



**Chemical vs. Sonochemical Synthesis and Characterization
of Silver, Gold, and Hybrid Nanoparticles**

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Mark H. Griep, and Shashi P. Karna**

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14. ABSTRACT Silver (Ag), gold (Au), and alloy nanoparticles synthesized chemically and Au-Ag core-shell sonochemically produced nanoparticles were investigated for their potential applications in solar cells, biology, transistors, and light-emitting diodes (LEDs). The alloy or core-shell structure can be useful for creating new particles that have the properties of both the core material and the shell material. The Au, Ag, and Au-Ag nanoparticles were characterized optically and structurally by using ultraviolet-visible (UV-Vis) spectroscopy and high resolution transmission electron microscope (HRTEM), respectively. A novel sonochemical approach was used in contrast to the chemical alloy method. The sonochemical approach was used with varying parameters to determine the optimal synthesis parameters for precise control of particle size, geometry, and electrical properties. It was determined that a longer duration of sonication decreased the particle size of the Au-Ag nanoparticles and that the core-shell particles exhibited absorption wavelengths similar to Au nanoparticles, suggesting that Au composes the core of the nanoparticle, but the Ag did not create a shell structure as hoped.				
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1. Introduction and Background Information

There are many different kinds of nanoparticles, quantum dots (QDs) being one of the popular names for nanodots or nanocrystals. QD are incredibly diminutive particles that act as one atom but are made up of more atoms. QDs are able to recreate certain characteristics of atoms and their nuclei, but are completely modifiable, unlike atoms. These dots can contain anywhere between a single electron to several thousand electrons (1). QDs can be synthesized in many different ways. These dots act as bulk semiconductors with discrete energy levels, which is why the electrical properties can be explored. QDs are composed of excitons (2), which react to the confinement effects, providing for electrical properties that can be expanded on. QDs have specific tunability properties in electrical, magnetic, optical, and chemical properties. As a result of the specific tunability properties, these nanoparticles have many applications in light-emitting diodes (LEDs), biomedicine, and solar panels (3).

Since QDs can be synthesized using various techniques, many methods were discussed to find a method that might best suit silver (Ag) nanoparticles. Previous research indicated that bismuth silver sulfate (AgBiS_2) was synthesized through the sonochemical (4) approach, explaining that the ultrasound techniques are applicable for this compound and produce an efficient way to have a control on increasing or decreasing particle sizes of dots. In addition to AgBiS_2 , Au-Ag core-shell bimetallic nanoparticles (5) were also synthesized at the University of Melbourne using sonochemistry, providing further evidence that Ag can be effectively synthesized using sonochemistry.

However, synthesis by sonochemistry frequencies of Au nanoparticles seemed to have no major effect on the particles except for the discovery that synthesis of particles at a certain peak frequency results in a higher concentration of particles of a certain size (6). Additional research also concluded that nanomaterials experiments were conducted in the 1980s under a different name, sols (7). The research of Lee and Meisel included a chemical synthesis approach explaining how to create Ag and gold (Au) nanoparticles.

The sonication approach was chosen as it is a novel method of synthesizing these nanoparticles and provides a simple and quick approach. This approach is compared to a number of chemical synthesis methods for Ag, Au, and Au-Ag nanoparticles, and shows the benefits and drawbacks of sonication.

2. Materials and Experimental Procedure

The materials used in this study are silver nitrate (AgNO_3) (Sigma-Aldrich), chloroauric acid trihydrate (HAuCl_4) (Sigma-Aldrich), sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$) (Sigma-Aldrich), poly(vinyl alcohol) (PVA) (Celvol 125, hydrolysis 99.8 mol %), sodium borohydride (NaBH_4) (Sigma-Aldrich), polyethylene glycol (PEG) (8000 MW), and ethylene glycol (EG). All were purchased from Sigma-Aldrich and used without additional purification. All ratios are given in terms of % (w/v), which refers to the weight-volume ratio (i.e., 1% sodium citrate = 1 g of granular sodium citrate in 100 mL of H_2O).

2.1 Chemical Synthesis Protocol

The chemical synthesis procedures were derived from Lee and Meisel's research. The first procedure, denoted as procedure (a) through this report, is achieved by adding 18% w/v of AgNO_3 to an aqueous solution, then adding 1% $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$ for the reduction process. This solution is boiled (to 100 °C) for 12 min to reduce the Ag to the desired nanoparticle size. The second method, denoted as procedure (b), reacts 20 mL of 5 mM AgNO_3 with 60 mL of a 2-mM NaBH_4 solution. The NaBH_4 solution is added portion wise over an ice bath. Then, 1% PVA was added after the reaction was complete to stabilize the solution. This is then boiled (to 100 °C) for 12 min to decompose any excess NaBH_4 . The solutions were then cooled and precipitated for 24 h, and finally stored in a dark area pending analysis.

The chemical synthesis procedure for Au nanoparticles was derived from Sethi and Knecht's research. Au nanoparticles were synthesized through a citrate reduction method. A solution of 1.00-mM tetrachloroauric [III] acid trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$) was heated to boiling. Once boiling, 10 mL of a 40-mM trisodium citrate dihydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$) solution was added and stirred constantly. A change of color from yellow to dark red occurred after about 15 min, at which time it was removed. The solution was then stored in a dark place and sonicated before characterization and analysis.

The chemical synthesis procedure for alloy Au-Ag particles was derived from Zhang's research. The particles were synthesized via replacement reactions. Initially, Ag nanoparticles were created separately. Glass Pyrex beakers with magnetic stir bars were filled with 5 mL of 20-mM AgNO_3 , 2 mL of 20-mM potassium hydroxide, 83 mL of 18.3-M Ω filtered distilled water, and 5 mL of 0.2M poly(vinylpyrrolidone) (PVP). This polymer substance was used to protect the Ag nanoparticles from the reaction with the Au salts. The solution was stirred for 30 min. To complete the reaction, 5 mL of ice-chilled 0.1M NaBH_4 , was added into the solution. The solution was stirred for 1 h to complete the reaction. Afterwards, the solution was quickly removed, wrapped in non-transparent foil, and stored for 48 h in order to allow any residual NaBH_4 to precipitate. After this period, 20 mL of the solution was poured into beakers and

heated to 100 °C. Varying amounts between 3 and 5 mL of 1-mM HAuCl₄ were then added and stirred for 10 min. The solutions were quickly cooled to halt the reaction, rewrapped, and stored for 24 h.

2.2 Sonochemical Synthesis Protocol

The sonochemical synthesis procedures were derived from the University of Melbourne's research. Three different solutions were prepared for this experiment: Au, Ag, and Au-Ag hybrid nanoparticles. The Au stock solution was measured to 10 mL and 10 mL (20 mL total) of the PEG+EG solution is added to make the concentration of the solution to 0.02 mM, as stated in the literature. The same thing was applied to the AgNO₃ solution for the Ag nanoparticles. The Au-Ag hybrid nanoparticles have 10 mL of the Au solution and 10 mL (20 mL total) of the AgNO₃ solution to make the concentration of the solution to 0.02 mM, as stated in the literature. These three solutions are sonicated for 30 min over an ice bath in a Misonix Qsonica XL-2000 Ti-tip sonicator at 7 W.

Ultraviolet-visible (UV-Vis) spectroscopy for sample absorbance characteristics was performed on a Photonics[®] CCD Array spectrophotometer and a PerkinElmer Lambda 950 distilled water was used as a blank and absorbance levels were collected on high precision. Spectrofluorometry and emission level collection was performed on a SPEX[®] Fluoromax[®] – 3. Detailed particle size was analyzed with a high resolution transmission electron microscope (HRTEM).

3. Results and Discussion

3.1 Chemical Synthesis Analysis

3.1.1 Chemical Synthesis of Ag Nanoparticles

Chemical synthesis based on procedure (a) from Lee and Meisel yielded a nanoparticle solution with a greenish yellow color and procedure (b) had a brownish-black color. Occasionally, procedure (a) produced a clear solution; however, the TEM determined that the clear solution also contained nanoparticles. We attribute this finding to the fact that it is possible that the amount of C₆H₅Na₃O₇ used as a reduction agent may not have been adequate for each trial. It was found that the clear Ag solution had an average size distribution of around 28 nm (figures 1–2).

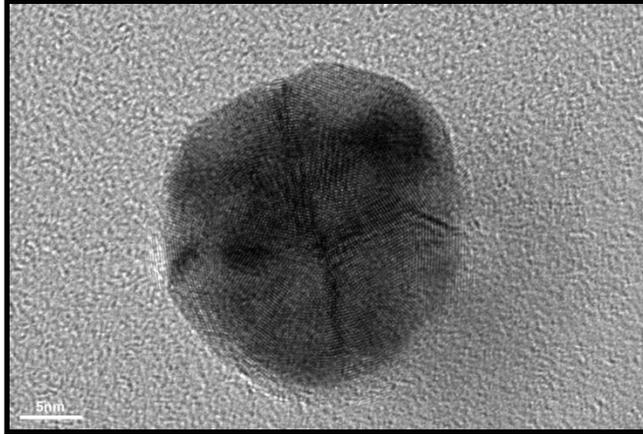


Figure 1. HRTEM image of Ag QD synthesized by procedure (a) (Ag QD Solution 3); average size distribution at 28 nm, view 1.

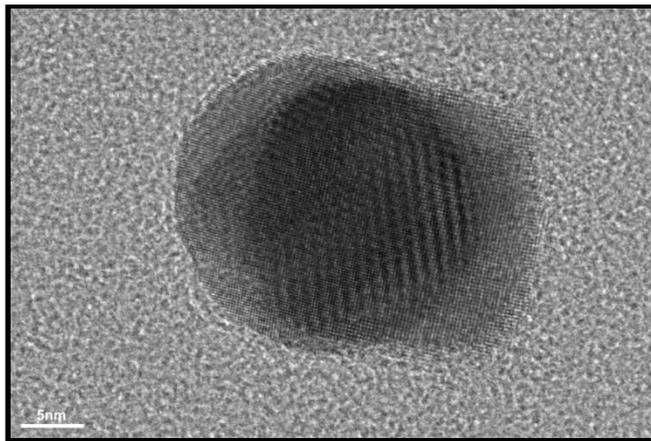


Figure 2. HRTEM image of Ag QD synthesized by procedure (a) (Ag QD Solution 3); average size distribution at 28 nm, view 2.

Following experimentation, we had the following solutions available for characterization (figure 3):

- Ag QD Solution 1 – procedure (a), boiled for 1 h (the solution evaporated);
- Ag QD Solution 2 – procedure (a), boiled for 14 min, resulted in green-yellow color;
- Ag QD Solution 3 – procedure (a), boiled for 12 min, resulted in clear solution;
- Ag QD Solution 4 – procedure (a), boiled for 20 min, resulted in darker green-yellow color;
- Ag QD Solution 5 – procedure (b), boiled for 20 min, resulted in dark brown color; and
- Ag QD Solution 7 – procedure (a), boiled for 3 min, resulted in translucent clear yellow color.



Figure 3. All solutions lined up in order, from Ag QD Solutions 2–7.

Through UV-Vis spectroscopy, it was discovered that the clear solutions all had an absorption at around 210–217 nm, which was in the UV spectrum. The remaining solutions all ranged around 413–466 nm (figure 4) in addition to the UV spectrum. From fluorescence spectroscopy, it was determined that the clear solutions emitted at 423 nm (figure 5) and excited at 382 nm; the other solutions emitted between 456 and 478 nm and excited between 410 and 467 nm, indicating a broad size distribution in the procedure (a) synthesis methods that did not result in a clear solution.

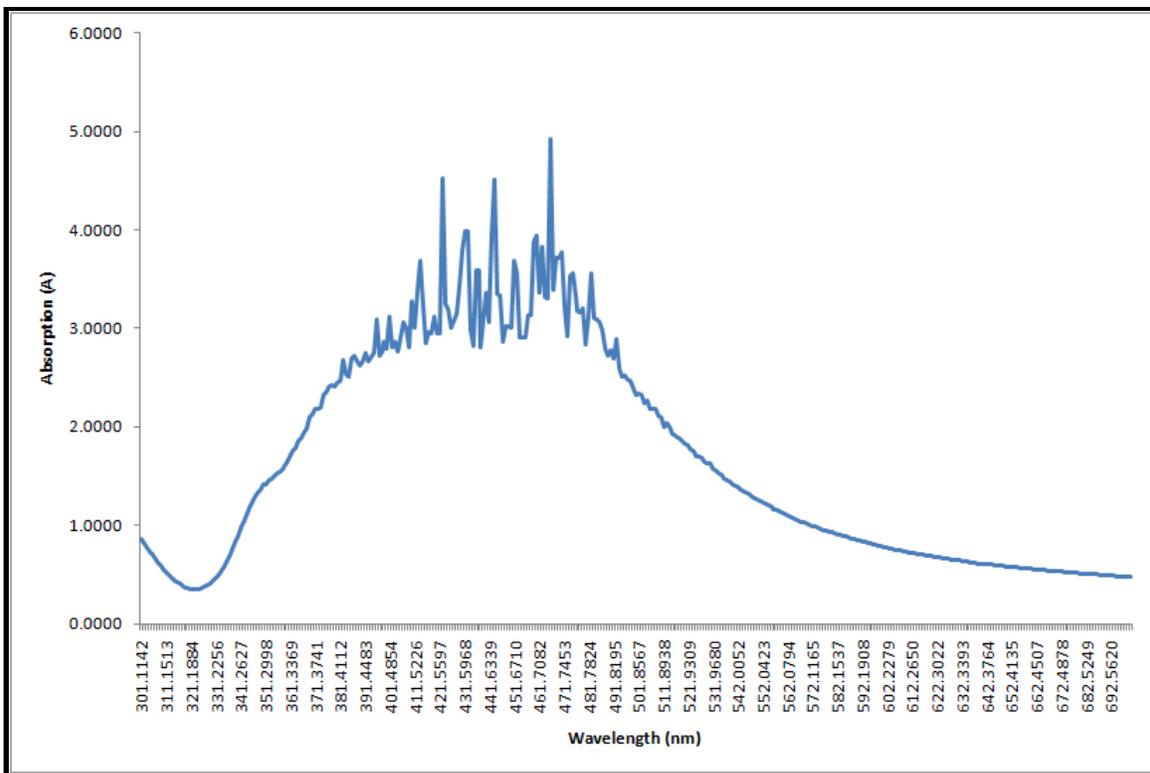


Figure 4. UV-Vis absorption on Ag QD Solution 2.

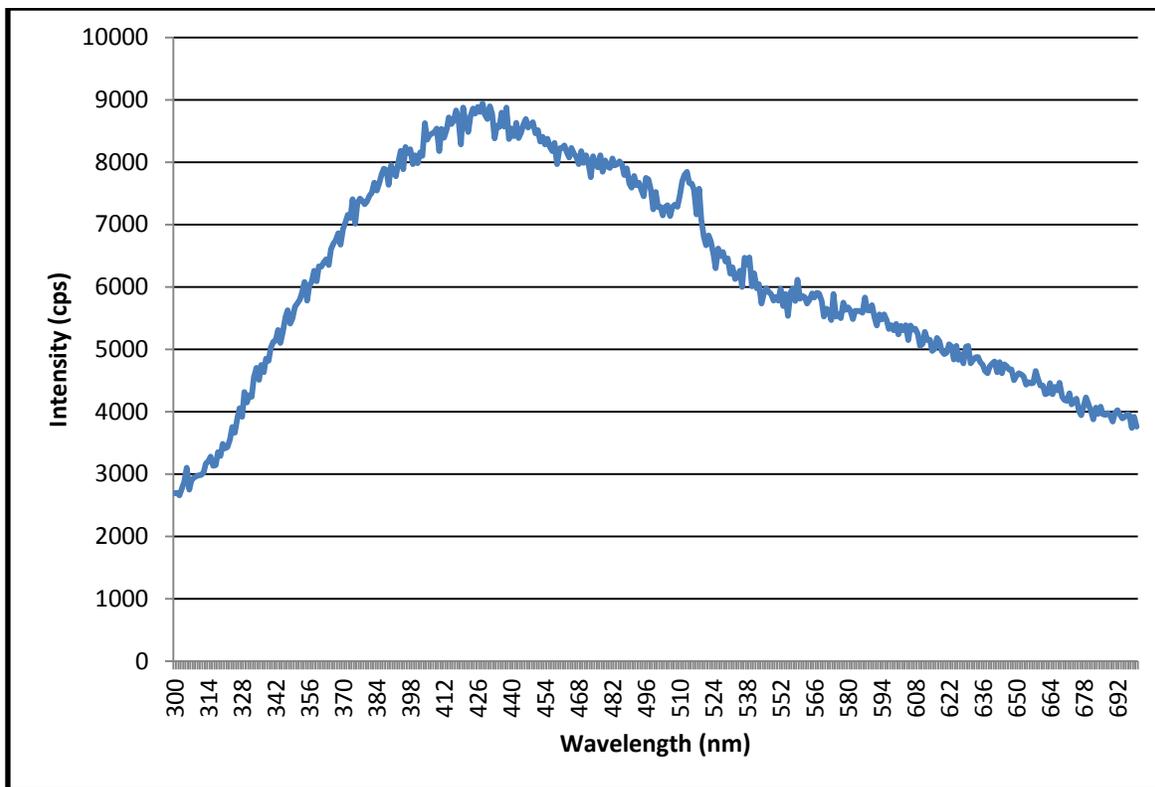


Figure 5. Fluorescence emission on Ag QD Solution 3; solution yields a peak emission at $\lambda = 423$ nm.

3.1.2 Chemical Synthesis of Au Nanoparticles

Au nanoparticles synthesized through the $C_6H_5Na_3O_7$ method by Sethi and Knecht produced a dark-red colored solution after boiling for 15 min, as shown in figure 6. Over time, the solution changed from clear to black to purple, and finally to the desired red color.



Figure 6. Au nanoparticle solutions after boiling for 15 min.

Through HRTEM, synthesis of Au nanoparticles was confirmed. The nanoparticles were found to be polycrystalline, varying shapes, and ranging in diameter from 6–12 nm with a high proportion at 8–9 nm, as shown in figures 7 and 8. Most particles were spherical, with few particles being pyramidal, egg shaped, or cylindrical. Some particles were clustered into groups of two or three, which may have been caused by aggregation over time.

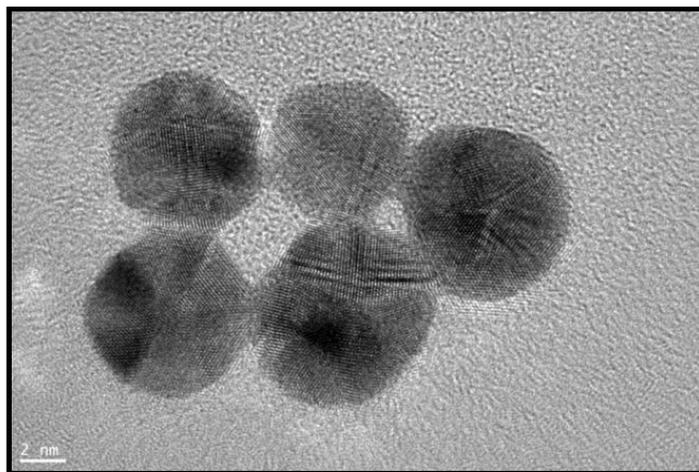


Figure 7. HRTEM images of Au nanoparticles, 2 nm scale

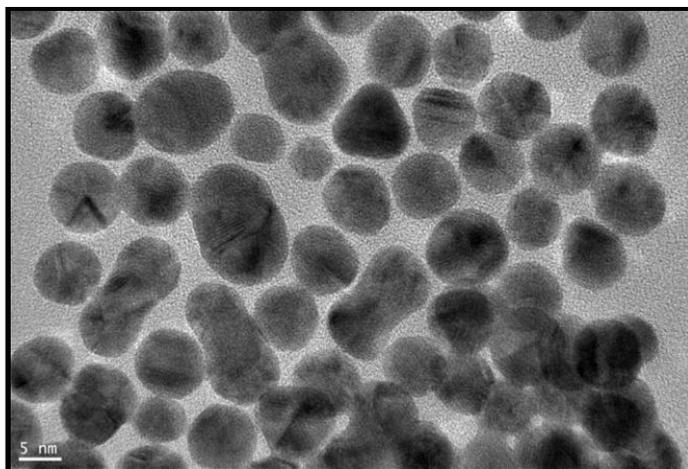


Figure 8. HRTEM images of Au nanoparticles, 5 nm scale

The Au nanoparticles were also found to have broad absorbance peaks at 220 and 521 nm and sharp emission peaks at 314 and 630 nm through the use of UV-Vis and fluorescence spectroscopy, as shown in figure 9.

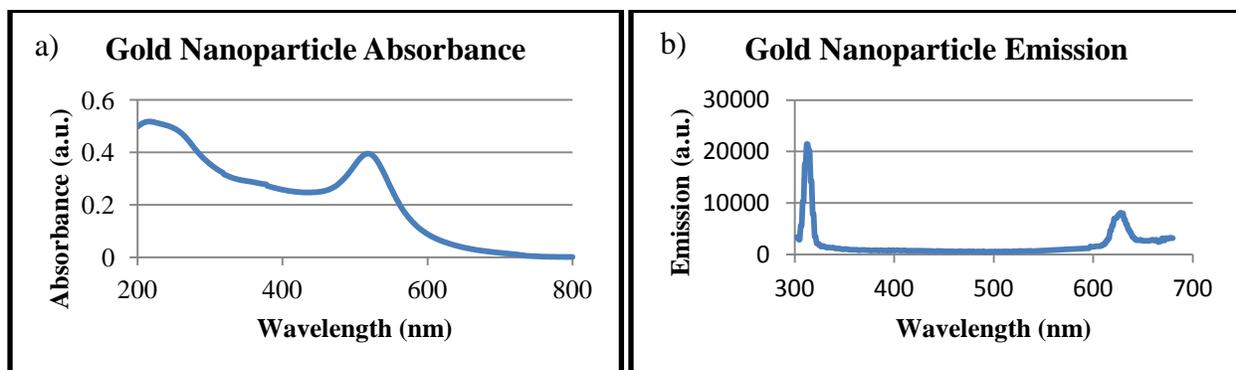


Figure 9. (a) Au NP absorbance at 220 and 521 nm and (b) Au NP emission at 314 and 630 nm.

3.1.3 Chemical Synthesis of Au-Ag Hybrid Nanoparticles

Chemical synthesis based on the procedure by Mallin and Murphy resulted in dark-red-colored solutions, which grew lighter as the amount of Au salt added decreased. UV-Vis spectroscopy performed on the samples was run in the visible spectrum. The absorbance spectrum, as shown in figure 10, displays a direct correlation with the amount of chlorauric acid (Au) and the absorbance peak of the sample. The peak for the 2-mL sample was 531 nm, which increased to 534 nm for the 3-mL sample, which increased again to 540 nm for the 4-mL sample. Each sample displayed a broad absorbance peak ranging approximately 40 nm. In general, as the amount of chlorauric acid added to the solution increased, the absorbance peak shifted to the right, closer to the pure Au spectrum and closer to the red portion of the visible spectrum.

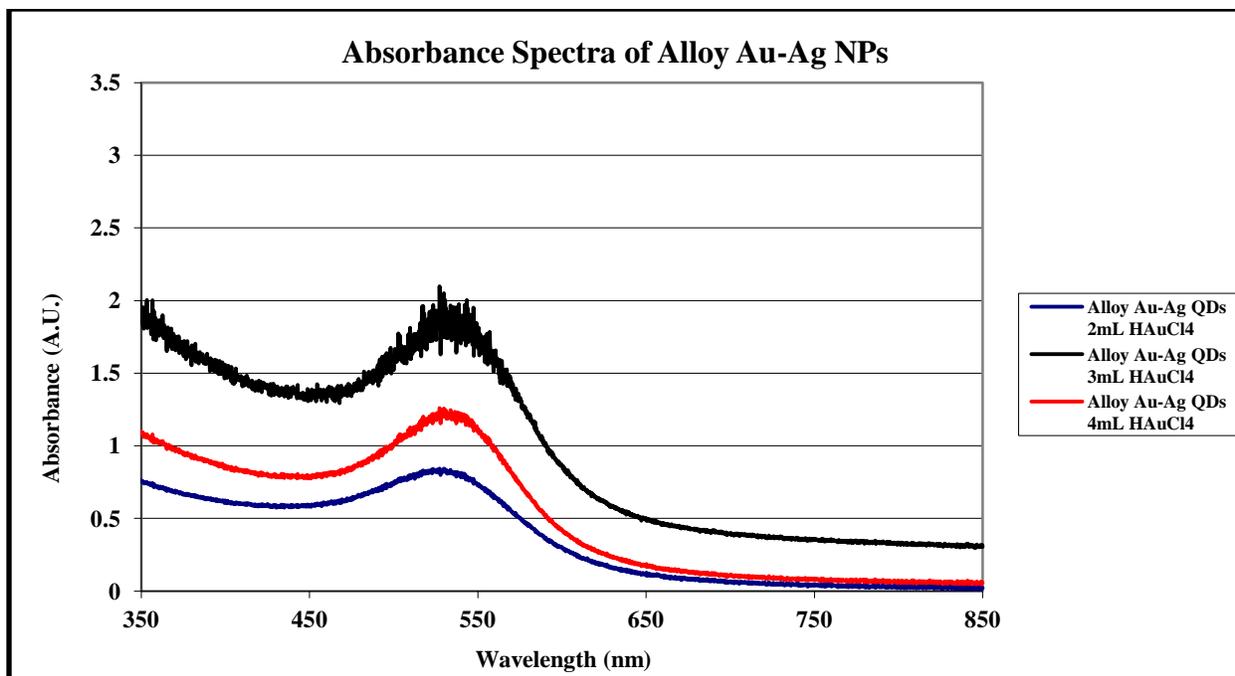


Figure 10. UV-Vis absorption on hybrid Au-Ag nanoparticles.

Emission scans were also performed on the alloy samples. These scans found that the alloy samples had two excitation peaks and two corresponding emission peaks, regardless of the amount of Au salt added. Emission intensity spectra as performed on the 3-mL sample are shown below. Figures 11 and 12 show that when alloy samples were excited with green light (495–570 nm), they were seen to emit red light at 658 nm. Additionally, alloy samples were seen to have a second excitation/emission peak. When excited at UV wavelengths (10–400 nm), alloy samples would emit violet light at a peak wavelength of 435 nm.

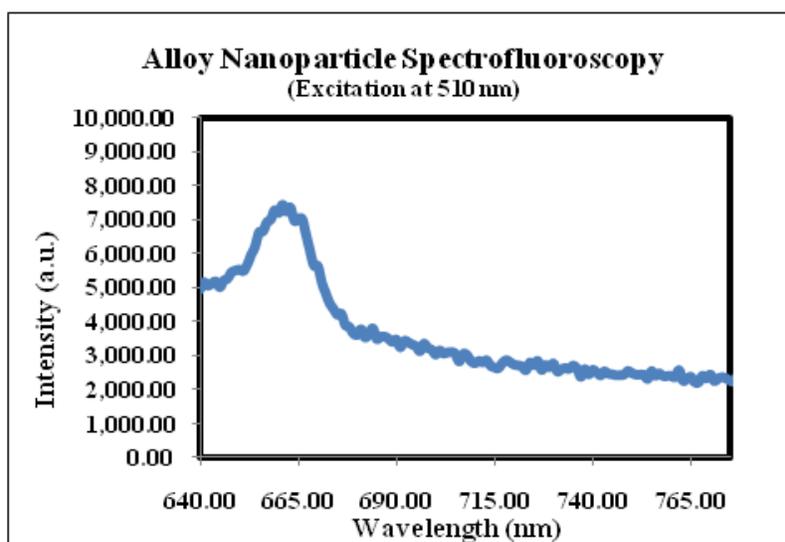


Figure 11. Alloy nanoparticle emission at 300 nm.

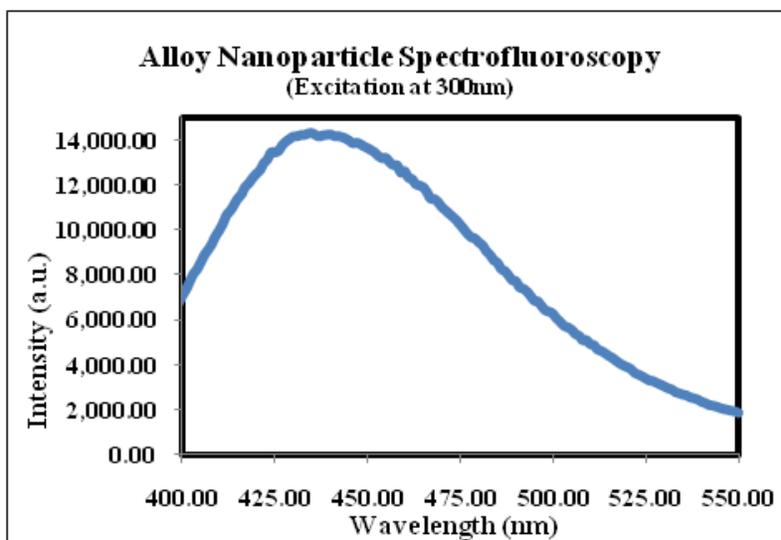


Figure 12. Alloy nanoparticle emission at 510 nm.

TEM was also used as a primary method to determine physical characteristics. Image scans were run at varying scan sizes, as shown in figures 13 and 14. The resulting images confirm the synthesis of alloy Au and Ag nanoparticles. The synthesis procedure also yielded fairly consistent particle diameters, with an average particle diameter that fell within the QD range (6 nm). Alloy samples are seen to form in circular patterns. Some particle aggregation was present in the samples, which may have occurred after the final reaction completed. Outside of these circular constructs, partially formed particles are seen to exist. Larger particles seem to move towards the exterior of the circle, while newer particles are seen to form along the interior of the circle. These artifacts may be remedied with a longer boiling process or a different ratio of materials.

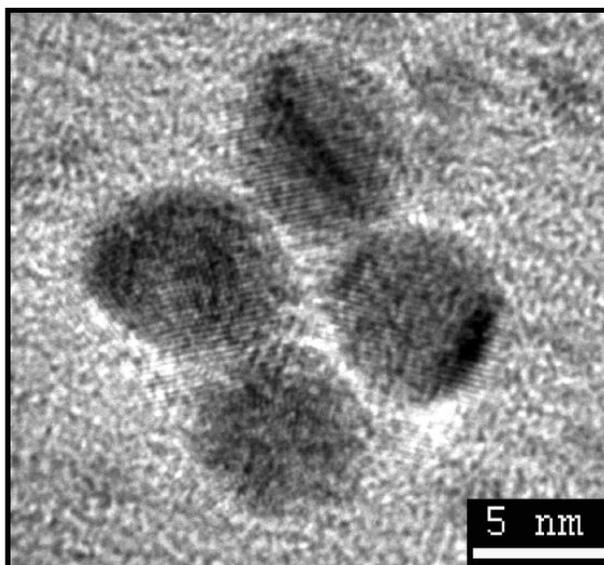


Figure 13. TEM image of alloy Au-Ag nanoparticles, 50 nm scale.

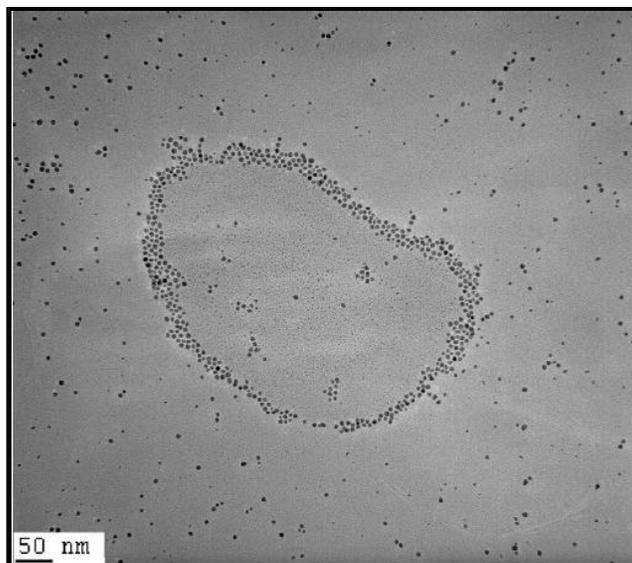


Figure 14. TEM image of alloy Au-Ag nanoparticles, 5 nm scale.

3.2 Sonochemical Synthesis Analysis

Through UV-Vis spectroscopy, the Ag solution had an absorption peak at 430 nm, the Au at 546 nm, and the Au-Ag at 557 nm (figure 15). The data are slightly higher than the literature states, but well within the range of the respective absorptions of the metals.

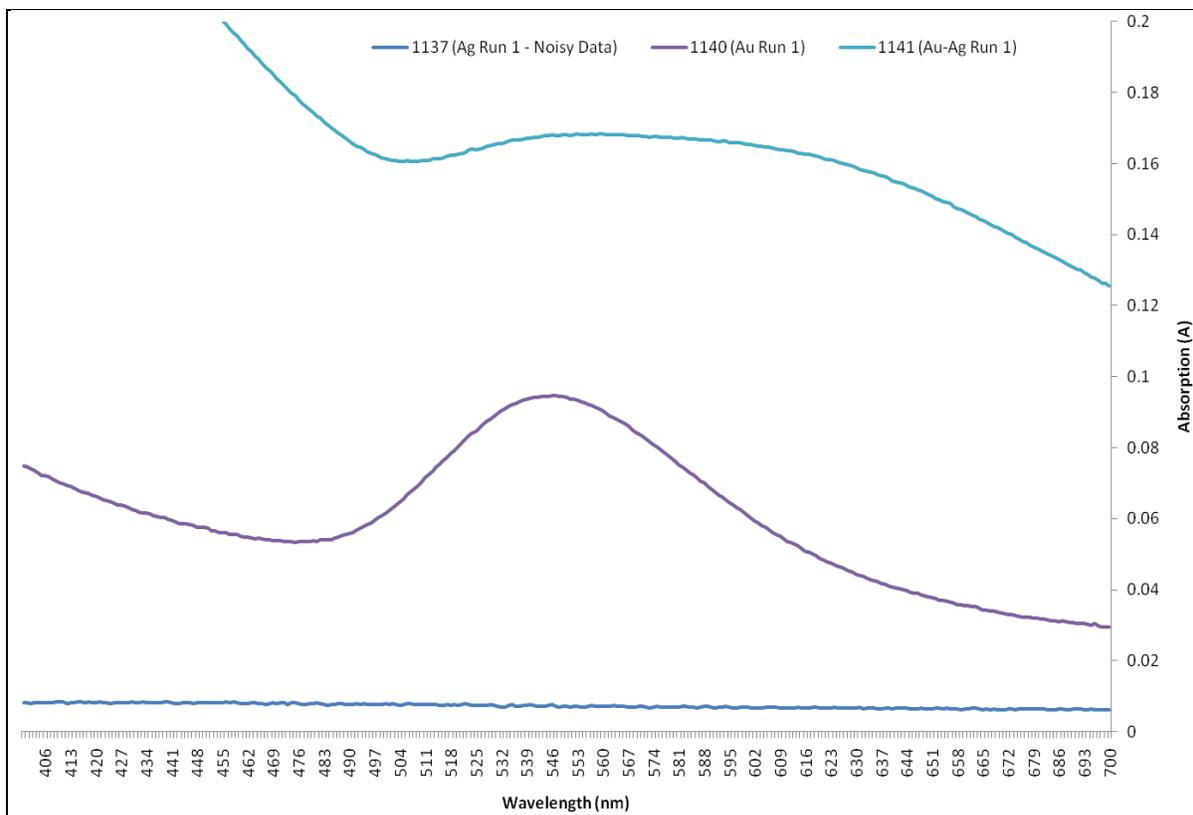


Figure 15. UV-Vis spectroscopy absorption on sonochemically synthesized Ag, Au, and hybrid nanoparticles.

3.2.1 Sonochemical Synthesis of Ag Nanoparticles

The Ag solution was clear, which did not show a significant sign of nanoparticle growth, but instead may have had aggregate Ag particles that were not reduced. The TEM images of the Ag nanoparticles showed that a great deal of aggregation had occurred and was likely the reason the UV-Vis spectroscopy was not definitive (figure 16).

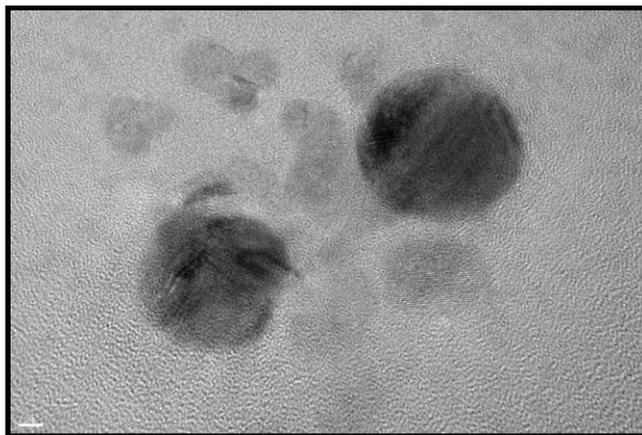


Figure 16. HRTEM image of Ag nanoparticles synthesized sonochemically; average size distribution at 10 nm.

3.2.2 Sonochemical Synthesis of Au Nanoparticles

The Au solution is a rose-pink color, clearly displaying nanoparticle properties when the particles are in solution. The Au nanoparticles showed an interesting size and shape distribution between 30–60 nm, which was not expected for sonochemically produced nanoparticles (figure 17). Nanopyramids, nanowires, and hexagonal shapes are seen here, possibly making a sonochemical synthesis approach a new way to synthesize new nanoshapes for new applications.

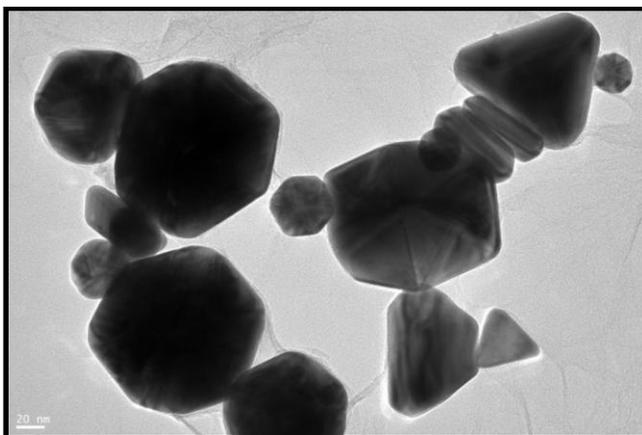


Figure 17. HRTEM image of Au nanoparticles synthesized sonochemically; average size distribution at 30–60 nm.

3.2.3 Sonochemical Synthesis of Au-Ag Hybrid Nanoparticles

The Au-Ag nanoparticles exhibited a deep purple solution color, signifying that the Au and Ag had reacted and reduced. The hybrid nanoparticles were around 12 nm in size (figure 18), but there was no real core-shell structure as explained by the literature.

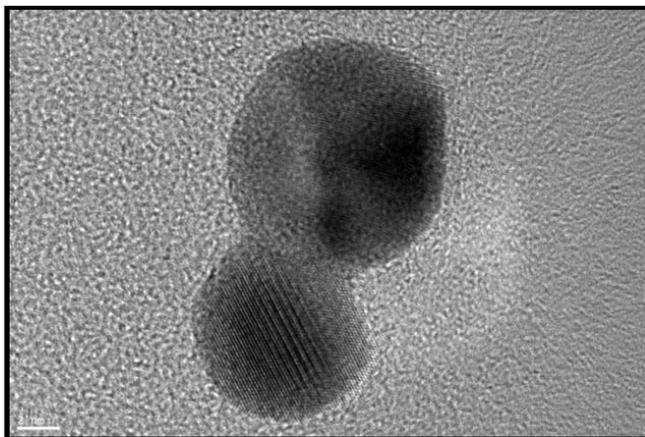


Figure 18. HRTEM image of Au-Ag nanoparticles synthesized sonochemically; average size distribution at 12 nm

4. Summary and Final Conclusions

We created Ag, Au, and hybrid alloy nanoparticles by chemical synthesis and Ag, Au, and hybrid core-shell nanoparticles were synthesized using the novel sonication method as studied by the University of Melbourne (5). Two different Ag chemical procedures were used, one with $C_6H_5Na_3O_7$ as a reduction agent and the other with $NaBH_4$, and one Au chemical procedure was used with $C_6H_5Na_3O_7$. It was found that the average size distribution was around 28 nm in size for Ag chemical synthesis, 8 nm in size for Au, and 8–9 nm for the alloy nanoparticles; however, the results are not conclusive as further characterization should be conducted. In the sonochemical approach, the reduction agent (PEG/EG) seemed to not have a significant enough impact on $AgNO_3$ reduction to make 5 to 25 nm size particles show the yellowish color that was stated in the literature. Instead, a wide variety of size distributions was seen in Au and Ag nanoparticles. One possible explanation is that the molecular weight of the PEG was not heavy enough and did need to have a long enough chain polymer to reduce the particle size even more. The Au and the hybrid nanoparticles did reduce under the reduced molecular weight from the literature, but significant physical characterization needs to be done in order to assure that the particles were reduced down to their ideal sizes for future applications.

The previous research that included these characterization methods now has some evidence why their solutions turned different colors. Those changes are attributed to the size and absorption of the nanoparticles, as found in UV-Vis spectroscopy and HRTEM imaging.

While the above synthesis procedures are practical and not time consuming, additional methods should be investigated as these solutions exhibited only certain characteristics but not others. A more in-depth analysis is required to understand all the properties of Ag QDs. For further studies, further characterization on electrical properties and height profiles should be conducted.

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List of Symbols, Abbreviations, and Acronyms

Ag	silver
AgNO ₃	silver nitrate
Au	gold
C ₆ H ₅ Na ₃ O ₇	sodium citrate
EG	ethylene glycol
HAuCl ₄ · 3H ₂ O	tetrachloroauric [III] acid trihydrate
HAuCl ₄	chloroauric acid trihydrate
HRTEM	high resolution transmission electron microscopy
Na ₃ C ₆ H ₅ O ₇ · 2H ₂ O	trisodium citrate dihydrate
NaBH ₄	sodium borohydride
NP	nanoparticle
PEG	polyethylene glycol
PVA	poly(vinyl alcohol)
PVP	poly(vinylpyrrolidone)
QDs	quantum dots
SEM	scanning electron microscopy
UV	ultraviolet
Vis	visible

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