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Seeded-Growth Experiment Demonstrating Size- and Shape-Dependence on Gold Nanoparticle-Light Interactions

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Abstract

Gold nanoparticles are exciting materials in nanotechnology and nanoscience research and are being applied across a wide range of fields including imaging, chemical sensing, energy storage, and cancer therapies. In this experiment, students will synthesize two sizes of gold nanospheres (~20 nm and ~100 nm) and will create gold nanostars utilizing a seed-mediated growth synthetic approach. Students will compare how each sample interacts differently with light (absorption and scattering) based on the nanoparticles' size and shape. This experiment is ideal for high-school and early undergraduate students since all reagents are non-toxic, affordable, and no special characterization equipment is required.

Graphical Abstract

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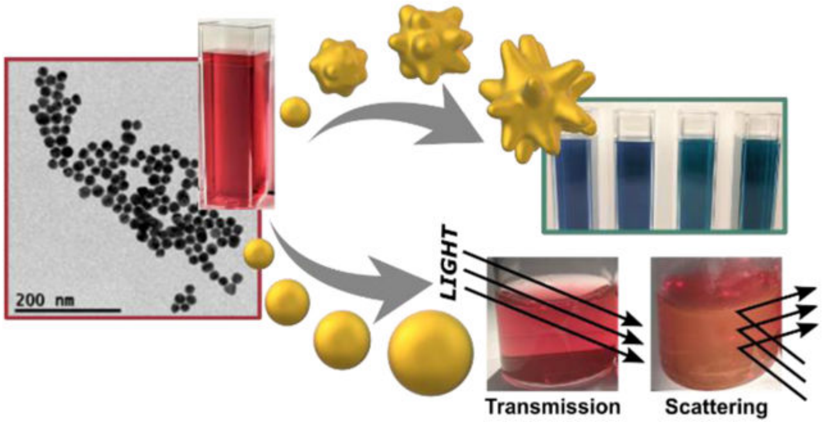
Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.0c01150.

Student Lab Manual

Instructor Lab Manual with chemical reagent purchase information

High school summer program drawing assignment prompt



Keywords

High school/Early Undergraduate; Nanoscience; Hands-On Learning / Manipulatives; Plasmonics, Nanoparticle Synthesis

INTRODUCTION

Nanoparticles are materials that have physical dimensions on the nanometer scale in three dimensions, and possess unique size-related characteristics, such as high surface areas,[1] unique magnetic properties,[2] and interactions with light[3] that differ from their bulk counterparts. In this experiment, students will explore how the sizes and shapes of gold nanoparticles affect their interactions with light, including visible color, the wavelengths of light transmitted/absorbed, and the probability of light scattering. The bright colors observed in gold nanoparticle suspensions are due to plasmons, which are defined as collective oscillations of loosely bound electrons in response to electromagnetic waves (i.e., light). When the frequency of the incident light wave matches the frequency of the plasmon, the oscillating electric field from the light can move the electrons back and forth, causing the light to interact with the nanoparticle (*e.g.* by absorption or scattering). This phenomenon is called a localized surface plasmon resonance (LSPR). The relationship of nanoparticle shape, composition, and local dielectric environment to their LSPR is well understood and can be utilized in nanotechnology.[4] In this work, we designed and implemented hands-on experiments introducing nanoscience and plasmonics to high-school and early undergraduate-level students, connecting students to this active research topic.

Bottom-up synthetic methods have been utilized to create nanoparticle suspensions with tailored plasmonic properties for a wide range of applications, including cancer therapies,[5] drug delivery,[6] and chemical detection.[4] Here, we use a method called seed-mediated growth, where small nanoparticles are first synthesized and then grown into large particles in a second step. This strategy enables precise tailoring of nanoparticle sizes and shapes for different applications.[7] During synthesis, small gold nanoparticle clusters (also called nuclei or seeds) form from gold atoms. After the nucleation step, seeds, which are usually below 20 nm in diameter, are injected into a separate solution containing ‘shape-directing reagents’, which are molecules that will bind to the growing nanoparticle surface and dictate the shape of the particle as it grows. Shape-directing reagents can include other metal ions, reducing agents, acids, and surfactants (we discuss this in more detail throughout the Experimental and Results & Discussion sections). This approach enables the precise control of the chemical solution for the two separate steps, nucleation and growth, so that the final shape of the nanoparticles is directed and better controlled. The development of this method has led to the uniform synthesis of many different nanoparticle shapes, including rods,[8] wires,[9] stars,[10] cubes,[11] and triangles.[12]

Currently, educational experiments involving gold nanoparticles primarily focus on testing their stability in solution,[13–15] utilizing them as colorimetric sensors,[16–18] and bottom-up synthetic approaches.[15,19–22] Although some educational experiments focusing on nanoparticle shape control[20] and seed-mediated growth[22] have been implemented previously, protocols that allow for the formation of complex shapes are generally not applied in high-school level settings due to the use of toxic chemicals and the need for characterization equipment such as UV-visible spectroscopy and electron microscopy, which may not be available in most high-school settings. The experiments presented here do not require complex instrumentation and involve optimized robust synthetic seed-mediated protocols for preparing gold nanostars and 100 nm nanospheres. Students will visualize the effects of nanoparticle size and shape on their optical properties. Additionally, students will compare different light interactions, such as absorption and scattering, on solutions containing different particle sizes. Overall, this experiment provides an opportunity to introduce students to several topics currently studied in research labs across the globe, including nanomaterials fabrication, surface area and colloidal stability, and the effect of size and shape on nanoparticle-light interactions.

EXPERIMENTAL

Students will learn and use basic concepts and models, such as the wave model of light, physical examples of a resonance, and the color wheel to understand nanoscience concepts, including interactions of plasmonic nanoparticles with light, bottom-up synthetic approaches, and the roles of surface energy in nanoscale objects. The laboratory consists of three experiments, which can be performed in one or multiple sessions. Preparation of reagent stock solutions require at most 1 h by the instructor (to perform dilutions) and can be done up to a week before the experiment. The experiments were designed for groups of 2–5 high school students to complete within 2–3 h (depending on the depth of the explanation). Parts I, II, and III take ca. 30 min each to perform. In our workshops, the discussion and explanation of the concepts took an additional 45 min – 1 h in total, but this timing can be adjusted at the discretion of the instructor, based on the backgrounds of the students. All chemical reagents were purchased from Millipore Sigma, and detailed experimental procedures are provided in the Supporting Manuals.

Turkevich synthesis of gold nanospheres

In this experiment, students utilize a ‘bottom-up approach’ to grow small gold nanoparticles (~15 nm), which exhibit bright red coloration due to their plasmonic properties using the Turkevich-Frens method (Figure 1A).[23,24] An aqueous solution of the gold precursor, 25 mL of 0.5 mM $HAuCl_4$ (≥99.9%), is heated to a gentle boil, and sodium citrate (2.5% wt, 0.5 mL) is added as a reducing agent and acts as a surfactant. The introduction of surfactants reduces surface tension and stabilizes the surface of the nanoparticles, which have high surface energy, to generate a colloidal suspension. Reducing agents are required in order to “reduce” the oxidation number of the gold ions in solution, since nanoparticles are comprised of neutral gold atoms. The high temperature causes the nuclei to grow quickly and uniformly. As the growth progresses, the solution changes color from faint yellow, to clear, then to black/blue, purple, and finally to a deep red. The students will note the color changes they observe at different times as the particles are formed, and each student should note at least 4 color changes. As an optional activity, once the particle solution has stopped changing color and has cooled to room temperature, two 5 mL aliquots of the solution will be separated into two vials. Liquid dish or hand soap will be added to one of the vials, and subsequently a table salt solution will be added to both aliquots. Students will record the color changes over time and discuss how the addition of soap (surfactant) and salt affect the colloidal stability of the nanoparticles.

Seed-mediated growth of nanostars

The particles from the first part of the experiment are used as seeds to synthesize nanoparticles with different shapes, using seed-mediated growth. The shape-directing reagents $AgNO_3$ and ascorbic acid (acting as a reducing agent) will be utilized in the growth step to facilitate nanostar formation (Figure 1B, top). Specifically, students prepare a solution containing 5 mL of 0.5 mM $HAuCl_4$, 0.2 mL of 10 mM $AgNO_3$, and 0.4 mL of the Turkevich seeds from Experiment 1 and combine this with 5 mL of a solution containing 1 mM ascorbic acid and 16 mM HCl. The students will record the final color of the solution. This part of the experiment can be combined with UV-visible spectroscopy, if it is available, but it is not necessary for understanding which colors are absorbed and transmitted or interpreting data based on changes in particle shape.

Seed-mediated growth of 100 nm nanospheres

In addition to absorption and transmission, this experiment will enable students to explore the differences between light absorption and scattering. Students will again apply seed-mediated growth by adding 0.120 mL of the seeds synthesized in the first part of the laboratory to a solution containing 6.5 mL 1.92 mM $HAuCl_4$, 0.4 mL 0.75% wt sodium citrate, followed by the addition of 5 mL of 4 mM ascorbic acid as a reducing agent (Figure 1B, *bottom*). Once the growth is complete (<5 min), the students can observe the difference in scattering intensity between the small and large nanoparticle suspensions by shining a flashlight onto the vial. Students will record their observations and rationalize their results based on the particle size.

HAZARDS

Personal protective equipment will be worn by students at all times during the experiment, including lab coats, goggles, and gloves. Although non-toxic materials are utilized in this experiment, both tetrachloroauric acid and silver nitrate can cause stains to clothes and skin. The synthesis also uses a small amount of 16 mM HCl, which can cause skin irritation. The

HCl should only be handled by the instructor during the pre-laboratory preparation period. When performing the Turkevich synthesis, the solution should be brought to a gentle boil and handled carefully. No fume hoods are necessary, and all reagents are non-toxic.

RESULTS & DISCUSSION

Observations of the synthesis in Experiment I will help students establish the idea that gold nanoparticles, due to their small size, appear brightly colored instead of the metallic yellow color characteristic of bulk gold. These observations will then be utilized in a discussion led by the instructor, who should then define the key terms ‘plasmon’ and ‘localized surface plasmon resonance.’ Following completion of Experiment I, students should have recorded data indicating the color change at different time points of the Turkevich synthesis (example shown in Figure 2A). The observed bright colors that arise as nanoparticles are formed can be explained using the wave model of light: the electric fields in electromagnetic waves can collectively push weakly bound electrons in the metal nanoparticle back-and-forth as the electric field oscillates. When the light wave frequency is in resonance with the inherent oscillation frequency of the electrons in the nanoparticle (called the plasmon), the light is absorbed. This absorption is referred to as a localized surface plasmon resonance (LSPR) because the process is localized on a single nano-sized object. Physical models, such as resonant pushing of a swing in motion, can be applied to explain the LSPR phenomena to students. In this model, when a person on a swing is pushed at exactly the right time, their motion can increase, representing absorption of the matching frequency of light (see Supporting Materials). If the swing is pushed either too early or too late, however, the force instead slows down the motion of the swing; this off-resonance pushing corresponds to light with either too low or too high a frequency, which is not absorbed by the nanoparticle. Moreover, students will learn the basic procedure for bottom-up nanoparticle synthesis, which can be expanded to discuss chemical oxidation/reduction and the role of capping molecules to stabilize colloidal nanoparticle suspensions.

Once students have been introduced to the key terminology, color complementarity (using the color wheel) provides a shortcut to enable students to predict the position of the LSPR peak, and thus the approximate wavelengths of absorbed and transmitted light. The final ~15 nm particle solution exhibits a red color, due to their LSPR peak at ~512 nm (Figure 2B–C). This is because the LSPR causes absorption of the green part of room light causing the student to perceive the red light that is not absorbed (Figure 2B). For more advanced students, addressing the color changes (black/blue, purple, to red) throughout the synthesis can reinforce the relationship between size and absorbed wavelengths, as well as the concept of small particles having high surface energies. As particles grow in size, the resonant frequency of their plasmon decreases, leading them to absorb longer wavelengths and shifting the LSPR peak to the red. Therefore, a solution of large particles that absorbs more in the yellow region instead of green would have a more purple coloration to it based on the color wheel. As small particles form, they are unstable due to their high surface-to-volume ratio, meaning that a higher percentage of their total atoms are on the surface (see Supporting Manuals). To reduce their high surface energy, the small nanoparticles form clusters. The clusters effectively absorb light as if they were large particles with lower plasmon resonance frequencies, causing absorption at longer wavelengths (Figure 2A: black/

blue, purple). As the individual particles grow in size, they become more stable as their surface area-to-volume ratio decreases and eventually the clusters separate (Figure 2A: red).

In this part of the laboratory, students will also learn about the required components for the bottom-up synthesis of gold nanoparticles: (i) gold salt (source of gold ions), (ii) a reducing agent (to turn gold cations into Au^0 atoms so nanoparticles can form), and (iii) a surfactant that binds to the surface of the nanoparticle (also referred to as a “capping” molecule). The gold cations need to be reduced because metallic nanoparticles are composed of neutral Au atoms. This is because it is unfeasible to form a solid material composed of charged atoms. The surfactant lowers the surface energy and allowing the particle to retain nanoscale dimensions. The initial color change in the Turkevich synthesis from yellow to clear (Figure 2A) is due to the reduction of Au^{3+} following the addition of reducing agent sodium citrate. In this synthesis, sodium citrate also acts as a surfactant or capping molecule (see Supporting Manuals for detailed discussion).

Expanding upon the idea of surface energy for advanced students, the additional soap/salt colloidal stability activity in Experiment I tests the surface stability of the nanoparticles following addition of surfactants, which acts as a stronger surfactant for stabilizing the particles and preventing them from aggregating following the addition of table salt, which causes aggregation due to electrostatic interactions. This concept has been documented in previous educational lab experiments[13–15] and is a general phenomenon of nanomaterials that are stabilized in solution by putting charges on their surfaces.

In Experiment II, students test the effects of nanoparticle shape on the observed color and LSPR peaks. This experiment uses the seed-mediated growth method, where the nucleation step (initial formation of small gold clusters <20 nm in diameter, also called nuclei or seeds) and the growth step (increased reduction of gold ions onto the seeds) are performed separately. Synthesis of uniform nanoparticle suspensions can be done through the rapid and uniform reduction of gold salt. In the Turkevich synthesis, heat is used to achieve quick, uniform nucleation in solution. Various nanoparticle shapes can be produced through addition of various surfactants, salts, and metal ions, and other shape-directing reagents. However, the presence of these reagents would also affect the nucleation step. So, rather than performing the nanostar synthesis in one single step, we instead perform the nucleation step first, then add the seeds to a separate growth solution where shape-control is performed (Figure 1B). This so-called seed-mediated growth method enables improved control over each synthesis step and is reliable for generating uniform suspensions of different nanoparticle shapes.[7–12]

A photograph of a typical nanostar solution synthesized via the seed-mediated method is shown in Figure 3A. The difference in color between the gold nanostars and the original seeds is due to the generation of a new LSPR peak at ~650 nm (Figure 3B). The arms/branches of the nanostar have a distinct shape compared the spherical “core” or center of the nanoparticle, and therefore the arms and core will have different plasmon resonance frequencies (Figure 3B: pink = LSPR for the core, blue = LSPR for the arms).[25] Since changing nanoparticle shape leads to the formation of new LSPRs, shape control can be applied to access LSPRs across the entire visible spectrum, and even into the near-infrared regime.

When developing experiments for high-school and undergraduate students, it is important to consider aspects in the procedure that may lead to variations in the final products. The size of the arms in the final products depends on the accuracy in timing the addition of growth reagents, which can vary between student groups. Figure 3C shows transmission electron microscopy (TEM) images of gold nanostars with different arm lengths. In Figure 3D, we show a representative set of final nanostar products that are ordered in color from smallest to largest branches, and their corresponding UV-visible spectra. Due to yield differences, the student samples can range in color from purple (shortest arms) to black (longest arms).[26,27] However, regardless of their yields, students can again utilize complementary colors to understand the size and shape effects on the optical property: purple color comes from a combination of complement pairs green-red and orange-blue. Particles with a darker blue color can be attributed to longer arms and thus higher absorption in the orange/red region of the spectrum. Thus, this reasoning relating nanostar arm length to the observed color, can be applied to infer particle shape. Student groups can compare and rank the lengths of the arms of their nanostars without UV-visible spectroscopy or TEM analyses, which are generally not available to high-school students.

In Experiment I, students discuss the relationship between nanoparticle size and the absorbed wavelength. Here, students will revisit nanoparticle size in the context of evaluating different light-matter interactions, namely transmission (light passing through the sample) and scattering (light bouncing back from a sample). Light transmission can be observed by holding a light source (smartphone light, white light-emitting diode (LED), or flashlight) behind the nanoparticle solution, as shown in Figure 4A. The nanoparticle solution coloration from this viewing angle is a direct result of the color of light that is being absorbed. When the illumination direction is changed so that the light source is moved to the same side as the viewing angle, the effect of nanoparticle light scattering can be observed (Figure 4B). The scattering is a result of the condition that the particles are much smaller than visible light wavelengths. Following the synthesis of large spheres in Experiment III, students will observe that within this size regime, larger particles preferentially scatter light with more intensity than smaller particles. Both the large and small particles will appear red in the transmission setup (Figure 4A,C,D). In contrast, when the light source and viewing position are in the same direction, the ~100 nm spheres will appear a murky green or brown color due to scattering, where the ~15 nm seeds will still appear red (Figure 4E). The green/brown color is due to preferential scattering of green light, which, like the absorbed color, is based on the nanoparticle properties. Although the Turkevich seeds do scatter light, they do so with such low intensity that it cannot be detected by the naked eye, where the scattering for the ~100 nm particles is so intense that it can be perceived. In fact, the portion of incident light scattered by the nanoparticle increases with the particle radius to the sixth power. From this section, students will understand that particle scattering intensity depends heavily on the particle size, and that there are different ways in which light can interact with nano-objects.

As can be seen in the sample data shown in Figure 4D, variations in the color of the final products can arise due to addition of inexact amounts of citrate or poor stirring. These differences also lead to variations in the scattering intensity (Figure 4E). Although particle size differences will affect the scattering yield, students should nonetheless see noticeable differences between the particles synthesized in this step and those synthesized in Experiment I. Moreover, much like with the nanostar synthesis, the scattering variation in products between groups can be used to rank the sizes of each group's particles without the need for UV-visible spectroscopy or TEM (highest scattering intensity = largest particles). The instructor can further apply nanoparticle absorption and scattering concepts to connect to art history through the example of famous Lycurgus cup, which is colored by gold nanoparticles embedded in the glass and exhibits different coloration based on the direction of illumination.[28]

USE & ASSESSMENT

This experiment was developed as part of the UCLA California NanoSystems Institute (CNSI) Nanoscience Education Program targeting teachers from schools in the greater Los Angeles area. The experiment has been implemented with high school teachers for the last two years (2018 – 2020). This far, more than 35 teachers have participated in the three-hour workshop. The teachers' opinions, comments, and understanding of the concepts in the experiment was gauged through a "High School Teacher Evaluation" questionnaire following the experiment. In one of the questions, teachers were asked to list/describe three scientific concepts they learned from the experiment. This produced a range of responses, including statements comparing surface energy/stability of nanoparticles with different sizes, requirements for bottom-up nanoparticle synthesis, *etc*. For our analysis, we focus on assessing their understanding of the following main concepts: (1) Nanoparticle perceived color depends on size and shape and (2) collective oscillation of the particles' electrons leads to the absorption of specific colors.

Of the teachers that commented on concept (1), >90% produced a correct statement. Here we provide an example of a correct statement for concept (1): "*visible light interacts with nanoscale particles based on size, shape*." For concept (2), which is more advanced, 50% of teachers provided a correct statement. Looking more into the teachers' comments related to topic (2), we find a common misconception that the particle itself is moving/oscillating. For example, one Teacher wrote "*nanoparticles can oscillate with different waves.*" This response is incorrect since they imply the nanoparticle is oscillating or moving in space. Where it is actually the *particle's electrons* that are coherently oscillating, rather than the particle itself. In a couple other examples, teachers wrote: "*charged nanoparticles interact with waves*" and "*the frequency of light matches the frequency of each ion's oscillation."* This indicates that further explanation is required to differentiate plasmons from ions. Although the electrons on the particle are charged, and thus interact with light/ electromagnetic fields, the gold particles are made up of neutral gold atoms. Incorporating discussions about the results from the experiments in between each synthesis step could be useful for reinforcing the relevant concepts.

High school teachers from the workshops have implemented the experiment independently with their classes in 2018 and 2019. This workshop is easy to implement in high school settings due to the fact that no fume hoods or specialized equipment is required (only a hot plate with magnetic stirring is needed) and no toxic chemicals are used. Although gold and silver salts, and other reagents in the synthesis can be costly, we find that proper storage of the chemicals prevents the cost from becoming prohibitive to performing the experiment in high school settings. Aqueous solutions of tetracholroauric acid in distilled water (distilled water purchasable from any grocery store) can be stored away from light and in a designated chemical refrigerator (4 °C) for at least three years. Teachers additionally found that silver nitrate, sodium citrate, and ascorbic acid have greater longevity (~2–3 years) when kept as solids out of light at 4 °C (aqueous solutions of these last ~3 months under refrigeration). One gram of gold salt costing ~$134 is enough for ~300 repetitions of the entire experiment (enough for performing the laboratory ~10 times for classes of 30 students working in groups of 3, performing 3 repetitions). Furthermore, citrate-capped seeds are stable and can last for years, if kept refrigerated and out of the light (such as in aluminum-foil wrapped containers), and thus can be used to grow stars or large spheres at much later times. We have also found that off-the-shelf hand soap can be added to the synthesized stars and large spheres to preserve them for later demonstrations, if desired (they are then stable for more than 1 year).

This experiment has also been implemented in the 2019 UCLA CNSI High School summer nanoscience workshops. Thus far, two summer workshop sections, with 66 high school students total, have performed the experiment (3 students per group) over a 2-h period. As mentioned above, the synthesis itself is fairly forgiving, and all groups were able to synthesize seeds, stars, and large spheres. When students made mistakes, such as adding inexact amounts of reagents, adding reagents too slowly, or overheating their solutions, slightly different LSPR peaks in their final products and slight differences in scattering yields resulted, as shown in Figures 3 and 4. Following the laboratory, students were evaluated via a drawing assignment where they had to depict two nanoscience concepts they learned from the experiment (see Supporting Information for the prompts).

Overall, the feedback from instructors and students was extremely positive, and shows that this experiment is useful for introducing students to complex ideas in nanoscience and plasmonics.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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REFERENCES

(1). Chakraborty S; Ansar SM; Stroud JG; Kitchens CL Comparison of Colloidal versus Supported Gold Nanoparticle Catalysis. J. Phys. Chem. C 2018, 122 (14), 7749–7758.

(2). Reguera J; Jiménez de Aberasturi D; Henriksen-Lacey M; Langer J; Espinosa A; Szczupak B; Wilhelm C; Liz-Marzán LM Janus Plasmonic–Magnetic Gold–Iron Oxide Nanoparticles as Contrast Agents for Multimodal Imaging. Nanoscale 2017, 9 (27), 9467–9480. [PubMed: 28660946]

(3). Kristensen A; Yang JKW; Bozhevolnyi SI; Link S; Nordlander P; Halas NJ; Mortensen NA Plasmonic Colour Generation. Nat. Rev. Mater 2017, 2 (1), 16088–16102.

(4). Willets KA; Van Duyne RP Localized Surface Plasmon Resonance Spectroscopy and Sensing. Annu. Rev. Phys. Chem 2007, 58 (1), 267–297. [PubMed: 17067281]

(5). Huang X; El-Sayed MA Plasmonic Photo-Thermal Therapy (PPTT). Alex. J. Med 2011, 47 (1), 1–9.

(6). Wang C; Wang Y; Zhang L; Miron RJ; Liang J; Shi M; Mo W; Zheng S; Zhao Y; Zhang Y Pretreated Macrophage-Membrane-Coated Gold Nanocages for Precise Drug Delivery for Treatment of Bacterial Infections. Adv. Mater 2018, 30 (46), 1804023–1804031.

(7). Xia Y; Gilroy KD; Peng H-C; Xia X Seed-Mediated Growth of Colloidal Metal Nanocrystals. Angew. Chem. Int. Ed 2017, 56 (1), 60–95.

(8). Jana NR; Gearheart L; Murphy CJ Wet Chemical Synthesis of High Aspect Ratio Cylindrical Gold Nanorods. 2001, 105 (19), 4065–4067.

(9). Wang Y-N; Wei W-T; Yang C-W; Huang MH Seed-Mediated Growth of Ultralong Gold Nanorods and Nanowires with a Wide Range of Length Tunability. Langmuir 2013, 29 (33), 10491–10497. [PubMed: 23924308]

(10). Guerrero-Martínez A; Barbosa S; Pastoriza-Santos I; Liz-Marzán LM Nanostars Shine Bright for You. Curr. Opin. Colloid Interface Sci 2011, 16 (2), 118–127.

(11). Zhang J; Langille MR; Personick ML; Zhang K; Li S; Mirkin CA Concave Cubic Gold Nanocrystals with High-Index Facets. J. Am. Chem. Soc 2010, 132 (40), 14012–14014. [PubMed: 20853848]

(12). Scarabelli L; Coronado-Puchau M; Giner-Casares JJ; Langer J; Liz-Marzán LM Monodisperse Gold Nanotriangles: Size Control, Large-Scale Self-Assembly, and Performance in Surface-Enhanced Raman Scattering. ACS Nano 2014, 8 (6), 5833–5842. [PubMed: 24848669]

(13). Keating CD; Musick MD; Keefe MH; Natan MJ Kinetics and Thermodynamics of Au Colloid Monolayer Self-Assembly: Undergraduate Experiments in Surface and Nanomaterials Chemistry. J. Chem. Educ 1999, 76 (7), 949–955.

(14). McFarland AD; Haynes CL; Mirkin CA; Van Duyne RP; Godwin HA Color My Nanoworld. J. Chem. Educ 2004, 81 (4), 544A–544B.

(15). Mulfinger L; Solomon SD; Bahadory M; Jeyarajasingam AV; Rutkowsky SA; Boritz C Synthesis and Study of Silver Nanoparticles. J. Chem. Educ 2007, 84 (2), 322–325.

(16). Campos AR; Knutson CM; Knutson TR; Mozzetti AR; Haynes CL; Penn RL Quantifying Gold Nanoparticle Concentration in a Dietary Supplement Using Smartphone Colorimetry and Google Applications. J. Chem. Educ 2016, 93 (2), 318–321.

(17). Zarantonello F; Mancin F; Bonomi R Working in a Team: Development of a Device for Water Hardness Sensing Based on an Arduino–Nanoparticle System. J. Chem. Educ 2020, 97 (7), 2025–2032.

(18). Bai J; Flowers K; Benegal S; Calizo M; Patel V; Bishnoi SW Using the Enzymatic Growth of Nanoparticles To Create a Biosensor. An Undergraduate Quantitative Analysis Experiment. J. Chem. Educ 2009, 86 (6), 712–714.

(19). Paluri SLA; Edwards ML; Lam NH; Williams EM; Meyerhoefer A; Pavel Sizemore IE Introducing “Green” and “Nongreen” Aspects of Noble Metal Nanoparticle Synthesis: An Inquiry-Based Laboratory Experiment for Chemistry and Engineering Students. J. Chem. Educ 2015, 92 (2), 350–354.

(20). Jenkins JA; Wax TJ; Zhao J Seed-Mediated Synthesis of Gold Nanoparticles of Controlled Sizes To Demonstrate the Impact of Size on Optical Properties. J. Chem. Educ 2017, 94 (8), 1090–1093.

(21). Sharma RK; Gulati S; Mehta S Preparation of Gold Nanoparticles Using Tea: A Green Chemistry Experiment. J. Chem. Educ 2012, 89 (10), 1316–1318.

(22). Pérez-Mariño ÁM; Blanco MC; Buceta D; López-Quintela MA Using Silver Nanoclusters as a New Tool in Nanotechnology: Synthesis and Photocorrosion of Different Shapes of Gold Nanoparticles. J. Chem. Educ 2019, 96 (3), 558–564.

(23). Turkevich J; Stevenson PC; Hillier J A Study of the Nucleation and Growth Processes in the Synthesis of Colloidal Gold. Discuss. Faraday Soc 1951, 11, 55–75.

(24). Frens G Controlled Nucleation for the Regulation of the Particle Size in Monodisperse Gold Suspensions. Nat. Phys. Sci 1973, 241 (105), 20–22.

(25). Hao F; Nehl CL; Hafner JH; Nordlander P Plasmon Resonances of a Gold Nanostar. Nano Lett. 2007, 7 (3), 729–732. [PubMed: 17279802]

(26). Pallavicini P; Donà A; Casu A; Chirico G; Collini M; Dacarro G; Falqui A; Milanese C; Sironi L; Taglietti A Triton X-100 for Three-Plasmon Gold Nanostars with Two Photothermally Active NIR (near IR) and SWIR (Short-Wavelength IR) Channels. Chem. Commun 2013, 49 (56), 6265–6267.

(27). Casu A; Cabrini E; Donà A; Falqui A; Diaz-Fernandez Y; Milanese C; Taglietti A; Pallavicini P Controlled Synthesis of Gold Nanostars by Using a Zwitterionic Surfactant. Chem. - Eur. J 2012, 18 (30), 9381–9390. [PubMed: 22736477]

(28). Freestone I; Meeks N; Sax M; Higgitt C The Lycurgus Cup — A Roman Nanotechnology. Gold Bull. 2007, 40 (4), 270–277.

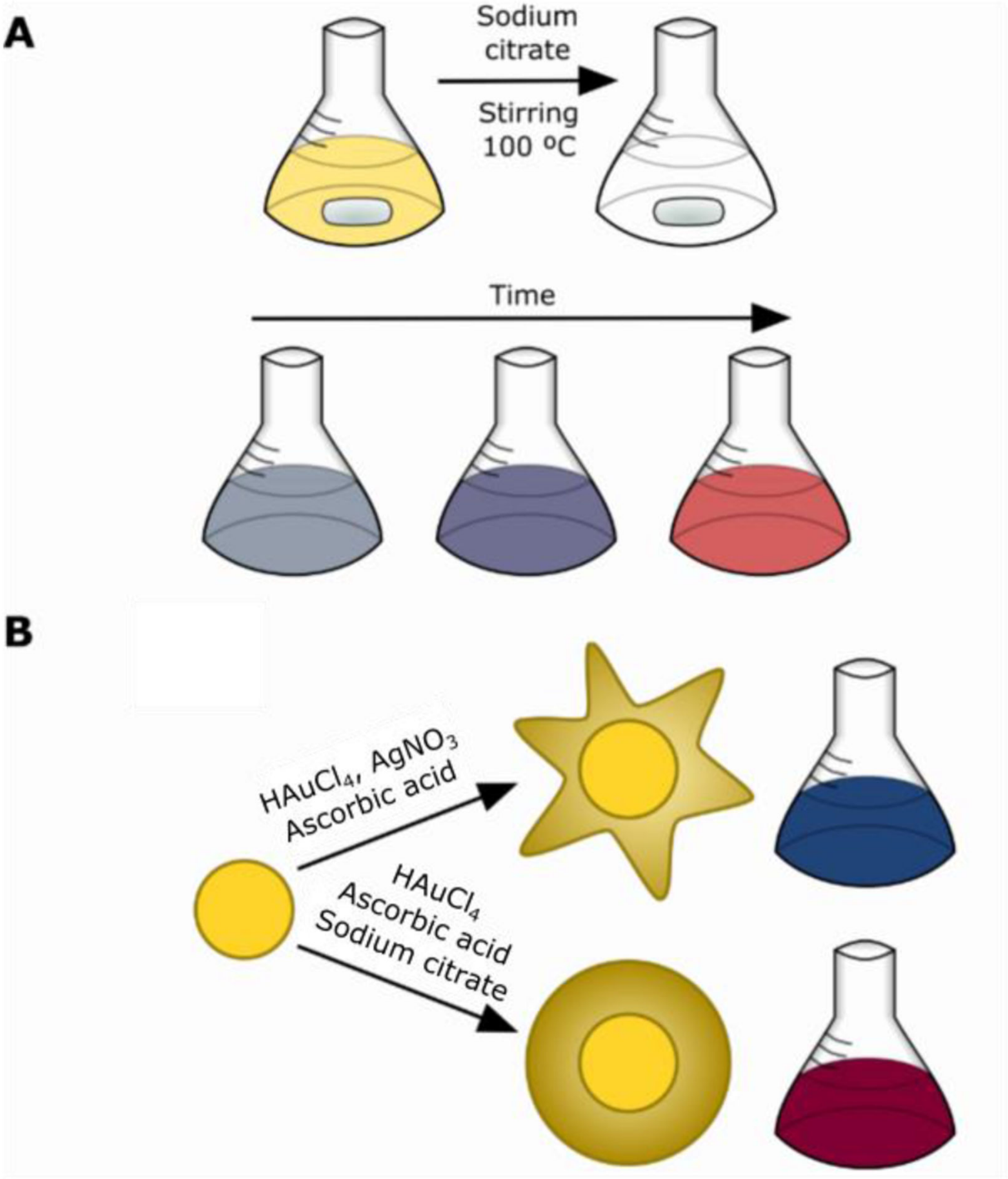

Figure 1.

Schematics of A: Turkevich seed synthesis and B: subsequent nanostar and large nanosphere growth utilizing the seed-mediated method.

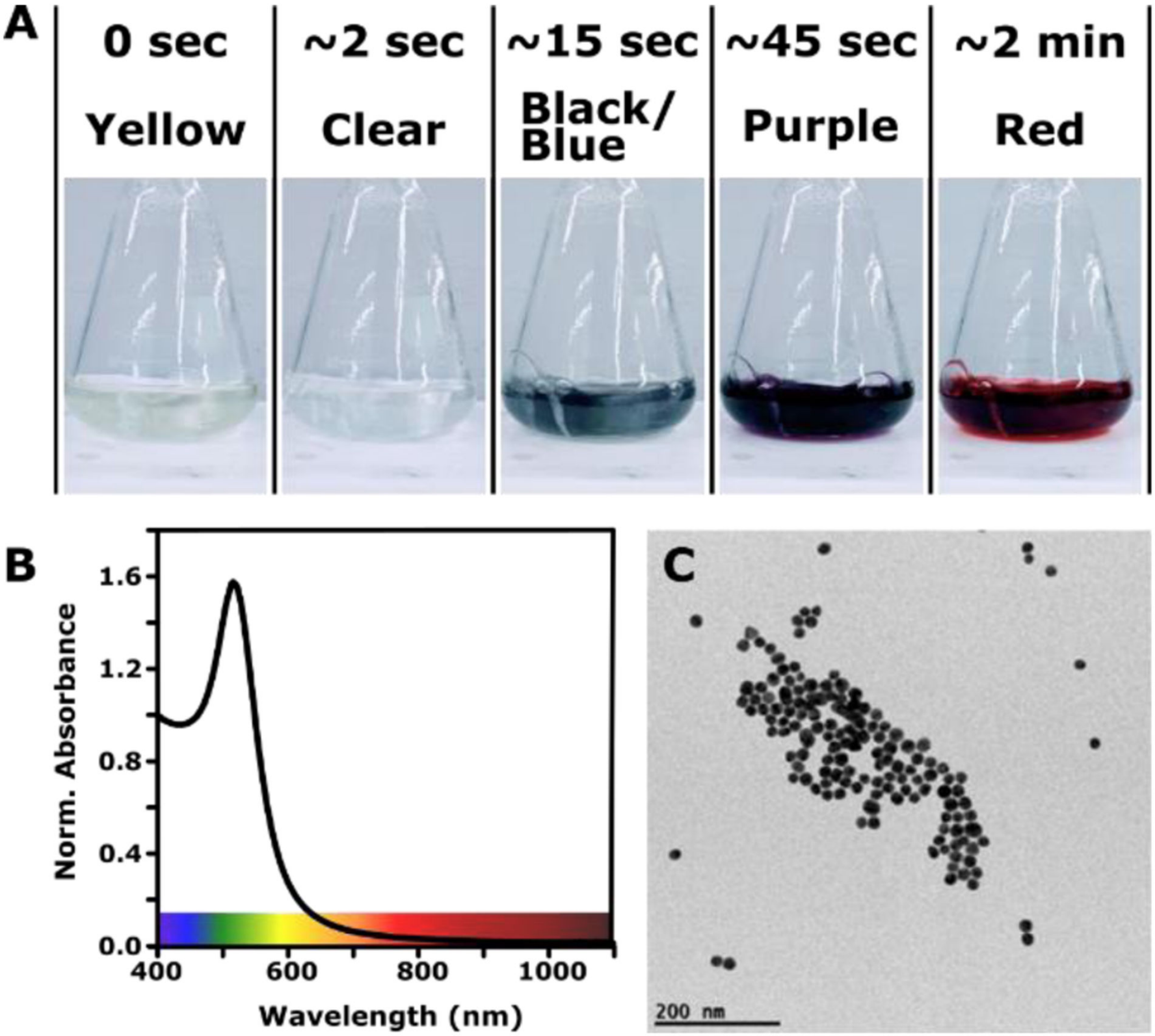

Figure 2.

A: Examples of typical student observations and data for the Turkevich synthesis. B: The UV-visible spectra showing maximum absorbance of the final products at ~520 nm. C: Transmission electron micrograph of a typical seed sample.

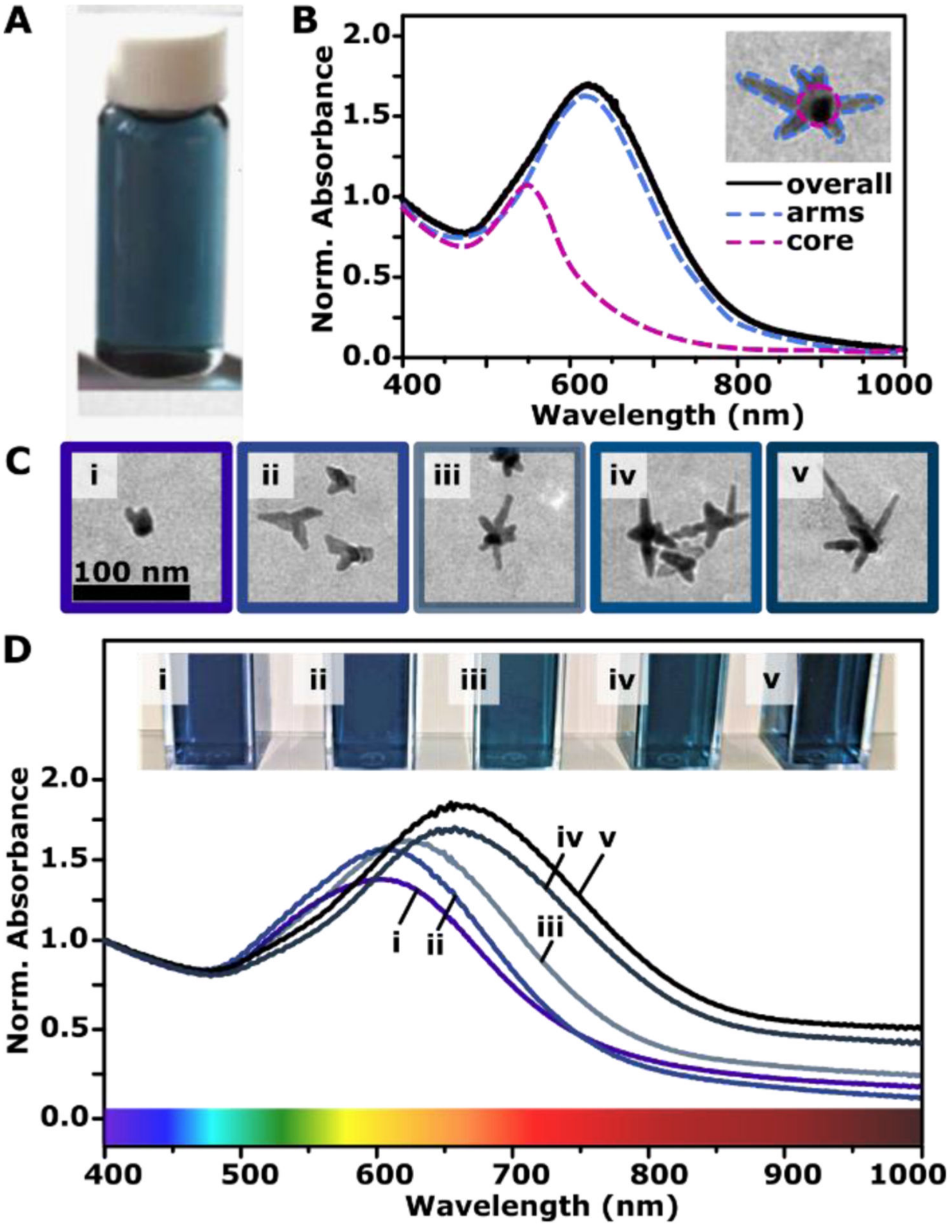

Figure 3.

A: Photograph of typical gold nanostar products and B: corresponding UV-visible spectrum (inset: diagram showing gold nanostar core and arms). C: Transmission electron micrographs showing variation in nanostar shape with longer and shorter branches, D: the color change resulting from the different shapes and their corresponding UV-visible spectra; longer branches cause the peak to shift to the right.

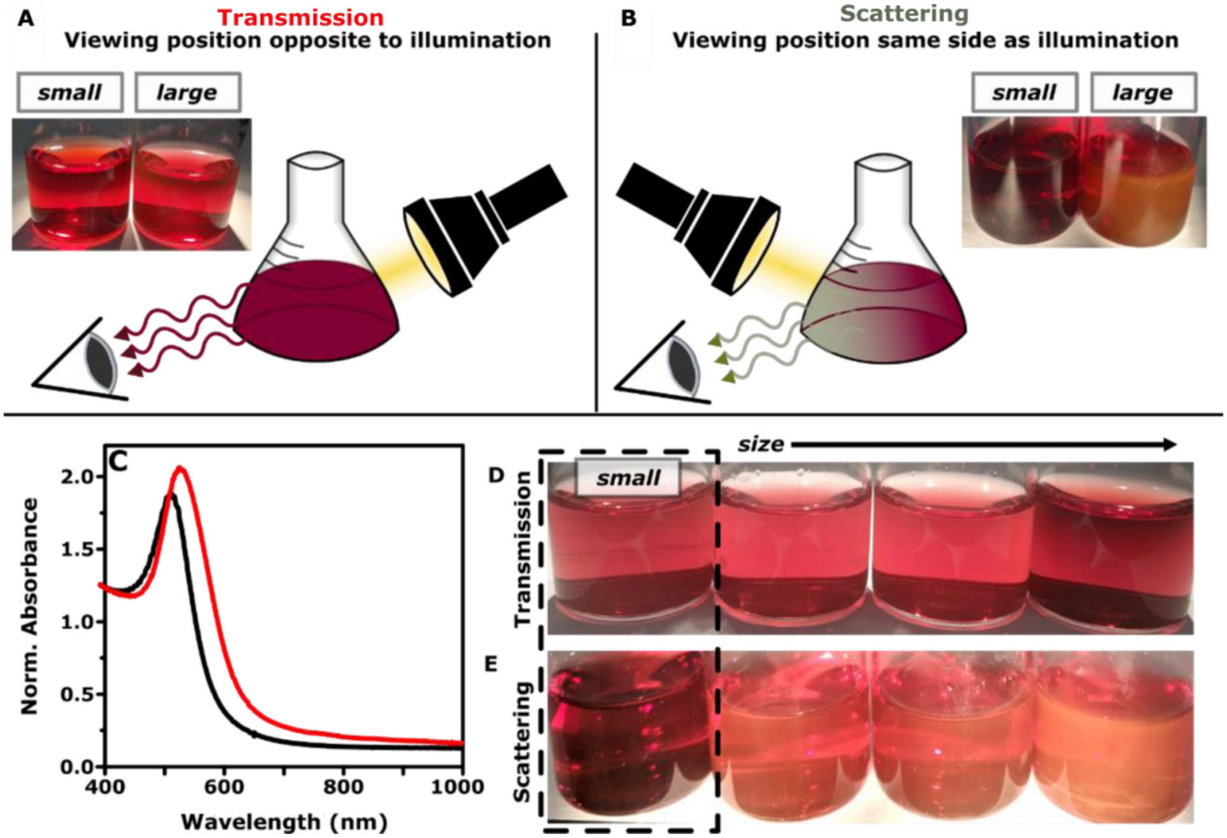

Figure 4.

A: Schematic showing illumination angle to observe color of transmitted light for small and large nanospheres (Flashlight=illumination source; eye=viewing position); inset: photograph of large and small samples viewed with transmitted light. B: Illumination schematic to evaluate scattering intensity for small and large nanospheres; inset: photograph of large and small samples viewed with scattered light. C: UV-visible spectra of small nanospheres (black) and large nanospheres (red). Photographs comparing nanospheres of different sizes. The photographs include images of the same samples viewed under transmitted light in part D and under scattered light in part E (different illumination direction/angle). Here, small = the Turkevich seeds. (Note: The difference in contrast for the first vials shown in panels D,E is due to the difference in lighting angle compared to the camera in the scattering *vs*. transmission geometry. For all other vials, the color difference is due to increased scattering from larger nanoparticles).