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Laboratory Experiment

Optical Properties of Alloyed Noble Metal Nanoparticles: A Nanotechnology Experiment for Chemistry and Engineering Students

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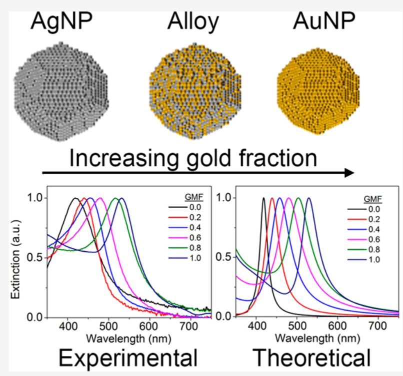
ABSTRACT: Nanoscale phenomena are under increasingly intense investigation both in academia and industry. The unique physical and chemical properties stemming from their high surface area and confined space lead to properties that are distinct from atomic and bulk materials. Students need experience in nanoscience to enter this growing field of nanoscience research. This laboratory experiment introduces the optical properties of noble metal nanoparticles and probes the effect that the metal composition has on these properties. An aqueous synthesis is performed, which allows for the control of the alloy composition of Au/Ag nanoparticles, while minimizing costs and hazardous waste. The composition of the synthesized particles is verified by mass analysis. Extinction spectra are recorded experimentally and determined *in silico*. The experimental and theoretical spectra are compared, and students are asked to identify causes for discrepancies on the basis of mass and particle size analysis. Students actively engage in identifying how the dielectric function of a nanoparticle affects the optical properties. By performing these experiments, students gain practical knowledge of the synthesis and characterization of metal nanoparticles, as well as an initial introduction to elements of theoretical chemistry. This experiment has been found to be easily reproducible; it utilizes primarily nonhazardous, nontoxic, green materials, and it can be performed with minimal added costs to normal budgets for lab courses.



KEYWORDS: *First-Year Undergraduate/General, Laboratory Instruction, Interdisciplinary/Multidisciplinary, Collaborative/Cooperative Learning, Nanotechnology, UV−Vis Spectroscopy, Colloids, Metals, Synthesis, Computational Chemistry*

■ INTRODUCTION

There has been an exponential growth in interest in nanoscience and nanotechnology over the past two decades, with the number of publications listed on PubMed containing the term "nanoscience" or "nanotechnology" in the title, growing from 3 in 1991 to 10,369 in 2018. This rapid growth is further evidenced by the budget of the National Nanotechnology Initiative, which increased from $989 million in 2004 to $1.7 billion in 2018. This interest is not limited to academia alone, with nanotechnology-based products accounting for $250 billion worldwide in 2009 and projected to exceed $3 trillion by 2020,[1] prompting the U.S. government to establish several guidelines and agencies to meet the regulatory needs of this influx of new products.[2,3] The growth of this new field presents an opportunity for students to engage in nanotechnology and develop marketable skills for both industry and academia.[4] Assimilating critical aspects of nanoscale phenomena in the chemistry curriculum, particularly the characterization and theoretical modeling of these materials, will equip students with basic skills in synthesis and characterization needed to succeed in the growing nanotechnology field.

Metal nanomaterials are utilized in a variety of biological and inorganic applications including as catalysts,[5,6] contrast agents,[7] and platforms for drug delivery[8] or chemical sensing.[9] Many of these applications rely on the unique optical properties of these kinds of nanoparticles: the localized surface plasmon resonance (LSPR), which is the collective oscillation of free electrons in the conduction band with incident light. The LSPR presents itself as a strong extinction peak, and nanoparticles that utilize the LSPR effect are characterized by UV−vis spectroscopy. The LSPR peak position is determined by several factors such as the particle size, shape, and metal composition.

A rapidly increasing number of undergraduate-level teaching experiments using gold and silver nanoparticles (AuNPs and AgNPs, respectively) have been developed with several

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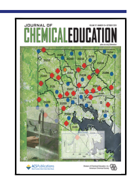

excellent modules focusing on the synthesis and optical characterization of particles of differing shapes and sizes.[10−14] To our knowledge, no teaching experiments have been developed that focus quantitatively on how the alloy composition affects the LSPR, despite the many intriguing properties of these alloys.[15,16] However, the relationship between the alloy composition and the LSPR is complex and difficult for undergraduates to comprehend and appreciate.

This laboratory experiment utilizes a series of teaching strategies to motivate and engage students to enhance their understanding of the LSPR phenomenon and factors that determine its peak position. The lab begins with prelaboratory (prelab) activities to prepare students for a fruitful learning environment.[17] The first activity is a quiz, which is used to provoke student thought for a discussion, where students are introduced to nanoscale phenomena, the growing nanotechnology field, and practical applications of LSPR-based nanomaterials. Students who comprehend the real-word relevancy of the material remain motivated and engaged.[18,19] During the discussion, a demonstration of the synthetic procedure for AuNP and AgNP is performed. The prelab activities prepare students for the laboratory experiment through multiple means. The activities introduce relevant experimental safety concerns and procedures, motivate students,[20] introduce students to the optical properties of noble metal nanoparticles, and offer the students the opportunity to ask questions to improve their understanding. Students that are prepared for a lab have been shown to have a more positive experience in the lab,[21] are more efficient with their time,[17] and have the potential for improved learning.[22] After the prelab activities, students synthesize alloyed AuAgNP whose compositions are predicted on the basis of the synthetic parameters and verified using mass analysis. The optical properties of these particles are then measured empirically by UV−vis spectroscopy and compared with theoretical determinations of these spectra on the basis of Mie theory. Freely available software is used to generate the theoretical spectra and augment student knowledge of how metal content affects the LSPR peak position. Simulation software is a successful tool to guide higher-level understanding of complex chemical theory.[23] The guided series of learning events is expected to enhance students' understanding of the unique optical properties and potential applications of noble metal nanoparticles. Each student is guided though the process of hearing the discussion, seeing a demonstration, performing the experiment, thinking during the theoretical modeling and take-home assignment, and last, synthesizing the material by writing a formal lab report.

Upon completing this lab, students will be able to

- synthesize and characterize noble metal nanoparticles
- calculate the mole fraction of a metal in an alloyed metal NP from mass analysis data
- describe how alloy composition affects the LSPR peak position for noble metal NPs
- apply theoretical calculations to compare with experimental results
- interpret and present complex data in a written report

■ EXPERIMENTAL OVERVIEW

Sophomore and junior undergraduate students in an analytical chemistry lab synthesize alloyed AuAg particles *via* the Turkevich method[24] and are introduced to nanoparticle characterization and Mie theory. The independent laboratory experiment can be implemented in two 3 h lab periods within an analytical chemistry lab course, or in a nanotechnology, general, inorganic, or physical chemistry laboratory course with slight modification. The approximate timetable for experiments is included in Table 1.

Table 1. Timetable for Laboratory Procedures

Period	Activities	Time, h
1	Prelab activities	1.0
	Nanoparticle synthesis	1.5
	Acquisition of UV−vis spectra	0.5
2	MiePlot simulations	1.0
	Preparing mass analysis samples and standards	1.0
	Acquiring mass analysis data and postlab quiz	1.0

The first period is devoted to prelab activities, the synthesis, and the initial characterization of the nanoparticles. The prelab activities should incorporate content from the corresponding lecture course, so that the lecture and lab reinforce one another. We have successfully implemented this lab during the introduction of spectroscopy in an analytical chemistry course, bolstering and expanding on molecular and atomic spectroscopy. Students should be familiar with Beer's law and molecular orbital theory and its relationship to the extinction spectrum prior to initiating this lab.

The second period is devoted to completing the characterization and simulation of spectra. Students are assembled into small working groups of 2−4 for the duration of the experiment. Full experimental details are included in the Supporting Information. This experiment has been deployed successfully three times at two different institutions with classrooms of 5−20 students in analytical chemistry. It was performed with a single instructor and no teaching assistants.

Chemicals and Equipment

All chemicals were used as received (see Supporting Information). Experiments were performed using deionized H_2O with resistivity of 18 MΩ. Stock solutions were prepared by the instructor prior to the class (see Notes for Instructors in the Supporting Information (SI)). The equipment used in this lab is common to many other standard general, analytical, or physical chemistry experiments or is readily available online. The only unique costs were those of chemicals, with an estimated cost of ∼$10 per deployment, so the module can be readily deployed even at sites with relatively modest budget availability.

Particle Synthesis

Au, Ag, and alloyed particles were prepared by the Turkevich method.[24] Briefly, 10 mL of water was brought to a rolling boil in a round-bottom flask under atmosphere. Solutions of $HAuCl_4$ and $AgNO_3$ (totaling 0.25 mM) were quickly added to the round-bottom flask and allowed 2 min to equilibrate. A solution of sodium citrate (0.5 mL, 57 mM) was then added to the flask with stirring. Pure particles were synthesized by the addition of $HAuCl_4$ or $AgNO_3$ only, while alloys were prepared by the addition of the two metal solutions in the appropriate proportion. Students made note of any color changes. After 20 min, the reaction was removed from heat and allowed to cool to room temperature. The citrate serves as both a reducing agent, which yields 0 valent metal atoms, and as a capping agent providing electrostatic stabilization of the particles. As an

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enrichment exercise, transmission electron microscopy (TEM) can be performed to determine the absolute size and heterogeneity of the synthesized particles. If TEM is unavailable, a 20 nm particle radius can be safely presumed on the basis of our studies during the development of this laboratory. Example images are provided in the SI as well as a walk-through for size calculations. Depending on the facilities and number of students available, synthesizing the following particles is recommended: Au, Ag, $Au_{0.4}Ag_{0.6}$, and $Au_{0.6}Ag_{0.4}$, while $Au_{0.2}Ag_{0.8}$ and $Au_{0.8}Ag_{0.2}$ can also be included to provide a more thorough analysis.

Optical Properties

Following synthesis, there are obvious differences in the color of the suspension on the basis of the alloy composition. Particles were transferred to a UV−vis cuvette. A spectrophotometer was used to record spectra between 300 and 900 nm, which had been previously blanked with H_2O. The intensity and location of the LSPR peak were recorded and clearly red shift with increasing Au content.

Mass Analysis

Residual metal ions were removed from solution by centrifugation of the particles (17000*g* for 20 min) and removal of the supernatant. A 5-fold concentrated solution of particles was digested in a glass vial with fresh *aqua regia* for 5 min. The sample was then diluted into 5% HNO_3 for mass analysis. The concentrations of Ag and Au were determined for the same sample, which were then used to determine both the mass ratio and the atomic ratio (on the basis of their atomic mass) of the two metals. Flame atomic absorption spectroscopy (FAAS) was used for this experiment, but other mass analysis techniques such as atomic emission spectroscopy (AES) or inductively coupled plasma mass spectrometry (ICP-MS) can be substituted.

Theoretical Modeling

Theoretical calculation of the extinction spectra was performed using MiePlot v4.6.14,[25] which is freeware developed by Philip Laven used to solve the Mie equation for a variety of spherical particles. Full details for the Mie equation can be found in the Supporting Information. The dielectric functions of alloys do not represent linear combinations of the components and must be uniquely calculated.[26] The wavelength dependent refractive index and extinction coefficient for a variety of Au/Ag alloys are freely available from Refractiveindex.info,[27] and MiePlot compatible files are included in the SI. Students entered the various parameters into the software under the intensity *vs* wavelength mode; particle radius and medium were selected, the dielectric functions were uploaded to the software, and spectra were returned. The goal of the theoretical modeling is to enable students to visualize the relationship between alloy content and the LSPR peak position and to provide assistance in analyzing their data, not to have the students fully comprehend all of the computational calculations.

Instructor Notes

It is highly encouraged that the instructor prepares the Au and Ag solutions immediately prior to the lab to minimize waste and variance between student groups. Synthetic failure can occur for a variety of reasons including, but not limited to, addition of sodium citrate at low temperature resulting in reduced silver reduction, unclean glassware or stir bars, or student errors, particularly those resulting in an incorrect ratio of Ag to Au due to pipetting error. Students should be trained on the proper use of micropipettes. In the event of failure to synthesize adequate NPs, two suggestions are offered: (1) clean the glassware (rinse extremely well to remove the acid) and attempt the synthesis again or (2) acquire data for the failed NP sample and obtain a good sample from the instructor for use in further experiments. A complete set of Instructor Notes is included in the SI.

■ HAZARDS

Personal protective equipment such as lab coats, gloves, and safety glasses should be worn during the synthesis and mass analysis components of the lab. The biosafety of metal nanoparticles is not fully understood, and $HAuCl_4$ and $AgNO_3$ stain skin upon contact. Glassware should be cleaned with *aqua regia* (3:1 $HCl:HNO_3$), which is highly corrosive and should only be used with caution in a fume hood and safely neutralized (with $NaHCO_3$) after completion of the lab. *Aqua regia* should be prepared fresh and cannot be stored in a closed container, as the gases it generates will cause the container to explode. Our experience has shown students to be capable of cleaning their own glassware and dissolving their own particles for mass analysis.

■ RESULTS AND DISCUSSION

Teaching Methods

This laboratory experiment engages students from every learning style through a series of guided instructional events. Before the experiment begins, students engage in a quiz and discussion where they are introduced to the unique optical properties of noble metal NPs. Real-world applications of NPs with a LSPR should be emphasized in the discussion. Students showed a particular interest in the application of NPs in medicine such as for photothermal therapy. Students then observe the relationship between the metal content in NPs and the optical properties with a demonstration. The demonstration of the synthesis is quick, ~10 min, and can be integrated as part of the discussion. A visual prelaboratory experience can enhance student confidence and increase student productivity in the lab.[21,28] Students then synthesize and characterize the alloyed NPs. Higher-level student learning is then stimulated by having the students simulate the extinction spectra with computer software, and having small groups discuss their results.

After completing the second lab period, a take-home assignment is given to the students, which is used to guide students through relevant calculations and to assist student comprehension as to the possible discrepancies between the theoretical and experimental spectra. Final student comprehension of the lab is evaluated with submission of a formal lab report.

Students interviewed during and after the experiment have expressed a favorable outlook on this experiment and have encouraged future implementation. During the lab students said that they particularly enjoyed the hands-on synthesis of the colorful nanoparticles, and learning about the practical applications of the synthesis and characterization of nanomaterials. After the lab, students identified that working in small groups during the theoretical calculations encouraged group discussion where they had the opportunity to develop questions and answers among themselves. The students also praised the example calculations for the gold mole fraction

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Table 2. Mass Analysis, TEM, and LSPR Data for Synthesized Particles

Particle GMF	Radius[a] (nm)	GMF Determined by Mass Analysis	Experimental LSPR Peak[b] (nm)	Theoretical LSPR 20 nm Radius	Theoretical LSPR Measured Radius[c] (nm)
0.0	22 ± 4	0.000	412 ± 2	415	418
0.2	21 ± 7	0.221 ± 0.034	438 ± 5	437	439
0.4	19 ± 3	0.329 ± 0.004	452 ± 3	459	458
0.6	14 ± 5	0.675 ± 0.001	479 ± 8	481	477
0.8	12 ± 4	0.874 ± 0.002	515 ± 3	507	504
1.0	8 ± 2	1.000	533 ± 5	533	529

[a]Particle diameters were measured from TEM images using ImageJ (NIH) by sizing at least 250 particles. [b]Average ± S.D., $N \geq 3$. [c]Theoretical LSPR based on the measured particle radius, using MiePlot v4.6.14.

(GMF) from mass analysis data, which is included in the Supporting Information.

Synthesis and Mass Analysis

Au, Ag, and alloyed nanoparticles were successfully synthesized by undergraduates following the protocol provided. The precursor ratio and the composition as determined by FAAS are included in Table 2 as well as size measurements from transmission electron microscopy (TEM) images. A photograph of vials containing these solutions is included in Figure 1A and shows a clear transition from yellow to red with

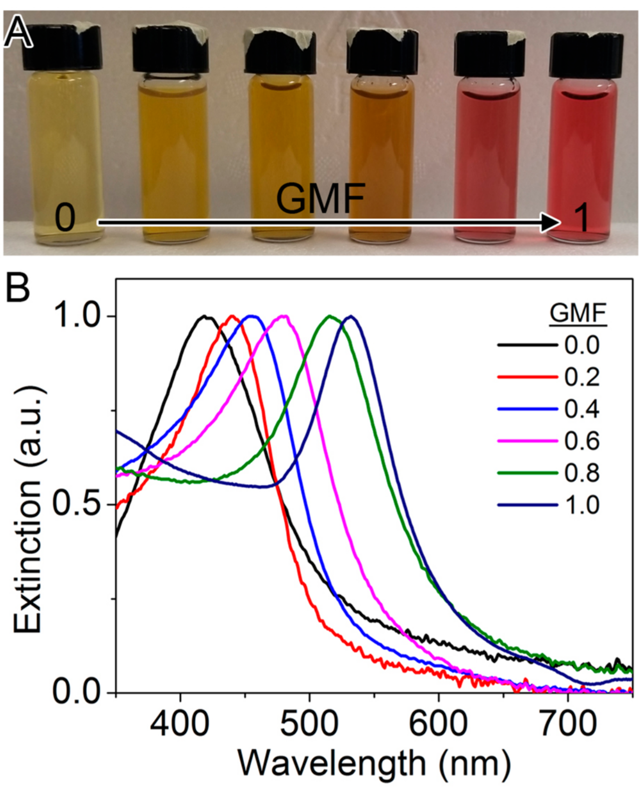

Figure 1. (A) Photograph and (B) extinction spectra of example nanoparticles, roughly 20 nm, synthesized by students with anticipated GMF values between 0.0 and 1.0. Spectra were normalized to a peak value of 1 to aid visualization.

increasing GMF. These measurements indicate that the radius of 20 nm can be reliably used for further calculations. Variance between the predicted and final alloy composition was minimal and expected. The experimental LSPR was within 2% of the theoretical LSPR, and the composition was consistently within 10%. The source of this discrepancy is likely explained by synthetic variance and student pipetting errors, and did not appreciably affect later results.

LSPR Measurement and Calculation

The extinction spectra of these particles were measured, and the peak positions are recorded in Table 2. The measured spectra can be found in Figure 1B. The calculated extinction spectra based on MiePlot analysis of different alloy compositions are included in Figure 2, with values for the

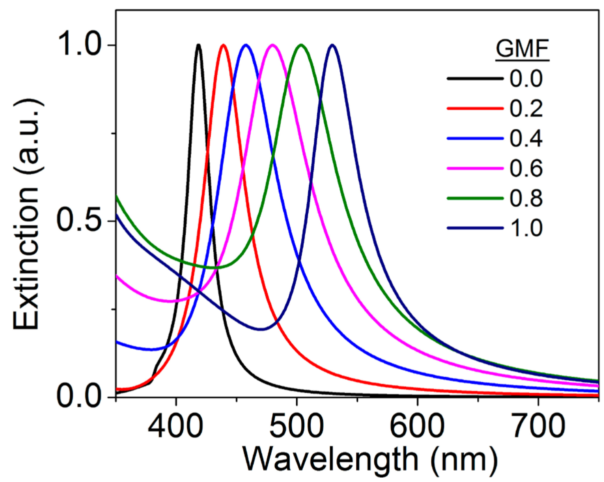

Figure 2. Theoretical UV spectra calculated using MiePlot with 20 nm radius particles with GMF between 0.0 and 1.0. Spectra were normalized to have a peak value of 1 to aid visualization.

extinction peak included in Table 2. The dependence of the LSPR peak wavelength on alloy composition is included in Figure 3 as both a function of experimental and theoretical mole fraction as well as on the anticipated and measured radius of the particles. The LSPR peak position was seen to shift linearly with composition, while the extinction coefficient was inversely correlated to the Au mole fraction. The experimental and theoretical spectra for a 20 nm radius particle are in close agreement, indicating successful validation of the theoretical model.

In this lab, particles with a radius ranging from 8 to 22 nm were synthesized, with larger particles corresponding to a lower GMF. The theoretical extinction spectra and LSPR peak positions for 10 and 20 nm radius particles are similar for all GMFs as displayed in Figures S1 and S2. The LSPR peak position for particles with a high GMF was found to be less sensitive to particle size as is displayed in Figure S3 and has been reported earlier.[29] Therefore the size of low GMF particles, 20 nm radius, was used for all theoretical calculations to avoid confusion. Discrepancies between the theoretical and

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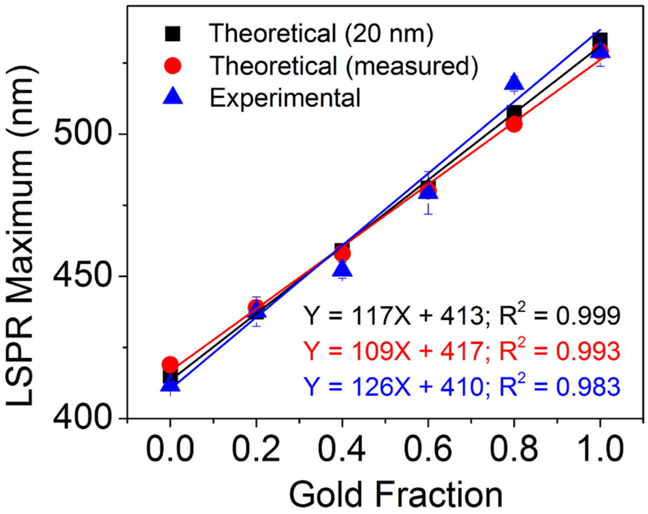

Figure 3. LSPR position as a function of gold fraction calculated for theoretical particles with 20 nm radius (black, ■), theoretical particles with the measured radius of the synthesized particles (red, ●), and the experimentally measured LSPR maximum of synthesized particles (blue, ▲). The lines represent linear fits of the data with corresponding R^2 values.

experimental spectra can be attributed to the heterogeneity of the nanoparticle size, the nonideal sphere morphology, and the deviation between the predicted and actual mole fraction of the metals; the size differential, while most obvious, had a significantly lower effect on the LSPR position than the metal composition.

Experimental Outcomes

The primary aims of this experiment were to guide students to understand the unique optical properties of metal NPs and the effect that the alloy composition has on the LSPR peak position. During the first lab period students synthesized the nanoparticles and characterized their particles with UV−vis spectroscopy. Students were excited to see the rapid and colorful synthesis reaction and curious to explore why the metal ratio affected the color so drastically. Students gained an empirical understanding of the unique optical properties of noble metal nanoparticles and saw how the composition of the particles affected these optical properties. The Turkevich synthesis of the alloyed particles is facile, with all student groups successfully synthesizing particles with roughly the anticipated LSPR peak.

In the second lab period, the students learned how to obtain theoretical extinction spectra of particles with varying Au/Ag compositions. They compared these spectra to their experimental extinction spectra. The students then measured the metal content by mass analysis. The students used the mass analysis data to identify causes for discrepancy in the LSPR peak position between the theoretical and experimental extinction spectra. Students were also provided example TEM images of particles to observe the dispersity in particle shape/size and how this dispersity affected their experimental spectra.

Formative Assessment

Upon completion of the experiment, a formative assessment was conducted using both a graded take-home assignment and formal lab report. Because the experiment involves evaluation of multiple learning goals, the assessments were broken down to focus separately on mathematical analysis and technical writing. To ensure comprehension of the calculations for mass analysis, a take-home assignment is first given allowing students to evaluate their own data using provided sample calculations as a reference. This assignment is graded and returned to students, who, after understanding the calculations, then proceed to write an individual formal laboratory report discussing the meaning of their results. Students should be capable of discussing the following in the laboratory report: the Turkevich synthesis, the importance of characterizing the LSPR peak position for noble metal NPs, and the relationship between alloy composition and the peak position. Additionally, students should utilize mass analysis data to identify discrepancies between the theoretical/experimental extinction spectra. The report enables the instructor to assess student understanding of the entire laboratory and offer feedback on their scientific writing skill.

■ CONCLUSION

This experiment introduces students to a quantitative analysis of alloyed Au and Ag nanoparticles synthesized using the citrate reduction method. The alloy composition is measured optically and by mass analysis and compared to the anticipated theoretical results. The visible differences in the LSPR position following synthesis provide a simple and direct means for students to observe the effects nanoparticle composition has on optical properties, which are confirmed experimentally and theoretically. By varying the alloy composition used among different student groups, students are able to compare results quickly and establish the correlation between composition and LSPR. This laboratory serves to introduce students to nanoparticles' unique optical properties, as well as introduce synthetic, characterization, and modeling techniques associated with nanomaterial research.

There are several additional modifications that could be made to this lab. The prelab activities could be assigned as a video prior to the lab in order to prepare them in advance. Prelab videos and video demonstrations that engage students outside of the class prepare them for the lab and have increased student performance, creating uniform prelab across multiple lab sections.[30] This lab could be modified to increase student comprehension of the Mie equation by having students calculate the real and imaginary components of the dielectric function using MATLAB,[26] instead of using the given scripts. Students could also use the software to explore the relationship between NP size and the LSPR peak position. Additionally, with slight modifications, this lab could be utilized at the beginning of a general chemistry II course. General chemistry students may require a more thorough discussion and introduction to MiePlot. In a general chemistry course this lab could be used to reiterate molecular orbital theory from general chemistry I and introduce new units of ppm/mol ratio.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available at https://pubs.acs.org/doi/10.1021/acs.jchemed.0c00125.

Instructor notes, cost estimate, experimental procedures, and student lab handout (PDF, DOCX)

MiePlot files of alloy refractive index (ZIP)

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Notes

The authors declare no competing financial interest.

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