both the core gold particles and shell species allowing for a more accurate investigation into the plasmonic enhancement of external chromophores.

Video Link

The video component of this article can be found at <https://www.jove.com/video/53383/>

Introduction

Gold and silver nanoparticles have potential for future technological advances in a variety of applications including photonics,¹ photovoltaics,² catalysis,³ chemical/biological sensing,⁴ biological imaging,⁵ and photodynamic therapy.⁶ Under visible excitation, the surface electrons can oscillate to form a resonance known as a localized surface Plasmon resonance (SPR), which can be utilized to concentrate incident radiation in the visible spectrum. Recently, noble metal nanoparticles have been combined with semiconductor or magnetic nanoparticles to produce hybrid nanoparticles with enhanced and tunable functionality.^{7,8} Recent literature, such as the study conducted by Ouyang *et al.*⁹ or Chen *et al.*¹⁰, has shown the possibility for the synthesis of these particles, but only limited control in the uniformity of the hybrid species is possible due to a distribution of gold nanoparticle sizes and compounded by the lack of optical characterization coupled with physical characterization at each stage of growth. Zamkov *et al.* showed similar uniformity in shell formation but only one shell thickness was utilized with different core sizes, with some shells not being fully formed around the nanoparticles. In order to effectively utilize these nanoparticles, the precise optical response must be known and characterized for a variety of shell thicknesses. Higher precision in shell thickness can be accomplished through the use of monodisperse, aqueous gold particles as the template, resulting in higher control over the final hybrid species. Interaction between the core and shell may show limited enhancement in absorption or emission rates due to the small amount of semiconductor material and the proximity to the gold core. Instead of interaction between the semiconductor found in the shell and the gold particle, the shell may be used as a spacer to limit the distance between an external chromophore.¹¹ This will allow for higher control over the spatial separation between the plasmon while, negating the consequences of direct contact with the metal surface.

The extent of the electronic interaction between the surface plasmon resonance and exciton produced in the chromophore, is directly correlated to the distance between the metallic and semiconductor species, the surface environment and strength of the interaction.¹² When the species are separated by distances greater than 25 nm, the two electronic states remain unperturbed and the optical response remains unchanged.¹³ The strong coupling regime is dominant when the particles have more intimate contact and can result in the quenching of any excitation energy via nonradiative rate enhancement or Forster Resonance Energy Transfer (FRET).^{14,15} Manipulation of the coupling strength, by tuning the spacing between the chromophore and metal nanoparticle, can result in positive effects as well. The nanoparticle extinction coefficient can be orders of magnitude larger than most chromophores, allowing the nanoparticles to concentrate the incident light much more effectively. Utilizing the increased excitation efficiency of the nanoparticle can result in higher excitation rates in the chromophore.¹² Coupling of the excitation dipole can also increase the emission rate of the chromophore which, can result in increase in quantum yield if nonradiative rates are unaffected.¹² These effects could lead to solar cells or films with increased absorbance, and photovoltaic efficiencies, facilitated by the increased absorption

cross-section of the gold and the ease of charge extraction from the semiconductor layer due to the existence of localized surface states.^{12,16} This study will also provide useful information on the coupling strength of the plasmon as a function of distance.

Localized surface plasmons have widely been used in sensing¹⁷ and detection¹⁸ applications due to the sensitivity of the plasmon resonance to the local environment. Cronin *et al.*, showed the catalytic efficiency of TiO₂ films can be improved with addition of gold nanoparticles. Simulations showed that this increase in activity is due to coupling of the plasmon electric field with excitons created in the TiO₂, which subsequently increases exciton generation rates.¹⁹ Schmittenmaier *et al.*, showed that the efficiency of Dye-sensitized (DSSC) solar cells could be improved with the incorporation of the Au/SiO₂/TiO₂ aggregates. The aggregates enhance the absorption through creation of broad localized surface plasmon modes which increase optical absorption over a broader range of frequencies.²⁰ In other literature, Li *et al.* observed significant reduction in fluorescence lifetime as well as distance dependent enhancement in steady state fluorescence intensity was observed through direct coupling of a single CdSe/ZnS quantum dot and single gold nanoparticle.²¹ In order to take full advantage of this plasmonic enhancement, there is a need for physical coupling with a set distances between the two species.

Synthesis of Hybrid Nanoparticles

Jiatiao *et al.*, described a method to coat semiconductor material onto gold nanoparticles via a cationic exchange in order to produce uniform and tunable shell thicknesses. The shells were uniform in thickness, but the gold templates were not very monodisperse. This will alter the semiconductor to gold ratio from particle to particle and therefore the coupling strength.⁹ An in-depth study on the optical properties of these core shell nanoparticles has been conducted, in order to develop a reproducible synthetic method. Previous methods rely on organic-based nanoparticle synthesis, which can produce samples with broad plasmon resonances due to inhomogeneity in the gold nanoparticle size. A modified aqueous synthesis of gold nanoparticles can provide a reproducible and monodisperse gold nanoparticle template with stability for long periods of time. The aqueous surfactant cetyl trimethyl ammonium chloride forms a double layer on the nanoparticle surface due to interaction between the long carbon chains of nearby cetyl trimethyl ammonium chloride molecules.²² This thick surface layer requires careful washing to remove excess surfactant and allow access to the nanoparticle surface, but can provide higher control over the nanoparticle size and shape.²³ The aqueous addition of a silver shell can be controlled with high precision leading to a more intimate correlation between shell thickness and optical properties.²³ A slower reduction via ascorbic acid is utilized to deposit the silver on the gold surface, requiring the addition of silver salt to be very precise in order to prevent formation of silver nanoparticles in the solution. The third step requires a large excess of sulfur to be added into an organic phase and a phase transfer of the aqueous nanoparticles must occur. With addition of oleylamine as an organic capping agent and oleic acid, which may act as both a capping agent and aid in phase transfer of the nanoparticles, a uniform, amorphous silver sulfide shell can be formed around the nanoparticles.^{9,24} The concentration of these molecules must be high enough to prevent aggregation of the nanoparticles in this step, but too much excess can make purification difficult. In the presence of tri butyl phosphine and a metal nitrate (Cd, Zn or Pb), a cationic exchange inside of the amorphous sulfide shell can be conducted. Reaction temperatures must be modified for the different reactivities of the metals⁹ and any excess sulfur must be eliminated to reduce the formation of individual quantum dots. Each step of the synthesis corresponds to a change in the surface environment of the nanoparticle, therefore, a change in plasmon should be observed due to the dependence of the plasmon frequency on surrounding dielectric field. A parallel study of optical absorption as a function of Transmission Electron Microscopy (TEM) characterization was used to characterize the nanoparticles. This synthetic procedure will provide us with well-controlled and uniform samples, providing better correlation from microscopy and spectroscopy data.

Coupling with Fluorophores

Applying a dielectric spacing layer between a plasmonic metal surface and a fluorophore can help to diminish losses due to nonradiative energy transfer of created excitons into the metal. This spacing layer can also aid in the study of distance dependence between the fluorophore and the plasmon resonance on the metal surface. We propose using the semiconductor shell of the hybrid nanoparticles as our dielectric spacing layer. The shell thickness can be tuned with nanometer precision with thicknesses ranging from 2 nm to 20 nm allowing precise distance correlation experiments to be conducted. The shell can also be tuned with Cd, Pb or Zn cations and S, Se and Te anions, allowing for control over not only the distance but also the dielectric constant, electronic band arrangement and even crystal lattice parameters.

Protocol

1. Synthesis of Gold Nanoparticles

1. Weigh the gold salt in the glove box and add to a vial previously cleaned with aqua regia before diluting with water in a volumetric flask. Prepare a 1 mM Gold (III) chloride trihydrate (393.83 g/mol) in 100 ml water for gold stock solution.
2. Weigh out 3.2 g solid CTAC (320 g/mol) and heat, in 25 ml water, to approximately 60 °C for dissolution. Cool to room temperature and dilute the mixture with to 50 ml with water in a volumetric flask to prepare a 0.2 M Cetyl trimethyl ammonium chloride (CTAC).
3. Mix 20 ml of 1 mM gold solution and 20 ml of 0.2 M CTAC solution inside a round bottom boiling flask and place in an oil bath set to 60 °C. Allow to mix for 10 min.
4. Add 1.7 mg (1:1 mole ratio) solid Borane tert-butyl amine (86.97 g/mol) to the gold/CTAC solution and let stir for 30 min.
Note: Solution should turn deep red. The resulting solution has a gold particle concentration of about 5 μM and can be stored for months at a time or used immediately for the next phase of reaction.

2. Coating with Silver

1. Use precise reagent amounts to coat the nanoparticles with a silver shell. The shell will provide the template for size and shape of the semiconductor shell. Precise reagent amounts will also help to prevent nucleation of silver particles.
2. First calculate the volume of the core, in cm³, and convert to mass per particle using the density of gold. For example, to calculate the core volume, assume a spherical nanoparticle with a diameter of 15 nm to give a volume of 1767.15 nm³ and then convert to cm³ (1.77 x 10⁻¹⁸ cm³). Multiply the volume by the density of gold (19.3 cm³) to calculate the mass per particle (3.41 x 10⁻¹⁷).

- Using 10 ml of a 5.3 μM gold nanoparticle solution, 5.30×10^{-8} moles of particles are present. Multiply by the molar mass gives to calculate the mass of gold present in the solution (1.04×10^{-5} g). Divide the mass of gold in the solution by the mass per particle to find the number of gold particles present (3.06×10^{11}).
- Calculate the volume of the nanoparticles with a 5 nm shell thickness, in cm^3 ($8.18 \times 10^{18} \text{ cm}^3$) and subtract this from the volume of the core nanoparticle ($1.77 \times 10^{-18} \text{ cm}^3$) to determine the shell volume (6.41×10^{-18}). Convert this volume to mass of silver by multiplying by the number of gold particles and the density of silver (2.33×10^{-4}). Shell thicknesses in the range of 1-10 nm will be utilized in this study.
- Convert the mass of silver to moles of silver needed for a 5 nm shell radius (2.33×10^{-4}). From this value, calculate the volume of 4.0 mM silver nitrate (540 μl) solution needed for the amount of gold utilized in the starting solution (10 ml).
- Prepare a 4.0 mM AgNO_3 (169.87 g/mol) solution in 5 ml water. In a 70 $^\circ\text{C}$ oil bath, mix 10 ml of stock gold nanoparticles with ascorbic acid to make a 20 mM solution.
- Add the silver solution drop-wise to the gold and ascorbic acid solution and allow the reaction to stir for 2 hr.
Note: The reaction will turn light orange (thinner shell) to dark orange (thicker shell) over the course of the reaction.
- Centrifuge the nanoparticles at 21,130 x g for 10 min and redisperse into clean water. Decant the supernatant from the pelleted nanoparticles to aid in removal of bare gold nanoparticles or silver nanoparticles which may have been formed.

3. Conversion of the Shell to Silver Sulfide

- Weigh elemental sulfur in a 200:1 molar ratio to the silver used in the previous stage of the experiment. For 10 ml of Au/Ag core shell particles and a 5 nm shell, dissolve 3 ml of oleylamine and 1.5 ml of oleic acid into 10 ml toluene.
 - Concentrate the silver colloids, via centrifugation at 21,130 x g for 10 min and disperse in 1 ml water.
Note: This step helps increase the efficiency of the extraction from the aqueous layer to the organic layer upon formation of the silver shell.
- Add the colloids, drop-wise to the sulfur solution under stirring for 1 hr.
Note: The solution will turn dark blue (thinner shells) to purple (thicker shells) as the sulfuration goes to completion.
- Centrifuge the colloidal solution at 4,000 x g for 10 min after the reaction has stirred 2 hr to remove the water and unreacted sulfur from the solution. Re-disperse the nanoparticles into clean toluene with sonication, if necessary.
 - Sonicate the nanoparticles in a bath sonicator for 30 sec to 1 min in order to disperse into toluene.
Note: Excess oleylamine or oleic acid may fall out of solution and can be removed after this step by decanting the solution from the white solid.

4. Cation Exchange

- Make the metal precursor by dissolving the metal nitrate into 1 ml of methanol, to make a 0.2 M solution of $\text{Cd}(\text{NO}_3)_2$ or $\text{Zn}(\text{NO}_3)_2$.
Note: a 0.8 M solution may be used for thicker shells to decrease the amount of methanol in solution.
 - Mix the metal solution with the silver sulfide-shelled nanoparticles in a 1:1 molar ratio with the silver. Heat to 50 $^\circ\text{C}$ for cadmium shell and 65 $^\circ\text{C}$ for zinc shells under a nitrogen atmosphere.
- Add tri-butyl phosphine in a 500:1 molar ratio to the metal precursor. The reaction times are 2 hr for Cadmium and 20 hr for zinc.
- Purify via centrifugation at 21,130 x g for 10 min in order to remove any isolated CdS or ZnS nanoparticles which may have been formed. Disperse the pelleted nanoparticles into a clean nonpolar solvent such as hexanes, toluene, or chloroform.

5. Ligand Exchange from Oleylamine

- Mix the nanoparticle solution with 1.5 times volume ratio ethanol to colloidal solution in toluene in a centrifuge tube. Centrifuge at 4,000 x g for 10 min to pellet the nanoparticles.
- Wash the nanoparticles with ethanol and centrifuge once more to collect the solid particles.
Note: The particles can be stored at this stage but removal of ethanol is necessary to prevent aggregation.
- Bind Ligands with a nucleophilic binding group to the surface via unbound cationic sites on the shell. 11-mercaptoundecanoic acid and 3,4-diaminobenzoic acid are appropriate molecules which leave the nanoparticles water-soluble.
 - Disperse the nanoparticles into the ligand solution in large excess, approximately 10 times higher concentration than the native oleate molecules. Stir the particles at room temperature overnight to allow displacement of any residual oleate molecules.
 - Centrifuge the solution at 4,000 x g for 10 min. Wash the pelleted particles with methanol and centrifuge at 4,000 x g for 10 min once more to collect the solid nanoparticles.

Representative Results

Normalized absorbance spectra of gold nanoparticles with three different surfactants are shown in **Figure 1**. The surfactants utilized are oleylamine, tetradecyl trimethyl ammonium chloride (TTAC), and cetyl trimethyl ammonium chloride. CTAC and TTAC surfactants show narrower plasmon resonance absorption band.

The amount of reducing agent not only affects the FWHM but the peak position of the resulting nanoparticle solutions. Investigation of **Figure 2** shows the peak narrowing with a lower amount of reducing agent.

Absorbance traces (**Figure 3**) were fit with a Gaussian and the FWHM was plotted versus the reducing agent to gold ratio. The sample with the narrowest FWHM was used to optimize the gold nanoparticle synthesis. From these data, a 1:1 molar ratio of reducing agent to gold produces the most monodisperse particles. The error in the plot is calculated from the deviation in the Gaussian fit to the data.

Synthesis of gold nanoparticles using TTAC as the surfactant, produces spherical particles with a diameter of about 25 nm. The images shown in **Figure 4** were analyzed using ImageJ software to find the particles to be single crystalline with lattice spacing of a approximately 2.3 Å (literature value = 2.355 Å).²² The nanoparticles showed a standard deviation of 0.02 nm.

Gold nanoparticles with a diameter of about 16 nm, were produced through synthesis with CTAC as the surfactant. The images in **Figure 5** were analyzed using ImageJ software to find the particles to be single crystalline with lattice spacing of a approximately 2.3 Å (literature value = 2.355 Å).²² The standard deviation of the nanoparticles was 0.4 nm.

The absorbance spectra of gold nanoparticles with silver shells of varying thickness (**Figure 6**), show a significant dependence of the plasmon resonance with the nature of the surface coverage. As the traces go from darker to lighter blue, the thickness of the silver shell increases. A blue shift in the spectrum of about 60 meV is observed for the surface plasmon resonance, from the characteristic gold peak at 2.38 eV to around 3.0 eV with the thickest silver shell.

We see the spectra produced when samples containing separate gold and silver nanoparticles in vary ratios in **Figure 7**. The blue shift of the surface plasmon resonance, seen in **Figure 6**, is due to silver coating as opposed to the formation of silver nanoparticles. The resonance doesn't shift as in the case for the silver shell but rather increases or decreases in intensity depending on which species is in excess. When silver is in excess the resonance around 3.0 eV is more prominent while the peak at 2.5 eV is prominent when the gold nanoparticles are in higher concentration.

TEM images of gold nanoparticles with 3 nm (top), 5 nm (middle), and 7 nm (bottom) radius silver shells were analyzed using ImageJ software. The particles, in **Figure 8** are single crystalline with lattice spacing of approximately 2.6-2.7 angstroms similar to that of fcc silver (2.5 Å)²⁵, as well as an absence of isolated silver particles. The inner gold nanoparticles were also analyzed to find that the spacing was slightly smaller than the bare gold nanoparticles with values around 2 Å. This could be due to a small amount of stress place on the nanoparticles when the shell is deposited. Overall the shell thickness seems uniform and mostly spherical with a few samples having a slightly asymmetric shell with one elongated end. This elongation is more pronounced in the smaller shell sizes, as the larger shell thicknesses seem to be more uniform.

The progression of the plasmonic peak with the addition of a silver sulfide shell is shown. Analysis of the spectrum in **Figure 9**, shows the plasmon peak red-shifting with increasing coverage of silver sulfide due to the effect of the larger refractive index of silver sulfide and contribution from the semiconductor band gap.

The absorbance spectrum of gold nanoparticles coated with silver shows a plasmonic peak centered around 400 nm. Analysis of **Figure 10** shows that after addition of sodium sulfide, in a 1:1 molar equivalent to the silver in the shell, a disappearance of any plasmon resonance occurs.

A featureless spectrum, similar to **Figure 10** is also observed, in **Figure 11**. Addition of the sodium sulfide solution to a colloidal solution of silver particles. This lead to the use of a different sulfur source for the reaction.

TEM images of nanoparticles shown in **Figure 12**, were analyzed using ImageJ software to find the particles to be amorphous or polycrystalline. In the majority of the nanoparticles, no crystal lattice fringes appeared in the shell due to the amorphous nature, however, a few small regions of crystallinity were seen with spacing of 2.38 Å, which is consistent to the literature values for monoclinic silver sulfide. In general the silver sulfide shell tends to be a little bit larger than the previous silver shells but very uniform and spherical with a standard deviation of 1.8 nm. The inner gold nanoparticles also retained their single crystallinity with spacing of 3.51 Å. This continued compression of the gold lattice supports the theory that increased stress from the shell is causing a compression of the gold particle.

The absorbance spectrum of gold nanoparticles coated with different thicknesses of CdS, in **Figure 13**, shows the plasmonic absorbance for thin CdS shell has broad peak centered around 2.25 eV. The absorbance becomes mainly featureless for thicker shells with broad shoulders forming around 2.5 eV. These shifts can be attributed to change in the refractive index and dielectric environment of the nanoparticle and the higher energy "humps" may be due to direct absorption of the semiconductor shell.

TEM images analyzed using ImageJ show that the shell may be affecting the lattice spacing of the inner gold particle with a similar trend observed in **Figure 14**. The inner gold particle, retained its single crystallinity but show a narrower lattice spacing of around 3.51 Å. The CdS shell analysis showed spacing of 6.00 Å on average, consistent with Zinc-Blende crystal structure.²⁶ The shells show high monodispersity at each thickness and no aggregation of the nanoparticle is observed.²⁷ A few nanoparticles showed a small spot where there seems to be a lack of shell coverage. This could be caused by an inability for the cation exchange to occur at that region due to the silver sulfide being crystalline in some regions as opposed to amorphous. A few particles seem to deviate from a spherical geometry with a slightly larger width, possibly structured after the silver sulfide template which had the larger deviation out of the three shell species.

Absorbance spectrum can be observed for gold nanoparticles coated with 10 nm of ZnS. Analysis of the spectra in **Figure 15**, shows the resonance is very similar to the CdS shell but with a plasmonic peak at 2.15 eV, which is blue-shifted by 100 meV from the CdS shell of the same diameter.

The inner gold particle of the ZnS coated nanoparticles retained its single crystallinity while continuing the trend of a slightly more narrow spacing of around 3.51 Å, seen in the TEM images shown in **Figure 16**. The ZnS shell analysis showed spacing of 5.31 Å on average, which is consistent with Zinc-Blende crystal structure.²⁶ The shells are uniform with an average diameter of around 10 nm. The shells are much thinner than the CdS shells which is due to the lower amount of electrons in the lighter Zn when compared to Cd. Inhomogeneities still occur on a few particles which could be due to either pre-existing defects in the silver sulfide shell or the longer reaction time and higher temperatures required for the ZnS cation exchange reaction.

FTIR spectrum of nanoparticles with mercaptoundecanoic acid and 3,4-diaminobenzoic acid can be observed in **Figure 17**. The molecules will bind via the thiol group for mercaptoundecanoic acid (blue) and the two amine groups for 3,4-diaminobenzoic acid (red). The spectra are compared to nanoparticles with oleylamine to confirm the varying surface coverage. The major feature present for the oleylamine-capped particles (black) is a very broad N-H stretch located around $3,450\text{ cm}^{-1}$. This could be due to an irregular stretching mode due to proximity of the nanoparticles to the protons on the amine nitrogen. The Carbonyl stretch is very prominent in the FTIR spectrum for the mercaptoundecanoic acid coated particles but is located around $1,550\text{ cm}^{-1}$. In the 3,4-diaminobenzoic acid-capped nanoparticles, a small carbonyl stretch is observed that is split into two bands but the main feature is the characteristic O-H stretch which occurs around $3,300\text{ cm}^{-1}$.

Nanoparticles with a 5 nm radius CdS shell and either oleylamine (black) or mercaptoundecanoic acid (red) as the surfactant are observed in **Figure 18**. The nanoparticles are dispersed in toluene for oleylamine and ethanol for mercaptoundecanoic acid. The surface plasmon resonance is nearly identical for both ligands with a slight broadening and red shift observed for the mercaptoundecanoic acid capped nanoparticles in ethanol.

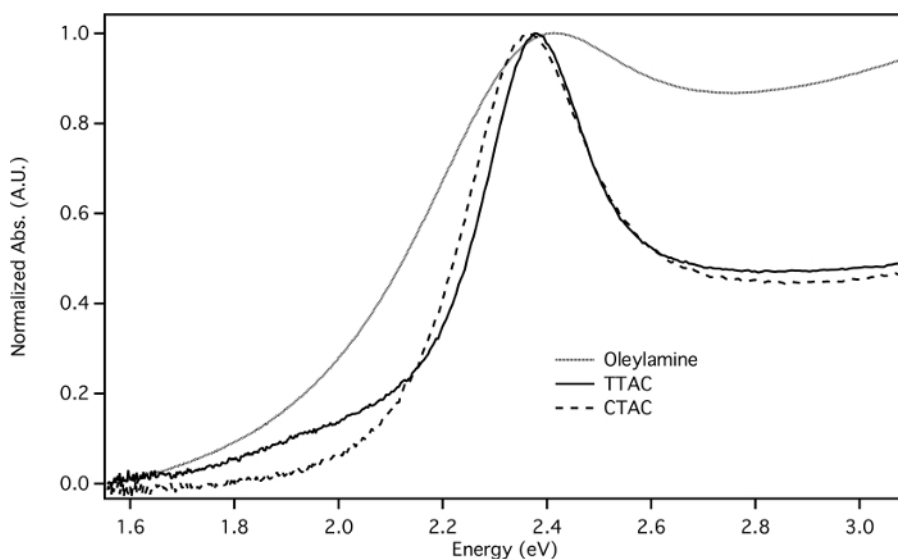


Figure 1: Absorbance spectra of gold nanoparticles. A comparison of absorbance spectra of gold nanoparticles synthesized with CTAC (dashed line), TTAC (solid line) and oleylamine (fine dotted) line surfactants.

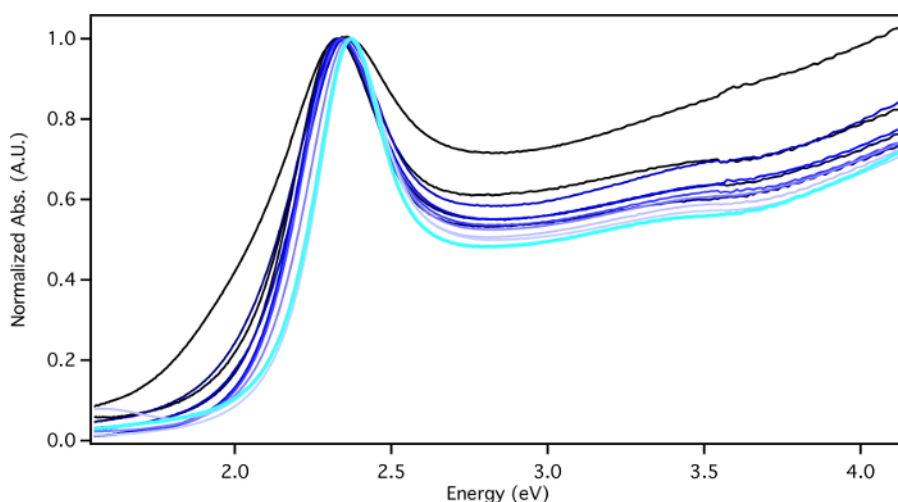


Figure 2: Absorbance spectra of gold nanoparticles synthesized with CTAC and varying ratios of borne tert-butyl amine reducing agent to gold precursor. The ratios range from 23:1 to 1:1. The black trace represents the 23:1 gold ratio and as the amount of reducing agent decreases the traces change from darker to lighter blue.

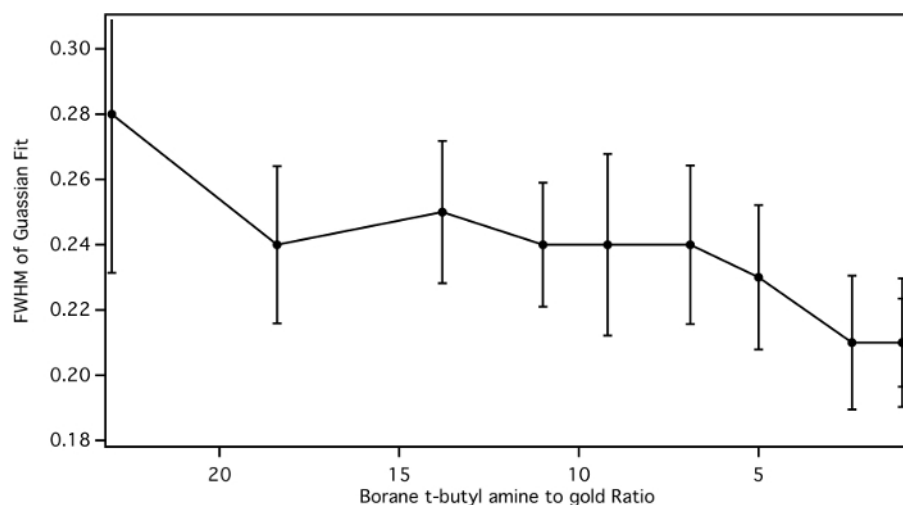


Figure 3: Comparison of full width at half-the maximum taken from a Gaussian fit of the absorbance line shape spectrum. The x axis represents the ratio of the reducing agent to moles of gold precursor in the sample and the y-axis is the FWHM of the Gaussian fit to the absorbance trace.

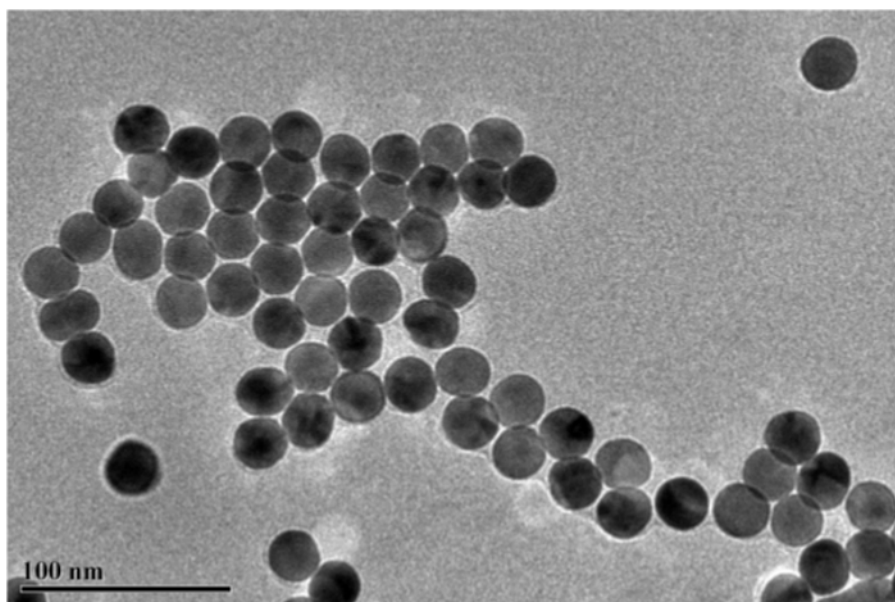


Figure 4: TEM images of synthesized gold nanoparticles with TTAC. The TEM images are acquired at 200 kV accelerating voltage and the scale bar is 100 nm.

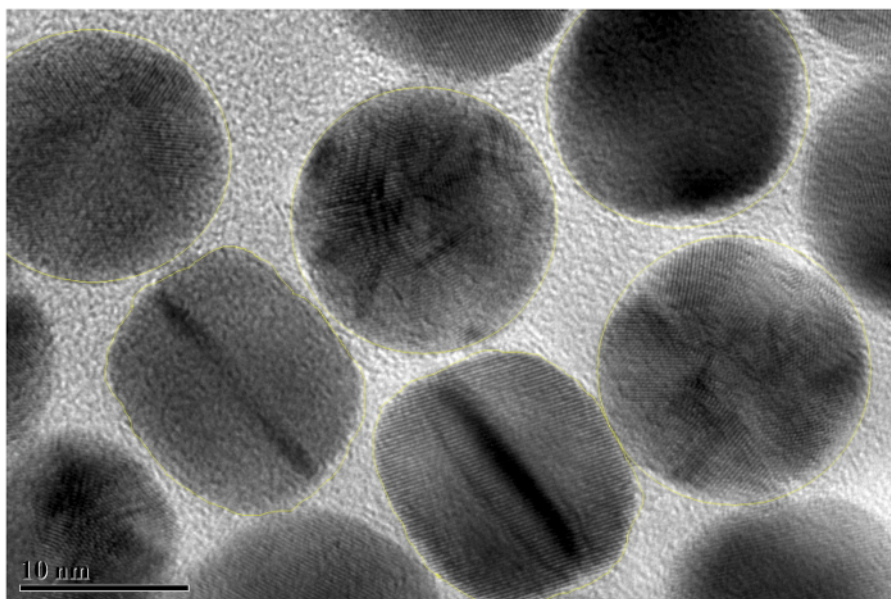


Figure 5: TEM images of synthesized gold nanoparticles with CTAC. The TEM images are taken at 200 KV acquired voltage and the scale bar is 10 nm.

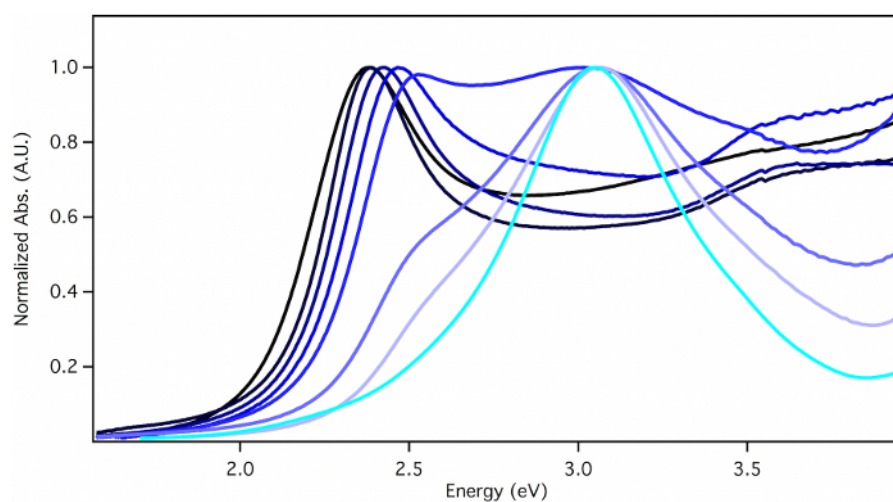


Figure 6: Normalized absorbance spectra of gold nanoparticles dispersed in water (far right black) and various silver shell thicknesses. Silver thickness increases from right to left (black to light blue).

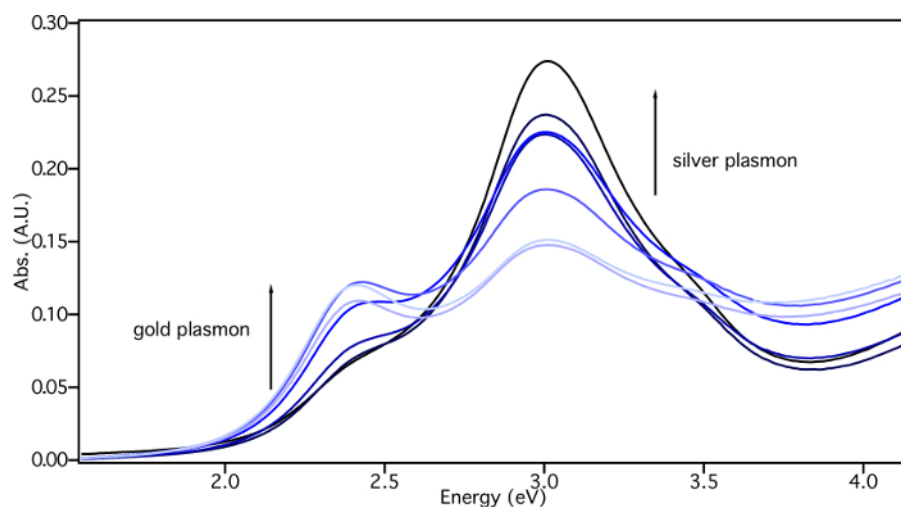


Figure 7: Absorbance spectra of mixtures of gold and silver nanoparticles at various ratios. The highest amount of silver particles is represented by the back curve and as the amount of gold particles increases, the traces become lighter blue.

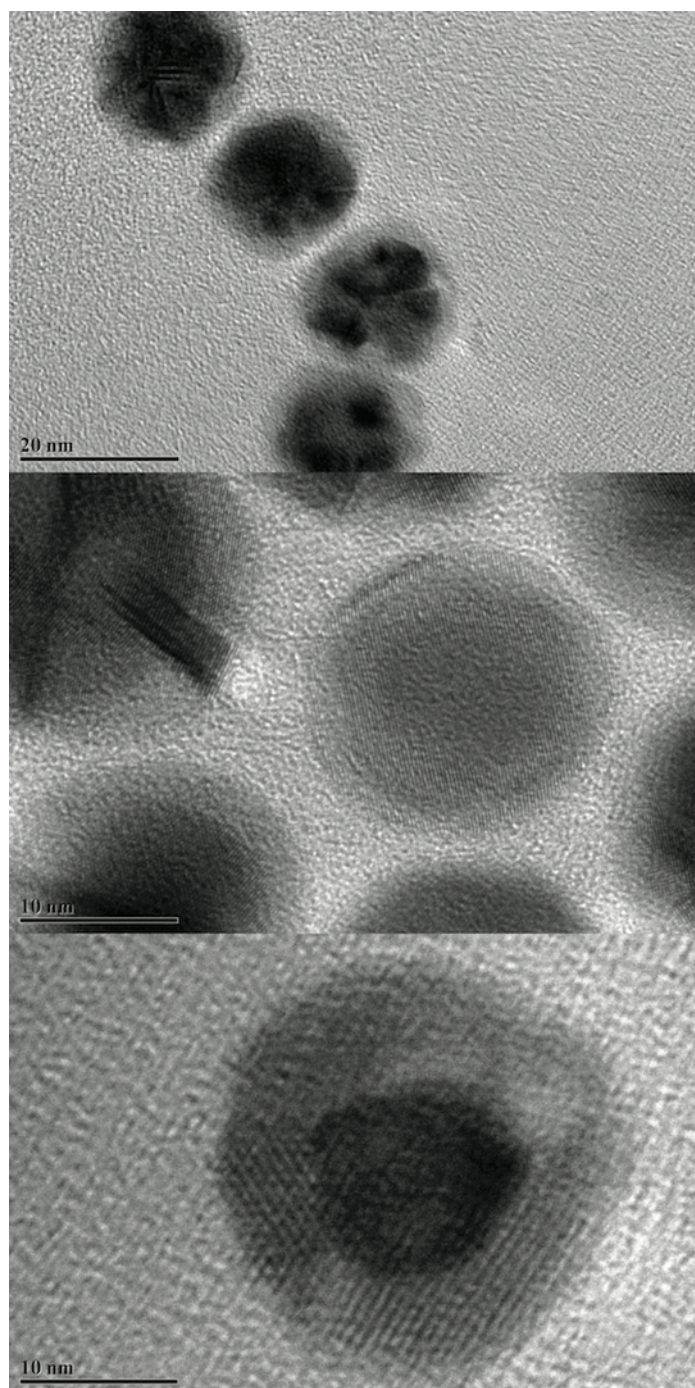


Figure 8: TEM images of synthesized gold nanoparticles coated with silver shell thicknesses of 3 nm in radius (top); 5 nm in radius (middle), and 7 nm radius (bottom). The TEM images are acquired at 200 kV accelerating voltage and the scale bars are 20 nm (top) and 10 nm (middle and bottom)

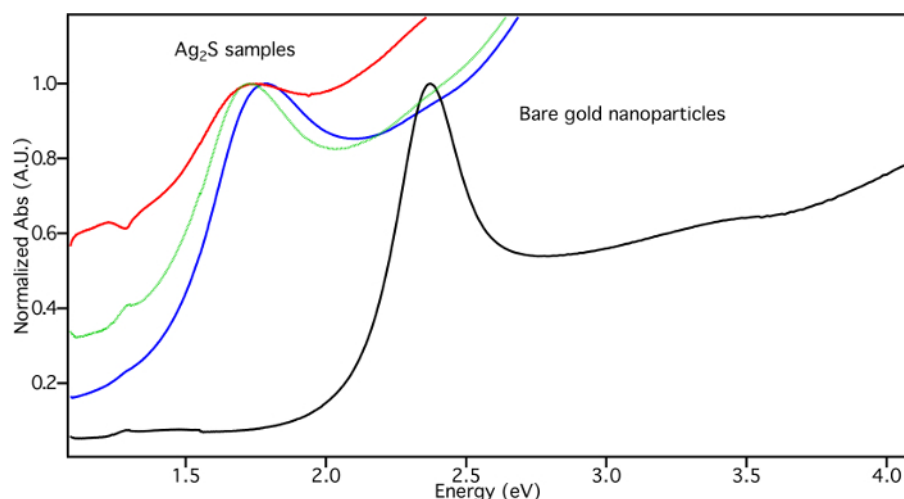


Figure 9: Normalized absorbance spectra of gold nanoparticles (black) with shells of silver sulfide (blue, green and red). The thicker the silver sulfide the lower the plasmon resonance.

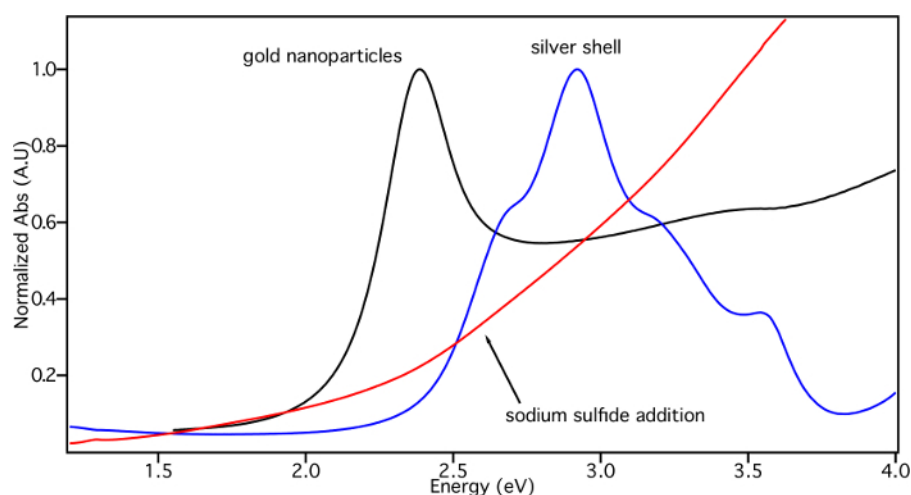


Figure 10: Normalized absorbance spectra of gold nanoparticles with a silver shell and after sulfur addition. The black trace represents gold nanoparticles, the blue is gold with a shell of silver and the red trace is after addition of sodium sulfide in a 2:1 mole ratio to silver in the shell.

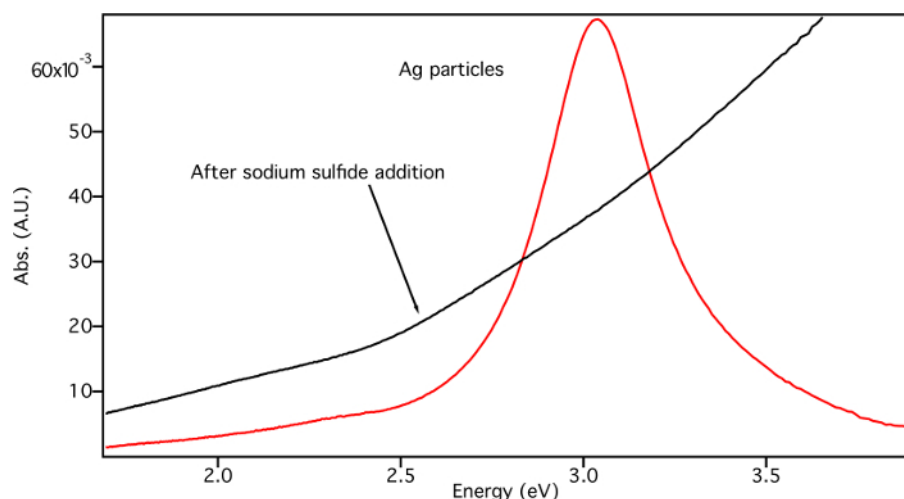


Figure 11: Normalized absorbance spectra of silver nanoparticles before (red) and after (black) addition of sodium sulfide. The nanoparticles are dispersed into water for the absorption experiments.

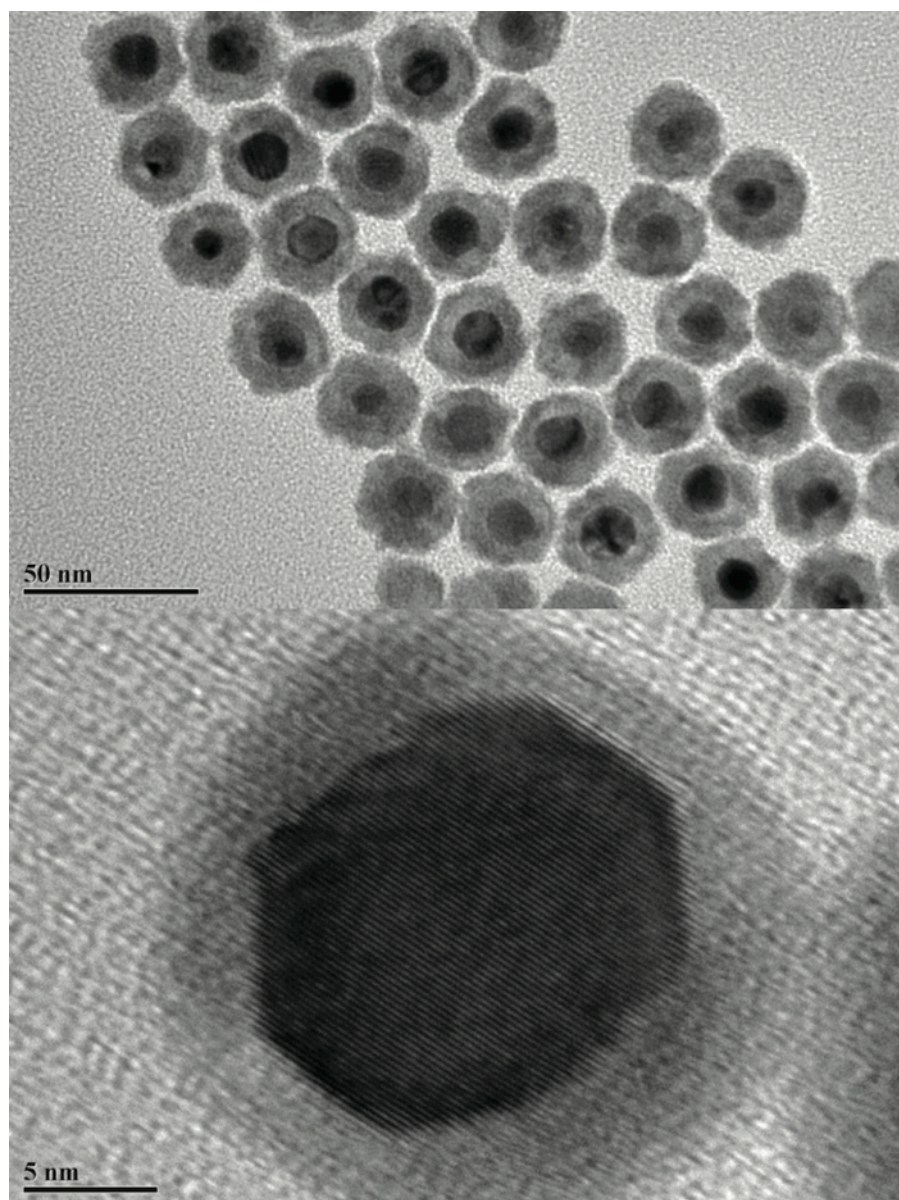


Figure 12: TEM images of synthesized gold nanoparticles coated with silver sulfide shell with 5 (top two images) and 15 nm thicknesses (bottom image). The TEM images are acquired at 200 kV accelerating voltage and the scale bars are 50 nm (top) and 5 nm (bottom).

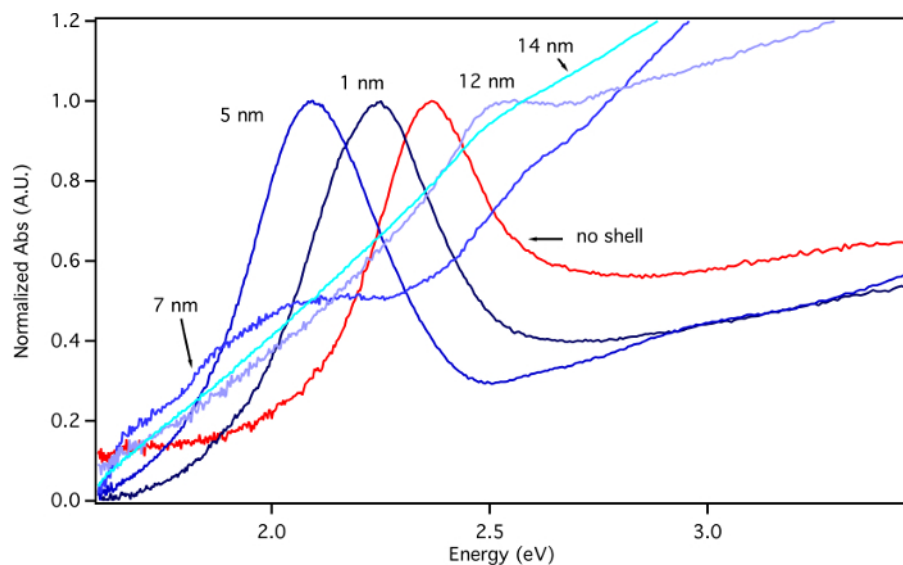


Figure 13: Normalized absorbance spectra of gold/CdS nanoparticles. Gold nanoparticles without CdS are shown in red. The thinnest CdS shell (1 nm radius) is shown in black and as the thickness increases, the traces go to a lighter blue.

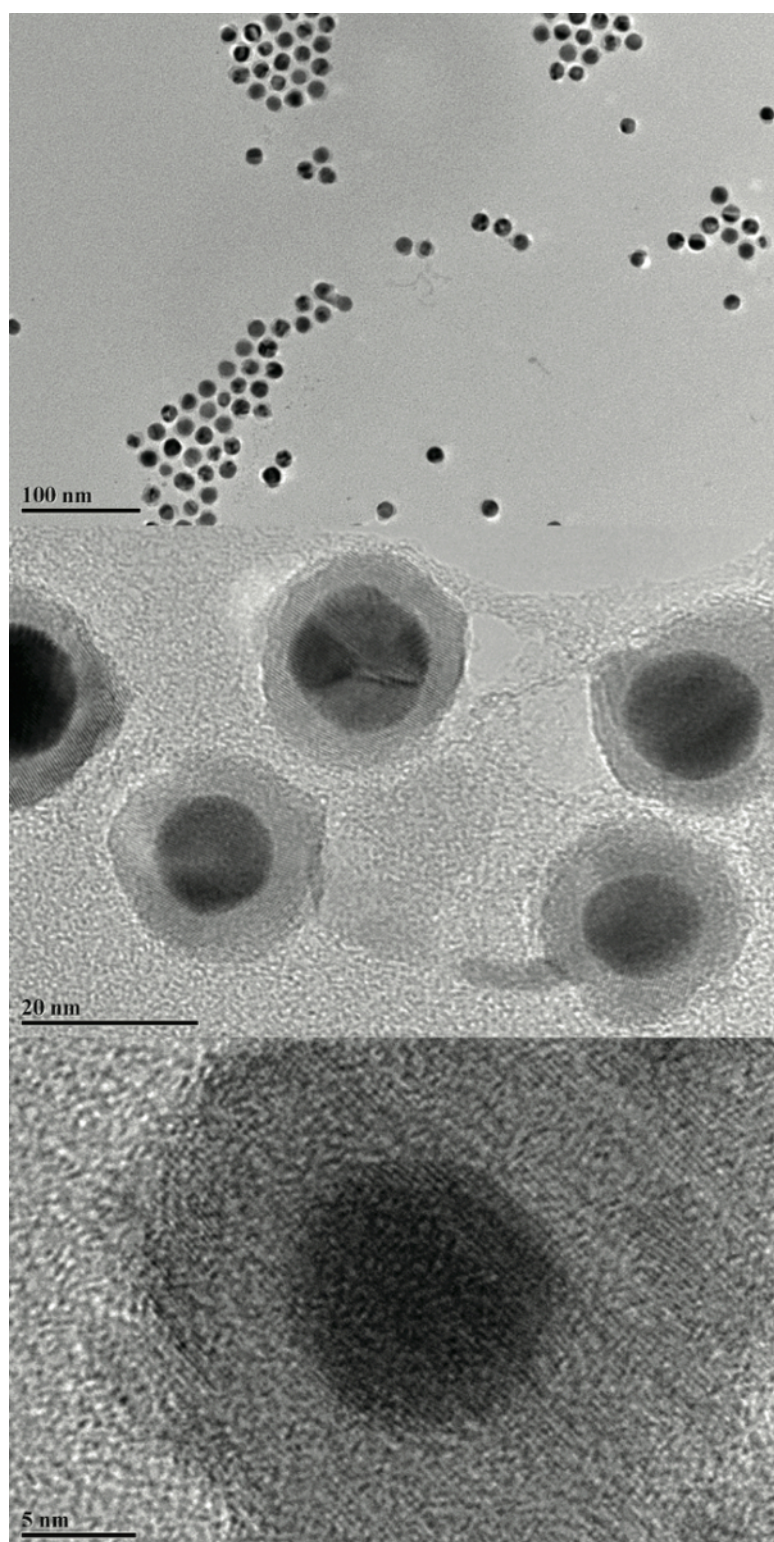


Figure 14: TEM images of synthesized gold nanoparticles coated with CdS shell thicknesses of 3 nm radius (top), 5 nm radius (middle), and 7 nm radius (bottom). The TEM images are acquired at 200 kV accelerating voltage and the scale bars are 100 nm (top), 20 nm (middle) and 5 nm (bottom).

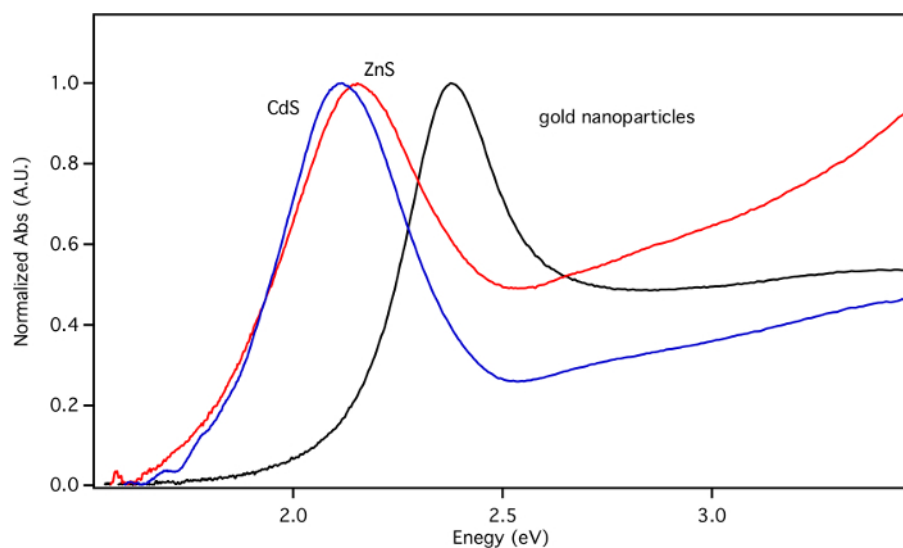


Figure 15: Normalized absorbance spectra of gold nanoparticles with a 5 nm radius ZnS shell (red trace). Gold nanoparticles without any shell are shown in black. The blue curve is the same gold nanoparticle sample coated with CdS of the same thickness.

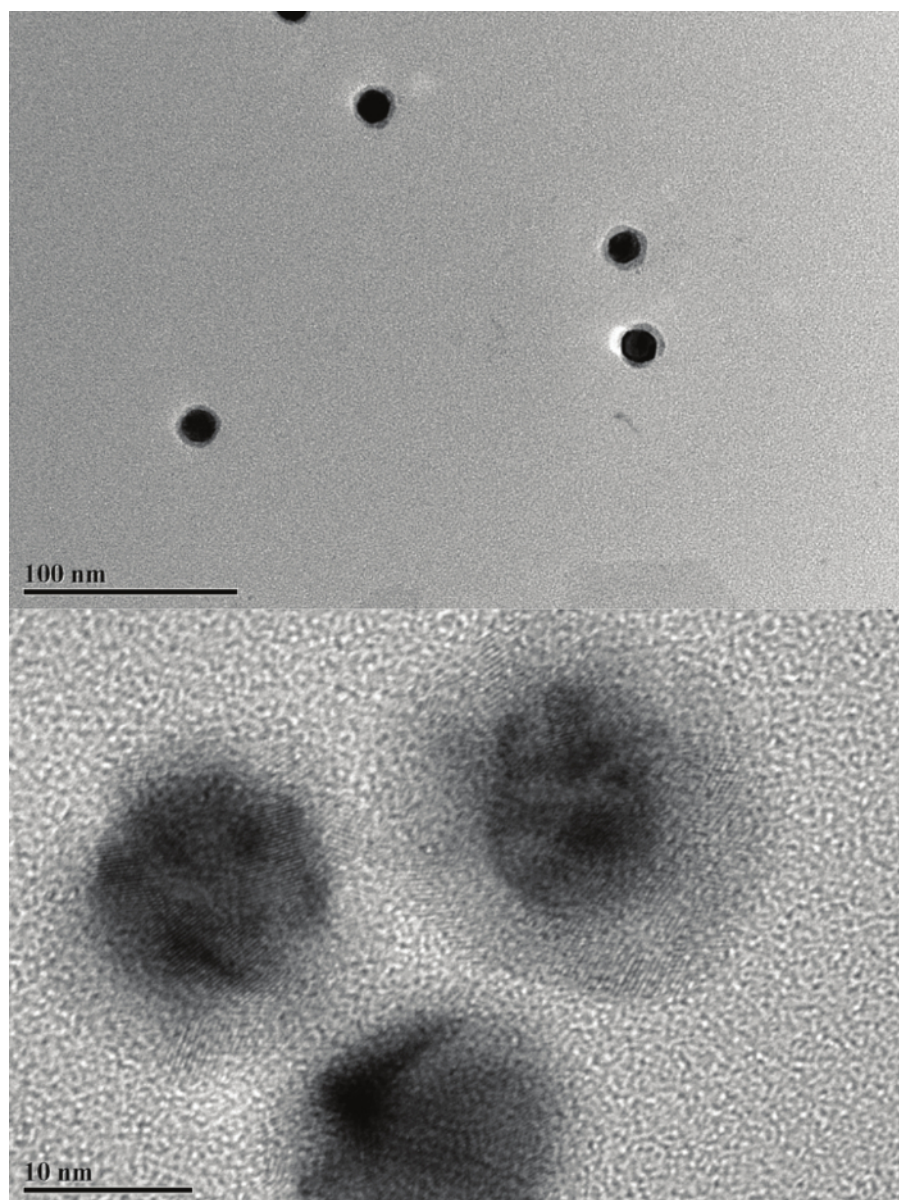


Figure 16: TEM images of synthesized gold nanoparticles coated with a ZnS shell with 5 nm radius thickness. The TEM images are acquired at 200 kV accelerating voltage and the scale bars are 100 nm (top), 10 nm (bottom).

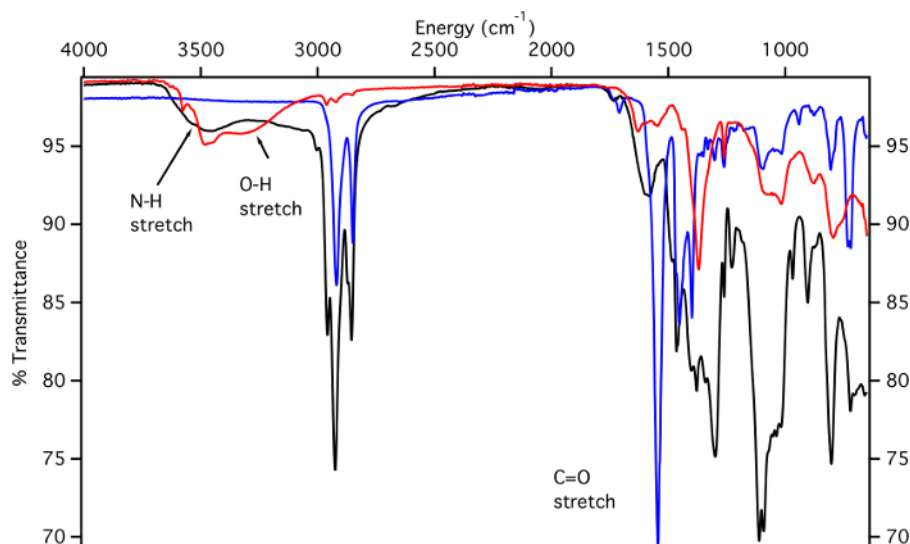


Figure 17: FTIR spectra of nanoparticles with oleylamine (black), mercaptoundecanoic acid (blue), and 3,4-diaminobenzoic acid (red) are shown. The FTIR spectra are taken on solid samples of dried nanoparticles.

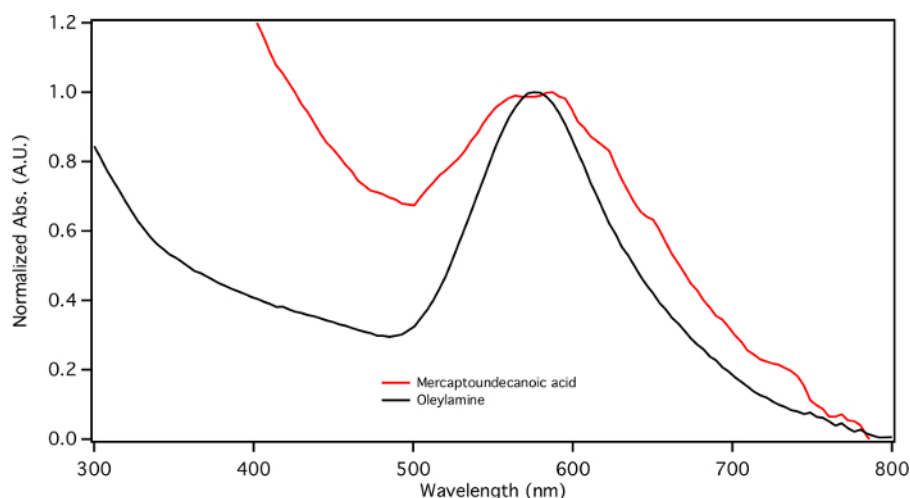


Figure 18: Normalized absorbance spectra of gold nanoparticles with a 5 nm radius CdS shell and different surface ligands, oleylamine in black and mercaptoundecanoic acid in red. The spectra are acquired in toluene (oleylamine) and ethanol (mercaptoundecanoic acid) solvents respectively. [Please click here to view a larger version of this figure.](#)

Discussion

Gold nanoparticles

In order to guarantee high quality core shell nanoparticles, a monodisperse sample of gold nanoparticles must first be synthesized as a template.^{28,29,30} We modified the gold nanoparticle synthesis to produce long-chain tertiary amines-capped nanoparticles instead of oleylamine-capped nanoparticles. Oleylamine-capped nanoparticles show a rather narrow plasmon resonance, indicative of monodisperse size range, but the particles synthesized via reduction using tert-butyl amine and in the presence of the produce long-chain tertiary amines-capped nanoparticle show a significantly more narrow resonance peak. The variability of sizes may provide inaccuracies in calculated precursor volumes for the shell materials. In order to further optimize the starting gold template, a study on the effect of reducing agent to gold ratio on FWHM of the colloidal gold solution absorption spectrum. The reducing agent amount also seems to affect the size of the resulting nanoparticles, the longest wavelength solutions also show a larger FWHM indicative of a large size distribution. The FWHM is directly dependent on the reducing agent ratio, with a ratio of 1:1 showing the smallest width. Ensuring there are stoichiometric equivalents of borane tert-butyl amine and HAuCl_4 may provide a more steady reduction rate and produce nucleates with a narrow size distribution. Little observable size or geometric variation is seen within the samples synthesized with CTAC or the shorter carbon chain TTAC, but the TTAC particles have a slightly larger diameter (25 nm) when compared to the CTAC coated particles (16 nm). The images were analyzed using ImageJ software to find the particles to be single crystalline with lattice spacing of approximately 2.3 Å (literature value = 4.07 Å). The particles are monodisperse with a standard deviation from the mean diameter of 0.02 nm for the TTAC samples and a slightly higher deviation of 0.4 nm for the CTAC samples. There is some particle overlap but overall, very little aggregation can be observed. Possible issues with this method lie in the accuracy needed in measuring the reducing agent. If too high a concentration of reducing agent is used, a polydisperse sample will be formed and too low a concentration will lower the reaction yield. This synthetic method for producing gold nanoparticles can be extended to studies on the effects of changing the carbon chain

length. Our data show a significant size dependence on the chain length. A 10 nm difference in the produced nanoparticle diameter is seen just by changing the carbon chain by two carbons.

Silver shell

Since the silver shells must also be transformed to an amorphous silver sulfide shell in the subsequent step, the synthesis method must be both robust and repeatable. It has been shown that particles coated with CTAC can provide a template for uniform growth of a silver nanocubes due to the formation of gold particles with both {100} and {111} crystal plane orientation and preferential growth on the {111} facets. The gold particles show mainly {111} facets. This allows for accelerated growth rates for the silver deposition. Here, this method has been utilized to produce tunable, spherical shells of silver onto gold nanoparticle cores. First, a series of shells with increasing thickness were produced in order to monitor the shift of the surface plasmon resonance. A blue shift in the spectrum of about 60 meV is observed for the surface plasmon resonance, from the characteristic gold peak at 2.38 eV to around 3.0 eV with the thickest silver shell. To ensure that this shift is not due to the formation of small silver nanoparticles, solutions with varying ratios of gold and silver nanoparticles are created and monitored using UV-Vis spectra. Observation of the plasmon shift with a mixture of gold and silver nanoparticle shows that the plasmon does not gradually shift to higher energies, but rather decreases or increases in intensity when the ratio of either nanoparticle is altered. If majority silver nanoparticles are present in the mixture, then the peak at 3.06 eV is more prominent, but no change in the position of the gold Plasmon occurs. When deposition of silver on the gold surface occurs, the gold Plasmon red shifts and broadens, until a second silver peak is formed. Finally with thick silver coverage, the gold plasmon is eliminated and only a plasmon peak at 3.06 eV is observed. TEM images were analyzed using ImageJ software to find the particles to be single crystalline with lattice spacing of a approximately 4.13-4.3 Å similar to that of fcc silver,³¹ as well as an absence of isolated silver particles. The inner gold nanoparticles were also analyzed to find that the spacing was slightly smaller than the bare gold nanoparticles with values from 3.6-4 Å. This could be due to a small amount of stress place on the nanoparticles when the shell is deposited. Overall the shell thickness seems uniform and mostly spherical with a few samples having a slightly asymmetric shell with one elongated end. This elongation is more pronounced in the smaller shell sizes, as the larger shell thicknesses seem to be more uniform. This procedure is simple but much care needs to be taken to ensure high precision in reactant amounts. The formation of isolated silver nanoparticles is possible if too high a reducing agent concentration is used or too high a silver ion concentration. The surfactant on the gold particles does not seem to affect the formation of the silver shells, but if the colloidal solution has been agitated the silver can become trapped in the bubbles that form on the top of the solution, lowering the precision of the added amounts. Nanocubes and other shapes can also form if the temperature of the solution is increased as well.

Silver sulfide shell

Once colloidal solutions of Au/Ag core shell nanoparticles are synthesized, the nanoparticle shell can then be converted to Ag₂S. Three separate routes to convert the silver, to silver sulfide were studied and characterized via UV-Vis absorption spectroscopy, in order to ensure a reproducible and robust conversion to an amorphous silver sulfide shell. The plasmon resonance of the nanoparticles has been reported to red shift with increasing shell thickness due to the change in the refractive index from Ag to Ag₂S and the band gap of silver sulfide, which is around 1.1 eV for bulk. The first method utilized was drop wise addition of aqueous sodium sulfide to the colloidal mixture of Au/Ag colloids. Sodium sulfide is a cheap sulfur source that would allow for the reaction to be conducted without a phase change. The plasmon peak red shifts with increasing coverage of silver sulfide due to the effect of the larger refractive index of silver sulfide and contribution from the semiconductor band gap. The amount of silver sulfide used is calculated based on the number of moles of silver present in the shell. An interesting phenomenon occurs when a large amount of sulfur ions, which would be necessary for thicker shells, are left in solution with the gold silver nanoparticles. The nanoparticles seem to dissolve, observed as an elimination of any Plasmon absorption. Once the sulfur solution is added to the colloids, a broad featureless spectrum is observed. To further study this phenomenon aqueous sodium sulfide is also added to a solution of silver nanoparticles. An alternate sulfur precursor is thioacetamide, which has been utilized as a sulfur ion source in various organic reactions. This may provide an aqueous and less reactive sulfur source providing more accurate shell control and eliminate the dissolution of the nanoparticles in solution. Conversion of Au/Ag colloids to Au/Ag₂S proved successful but the same phenomenon was observed using thioacetamide as the sulfur precursor. This issue could be avoided with careful attention to reaction amounts but an alternate method was utilized which offered equal control over sulfurization of the silver shell. When elemental sulfur was dissolved into a toluene solution with oleylamine and oleic acid, the silver shell can be converted to silver sulfide with oleate passivation. The resulting nanoparticles can then be isolated via centrifugation and redispersed into hexanes or toluene. The absorbance spectrum was similar to the ones shown in **Figure 9**. The nanoparticles were then analyzed via TEM. In general the silver sulfide shell tends to be a little bit larger than the previous silver shells but very uniform and spherical with a standard deviation of 1.8 nm. The inner gold nanoparticles also retained their single crystallinity with spacing of 3.51 Å. This continued compression of the gold lattice supports the theory that increased stress from the shell is causing a compression of the gold particle.

Cadmium Sulfide and Zinc Sulfide shell via cation exchange

The silver sulfide was subsequently converted to cadmium sulfide via the literature method.⁹ The absorbance becomes mainly featureless for thicker shells with broad shoulders forming around 2.5 eV. These shifts can be attributed to change in the refractive index and dielectric environment of the nanoparticle and the higher energy "humps" may be due to direct absorption of the semiconductor shell. These spectroscopic changes can be used to roughly estimate the produced shell thickness. The nanoparticles were further studied via TEM. The CdS shell analysis showed spacing of 6.00 Å on average, consistent with Zinc-Blende crystal structure. The shells show high monodispersity at each thickness and no aggregation of the nanoparticle is observed. A few nanoparticles showed a small spot where there seems to be a lack of shell coverage. This could be caused by a inability for the cation exchange to occur at that region due to the silver sulfide being crystalline in some regions as opposed to amorphous. A few particles seem to deviate from a spherical geometry with a slightly larger width, possibly structured after the silver sulfide template which had the larger deviation out of the three shell species. Significant changes in the absorption are observed after the cation exchange. The tails of both absorption spectrum begins to exponentially increase at energies higher than 2.5 eV with the ZnS shell showing double the absorption of the CdS shells. The nanoparticles were further analyzed using TEM. The ZnS shell analysis showed spacing of 5.31 Å on average, which is consistent with Zinc-Blende crystal structure. The shells are uniform with an average diameter of around 10 nm. The shells are much thinner than the CdS shells which is due to the lower amount of electrons in the lighter zinc when compared to cadmium. Inhomogeneities still occur on a few particles which could be due to either pre-existing defects in the silver sulfide shell or the longer reaction time and higher temperatures required for the ZnS cation exchange reaction. The shells can be changed to any group II-IV semiconductors, allowing for a more comprehensive investigation of physical and optical properties as a function of the local dielectric environment.

Ligand Exchange

Functionalization of the outer surface of the shell is accomplished via ligand exchange. FTIR served as the main characterization technique, to identify what chemical species is present on the surface. The use of nucleophilic binding groups ensures a strong bond to the shell surface that will not fall off over time. Two different types of functional groups were placed onto the particles, either a carboxylic acid or an amine. The nanoparticles were washed with methanol to remove any excess ligand present at the end of the exchange. Nanoparticles with oleylamine as the surface ligand were soluble in nonpolar solvents such as chloroform, hexanes or toluene. A complete ligand exchange can be confirmed through a change in solubility to polar solvents such as water or ethanol. The absorption spectrum shows that the particles maintain their plasmon resonance, around 550 nm for nanoparticles with a 5 nm shell of CdS. This ligand exchange can be conducted with dyes or other chromophore with similar nucleophilic functionalities. As with all ligand exchange procedures, irreversible aggregation is always a possibility and can be prevented by limiting the number of washing steps and supersaturating the solution with the desired ligand. The ligand which is wanted to be bound to the surface must also have a higher affinity for the nanoparticle surface than the native oleylamine.

This technique provides a simple modification of a previously developed procedure in order to produce high quality hybrid nanoparticles. The method has been discussed previously, however, issues which could prevent reproducibility, particle stability and monodispersity, still remained. This careful study reveals that a well characterized and monodisperse sample of gold must first be utilized in order to guarantee high quality samples. Using CTAC as the surfactant for the gold nanoparticles provides high monodispersity while also allowing easy deposition of silver with nanometer precision. Silver can be deposited onto the gold to form spherical shells with ranges of 1 to >20 nm in diameter and high stability in aqueous solutions. The silver shell is the template for conversion to an amorphous silver sulfide. The nanoparticles can then be transferred to the organic phase after sulfurization of the silver shell in the presence of oleate surfactant to produce an amorphous shell of slightly larger size than the previous silver shell. Characterization via UV-Vis absorbance spectroscopy and TEM allows for correlation of the Plasmon peak with physical size parameters. This robust procedure can also be extended to other shell species such as lead, or iron as well. This procedure can provide the platform for a new generation of devices where instead of having to add multiple species to optimize performance, the core shell species can be tailored instead allowing for more facile device design by lowering the amount of material needed. These particles will also provide a platform for binding of other materials for studies of distance-dependent plasmonic enhancement with the semiconductor layer acting as a spacer between the chromophore and gold surface.

Disclosures

Authors have nothing to disclose

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