Synthesis-Dependent Catalytic Properties of Gold Nanoparticles

Nanoscience is the study of materials that have dimensions, intuitively, on the nanoscale, typically between 1–100 nm. This field has received such intense research focus because these nanoscale materials (i.e., nanomaterials) not only exhibit physical properties that are drastically different from their bulk state counterparts but also present unique electronic, magnetic, photophysical, and/or catalytic properties.

Of the many different nanomaterials, colloidal (i.e., a homogeneous suspension of particles dispersed in another substance such as a solvent) gold nanoparticles (AuNPs) are one of the most well-studied due to the fascinating phenomena and properties that they exhibit, such as unique optoelectronic behavior and high surface-to-volume ratios, which can be exploited in a wide range of applications including catalysis, chemical and biological sensors, medicinal treatments, and nanoelectronics. The aforementioned photophysical properties and optoelectronic behavior arise from the nanoscale metal particles’ interactions with electromagnetic energy, specifically visible wavelengths of light. When a given metal particle’s size is decreased into the nano-regime, upon interacting with electromagnetic energy of an appropriate wavelength, the NPs experience a relatively uniform electric field, which results in an oscillation of the conduction electrons within the NP, as schematically shown in Figure 1. As the electromagnetic energy continually passes through the NPs, this oscillation results in a resonating effect in the conduction electrons, which is known as the localized surface plasmon resonance (LSPR). The specific wavelength at which this resonance occurs is then known as the LSPR frequency. LSPRs are not limited to AuNPs but are also observed in other colloidal suspensions of metal NPs, specifically those based on silver.

![Figure 1](image)

Since the LSPR is dependent upon the NPs’ size, by varying their size, morphology, and/or shape, this resonance can be tuned throughout most of the visible spectrum. Specifically, for colloidal AuNPs, the observed solution color can range from red to green to blue. For colloidal AuNP solutions where the particles are quasi-spherical in shape and roughly 10–20 nm in diameter, the SPR will appear between 500–525 nm and the solution will display an intense red color as observed in Figure 2A due to the AuNP solution interacting with the blue to green wavelengths and reflecting the complimentary color (i.e., red). As the quasi-spherical NP size increases to sizes between 20–100 nm, for the NPs to experience a relatively uniform electric field, the wavelength must also increase. This means that as the NP size increases, the SPR will shift to longer wavelengths, resulting in the solution color changing from red to purple to blue since the wavelength that is interacting with the particles and, therefore, the reflected wavelength are simultaneously shifting. This phenomenon is visualized in Figure 2A. As previously mentioned, the NP morphology or shape will also influence the SPR. As an example, AuNPs of a trigonal plate morphology...
often display a deep green color due to where the SPR occurs (i.e., the wavelength of light that interacts with this specific morphology).

The resulting AuNP size and, therefore, SPR are highly dependent upon the synthetic conditions employed. That is, the reaction temperature and pH, the reducing agent utilized, and the molar ratio of reducing agent to gold (defined as the “R value”) dramatically influence the resultant NPs and their properties. One of the simplest synthetic routes to AuNP formation is the reduction of a gold salt (\(\text{Au}^{3+}/\text{Au}^+ \rightarrow \text{Au}^0\)), typically chloroauroic acid (HAuCl\(_4\)), in the presence of both a strong reducing agent and a stabilizing agent to prevent the NPs from aggregating. With the proper selection of reducing agent, the need to employ two separate agents for stable AuNP formation can be circumvented since the reducing agent or its oxidized product (recall that if an atom or molecule is reduced, a different entity must simultaneously be oxidized) also functions as the NP stabilizer. Likely the most well-studied of these approaches is known as the Turkevich method, in which an aqueous solution of HAuCl\(_4\) is brought to a boil (100 °C) and an aliquot of sodium citrate at a concentration such that the final R value is approximately 3.4 is rapidly injected. These specific conditions result in quasi-spherical AuNPs in the 15–20 nm regime with the SPR appearing near 525 nm. Other molecules that function in the same manner as sodium citrate (i.e., a dual reducing and stabilizing agent) are NaBH\(_4\) (a strong reducing agent) and ascorbic acid (a mild reducing agent).

Since AuNPs are typically less than 100 nm, the best way to characterize their size and morphology are through electron microscopy techniques such as transmission electron microscopy (TEM). Representative TEM images of AuNPs are provided in Figure 2B–C. However, since their physical properties dictate their photophysical properties (i.e., the SPR), the optical characterization of the nanoparticles via UV-Vis spectroscopy can be employed as a powerful screening tool to make reliable inferences as to the nature of the NPs’ size and morphology. In addition to the SPR frequency providing information as to the approximate size of the resultant AuNPs, the peak shape (i.e., narrow vs. broad) provides insight into the polydispersity or size distribution of the NPs. Typically, a narrow or sharp SPR is indicative of monodisperse NPs or a small size distribution, while a broad SPR is indicative of polydisperse (i.e., large size distribution) or highly aggregated NPs.
The NP size dispersity strongly influences how the NPs behave in applications such as catalysis. Smaller, more uniform AuNPs can result in extremely fast catalytic reactions due to the increased surface-to-volume ratio, which provides a higher quantity of catalytic sites, while large and/or polydisperse NPs typically produce sluggish catalysis. The catalytic properties of the AuNPs can be evaluated through model dye degradation reactions such as the NaBH₄-assisted reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP). In this reaction, the addition of NaBH₄ to 4-NP produces the 4-nitrophenolate ion (4-NPO), which shows an absorbance maximum around 400 nm, resulting in a dark yellow solution. In the presence of a catalyst, such as AuNPs, the NaBH₄ reduces the yellow-colored 4-NPO to the colorless 4-AP, which can be monitored colorimetrically via time-dependent UV-Vis spectroscopy to assess the kinetics of the catalysis. In these model dye degradation reactions, NaBH₄ is used in excess (>200-fold with respect to 4-NP) to ensure that the reduction follows pseudo-first-order kinetics, making the rate calculations easier. Other model reactions that are often employed are the degradation of methylene blue and Congo red. A representative catalytic analysis of 4-NP reduction is provided in Fig. 3. Panel A displays the time-dependent UV-Vis spectra collected throughout the catalyst-mediated reduction of 4-NP. To determine the catalytic rate, a plot of ln(A₀/Aₜ) vs. time is generated as depicted in Panel B of Fig. 3. In this plot, A₀ is the initial absorbance at the wavelength of maximum absorption (Abs@λ_max) prior to the addition of catalyst and Aₜ is the absorbance (at λ_max) at time (t) after the addition of catalyst. The resulting slopes of these plots are equivalent to the apparent rate constants (k_app; in units of inverse time) for the AuNP catalysts.

In this experiment, you will synthesize two different sizes of AuNPs from a stock solution of HAuCl₄ using NaBH₄ and ascorbic acid as co-reducing and stabilizing agents. The NPs’ photophysical properties will be characterized via UV-Vis and you will make inferences as to their approximate size, size distribution, and morphology based on the solution color and SPR. You will then assess the catalytic properties of your two AuNP solutions by conducting model dye degradation reactions, specifically the NaBH₄-assisted reduction of methylene blue and Congo red.
Procedure

*Preparation of the solutions*

1. 6.5 mM HAuCl₄ solution will be provided.
2. 0.05 mM Congo red and methylene blue solutions will be provided.
3. Use 18.2 MΩ·cm water for **ALL** glassware cleaning and dilutions. If poor-quality water is used, or if your glassware is not properly cleaned, AuNP aggregation is likely to occur and your AuNP solutions will need to be re-made with freshly drawn ultrapure water.
4. Preparation of a 0.91 mM ascorbic acid solution:
   a. Accurately weigh approximately 0.4000 g of ascorbic acid (MW=176.12 g mol⁻¹) and record the mass to four decimal places.
   b. Quantitatively transfer the ascorbic acid to a clean 250-mL volumetric flask and add ~100 mL of water. Swirl to dissolve and dilute to volume with water.
   c. Using a 25-mL volumetric pipet, transfer 25 mL of this solution to a clean 250-mL volumetric flask and dilute to volume with water.
   d. Calculate the concentration of the solution.
5. Preparation of a 67.4 mM NaBH₄ solution (note that this solution is not stable long-term and is prone to bubble formation; therefore, it should be carefully mixed immediately before use):
   a. Accurately weigh approximately 0.0255 g of NaBH₄ (MW=37.84 g mol⁻¹) and record the mass to four decimal places.
   b. Deliver the NaBH₄ to a clean 20-mL scintillation vial and add 10 mL of water. Swirl to dissolve.

*Preparing gold nanoparticle (AuNP) solutions*

1. Preparation of ascorbic acid AuNPs:
   a. Deliver 25.0 mL of the ascorbic acid stock to a 50-mL falcon centrifuge tube.
   b. Add 1.0 mL of HAuCl₄ stock to the tube using a clean, dry 1-mL pipet, close the tube, and mix via rapid swirling.
2. Preparation of NaBH₄ AuNPs:
   a. Deliver 25.0 mL of water to a 50-mL falcon centrifuge tube.
   b. Add 1.0 mL of HAuCl₄ stock to the tube using a clean, dry 1-mL pipet.
   c. Add 1.0 mL of NaBH₄ stock to the tube using a clean, dry 1-mL pipet, close the tube, and mix via rapid swirling.

*Analysis of the surface plasmon effect*

1. Using transfer pipettes, transfer each AuNP solution into separate polymethylmethacrylate (PMMA) cuvettes. Analyze these solutions using your UV-Vis spectrometer.
2. Record the LSPR for each solution. This wavelength should lie somewhere between 500 and 550 nm for each solution.
   a. Make a comment about how the LSPR corresponds to the color of each AuNP solution and the respective particle sizes (i.e. which solution has smaller particles).
   b. If multiple peaks exist, record their approximate wavelengths as well and comment about particle morphology.
3. Approximate a full width at 0.75 max (FW@0.75 max) for each solution. Your TA will explain this approximation to you.
a. Comment about particle size distribution as it relates to this number.
4. If your spectra do not look like the ones present in this lab, be sure to let your TA know. Moving forward with poor AuNPs will negatively impact catalysis.

**Catalysis of Congo red reduction using AuNPs**
1. Prepare a fresh stock of 0.10 M NaBH₄ for catalysis. This solution will degrade rapidly, and is only usable for around 30 minutes.
   a. An adequate way of performing this is to weigh ~37.8 mg of NaBH₄ and 10.0 g of water into separate 20-mL glass scintillation vials. Prior to use, slowly pour the water directly onto the NaBH₄ solid and carefully mix to dissolve so as to minimize bubble formation. Use this solution immediately after all of the contents are dissolved and for up to 30 minutes post-mixing.
2. Using a 200-μL autopipettor, add 20 μL of 5.0 mM Congo red and 150 μL of 0.10 M NaBH₄ to a disposable PMMA cuvette.
3. Place this cuvette into the spectrometer and begin recording time-dependent absorbance values at 498 nm. Your TA will show you how to set up the spectrometer for this analysis.
4. Using a 200-μL autopipettor, add 200 μL of the 0.25 mM AA-stabilized AuNP solution.
5. Observe the decrease in absorbance at 498 nm as the Congo red is reduced. The reaction is complete once the absorbance is ~1% of the starting absorbance.
6. Perform this reaction in triplicate for AA-stabilized AuNPs, using fresh solutions and a fresh cuvette for each trial.
7. Repeat the above steps using NaBH₄-stabilized AuNPs.

**Catalysis of methylene blue reduction using AuNPs**
1. Prepare a fresh stock of 0.10 M NaBH₄ as above.
2. Using a 200-μL autopipettor, add 20 μL of 5.0 mM methylene blue and 150 μL of 0.10 M NaBH₄ to a disposable PMMA cuvette.
3. Place this cuvette into the spectrometer and begin recording absorbance at 664 nm.
4. Using a 200-μL autopipettor, add 50 μL of the 0.25 mM AA-stabilized AuNP solution.
5. Observe the decrease in absorbance at 664 nm as the methylene blue is reduced. The reaction is complete once the absorbance is ~1% of the starting absorbance.
6. Perform this reaction in triplicate for AA-stabilized AuNPs, using fresh solutions and a fresh cuvette for each trial.
7. Repeat the above steps using NaBH₄-stabilized AuNPs.

**Data Analysis**
1. Measure the LSPR (λmax) for each particle solution and compare them. The resulting wavelength gives insight into the particle size. Which reduction results in smaller particles?
2. Determine ~75% of the maximum absorbance for each particle solution. Measure the corresponding wavelength on either side of the LSPR, then subtract those values to determine the FW@0.75 max for each solution. The resulting number gives insight into the particle dispersity. Which AuNP solution is more monodisperse?
3. For each catalytic run, plot ln(A₀/Aₜ) vs. time. This plot should be linear, and the resulting slope represents k_{app}. Find the average rate and standard error for each dye and NP combination. Which AuNP solution is more catalytically active? Remember to include all plots in your final report!
Chemistry 3200
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Date: ___________ Lab Instructor: ____________________ Section: ________

**Synthesis of AuNPs**

Ascorbic acid mass: ______________

AA concentration: ______________ ± ______________

NaBH₄ mass: ______________

NaBH₄ concentration: ______________ ± ______________

AA AuNP LSPR: ______________

AA AuNP FW@0.75 max: ______________

NaBH₄ AuNP LSPR: ______________

NaBH₄ AuNP FW@0.75 max: ______________

**Catalysis and Dye Degradation**

Congo red $k_{app}$ (s⁻¹) using AA AuNPs: ______________ ______________ ______________

Average: ______________ ± ______________

Congo red $k_{app}$ (s⁻¹) using NaBH₄ AuNPs: ______________ ______________ ______________

Average: ______________ ± ______________

MB $k_{app}$ (s⁻¹) using AA AuNPs: ______________ ______________ ______________

Average: ______________ ± ______________

MB $k_{app}$ (s⁻¹) using NaBH₄ AuNPs: ______________ ______________ ______________

Average: ______________ ± ______________
Calculation of stock solution concentrations:

Calculation of $k_{app}$ values (include ALL catalysis plots in final report):

Calculation for error analysis (include a list of the errors and their sources):