

*ARMY RESEARCH LABORATORY*



---

## **Shape-Controlled Gold Nanoparticle Synthesis**

**by Hailey E. Cramer, Lily Giri, Mark H. Griep, and Shashi P. Karna**

---

**ARL-TR-6662**

**September 2013**

## **NOTICES**

### **Disclaimers**

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

# **Army Research Laboratory**

Aberdeen Proving Ground, MD 21005-5069

---

---

**ARL-TR-6662**

**September 2013**

---

## **Shape-Controlled Gold Nanoparticle Synthesis**

**Hailey E. Cramer, Lily Giri, Mark H. Griep and Shashi P. Karna**  
**Weapons and Materials Research Directorate, ARL**

<b>REPORT DOCUMENTATION PAGE</b>			<b>Form Approved OMB No. 0704-0188</b>		
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. <b>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.</b>					
<b>1. REPORT DATE (DD-MM-YYYY)</b> September 2013		<b>2. REPORT TYPE</b> Final		<b>3. DATES COVERED (From - To)</b> June 2012–September 2012	
<b>4. TITLE AND SUBTITLE</b> Shape-Controlled Gold Nanoparticle Synthesis			<b>5a. CONTRACT NUMBER</b>		
			<b>5b. GRANT NUMBER</b>		
			<b>5c. PROGRAM ELEMENT NUMBER</b>		
<b>6. AUTHOR(S)</b> Hailey E. Cramer, Lily Giri, Mark H. Griep, and Shashi P. Karna			<b>5d. PROJECT NUMBER</b> 622618		
			<b>5e. TASK NUMBER</b>		
			<b>5f. WORK UNIT NUMBER</b>		
<b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b> U.S. Army Research Laboratory ATTN: RDRL-WMM-A Aberdeen Proving Ground, MD 21005-5069			<b>8. PERFORMING ORGANIZATION REPORT NUMBER</b> ARL-TR-6662		
<b>9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b>			<b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>		
			<b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b>		
<b>12. DISTRIBUTION/AVAILABILITY STATEMENT</b> Approved for public release; distribution is unlimited.					
<b>13. SUPPLEMENTARY NOTES</b>					
<b>14. ABSTRACT</b> At the nanoscale, the optical, electrical, and catalytic properties of a material depend on its size and shape. Therefore, synthesis of nanoparticles with controlled size and shape is important for their application in biosensors, photonics, and other optoelectronic devices. Whereas the effect of size on the properties of nanoparticles has been extensively studied in the past two decades, similar studies on the shape of nanoparticles have received little attention. The specific goals of this research are to synthesize nanoparticles with desired shapes and investigate their structure-property relationships. Recently, we successfully synthesized colloidal gold (Au), silver (Ag), and mixed Au–Ag nanoparticles using aqueous chemistry. The particles exhibited a mixture of shapes, including spheres, rods, and prisms. In the present work, we synthesize Au nanorods, nanospheres, and nanotriangles using a wet-chemical, seed-mediated growth method employing the surfactant cetyltrimethylammonium bromide as a growth-directing micellar template. It was possible to obtain these shapes through precise tuning of thermodynamic and kinetic parameters and the addition of small concentrations of halide and metal ions. Characterization of the particles was performed using tunneling electron microscopy, energy-dispersive spectroscopy, ultraviolet-visible spectroscopy, and dynamic light scattering.					
<b>15. SUBJECT TERMS</b> nanoparticles, gold nanoparticle, nanosphere, nanoprism, nanotriangle, nanorod					
<b>16. SECURITY CLASSIFICATION OF:</b>			<b>17. LIMITATION OF ABSTRACT</b>  UU	<b>18. NUMBER OF PAGES</b>  24	<b>19a. NAME OF RESPONSIBLE PERSON</b> Mark Griep
<b>a. REPORT</b> Unclassified	<b>b. ABSTRACT</b> Unclassified	<b>c. THIS PAGE</b> Unclassified			<b>19b. TELEPHONE NUMBER (Include area code)</b> 410-306-4953

---

## Contents

---

<b>List of Figures</b>	<b>iv</b>
<b>List of Tables</b>	<b>v</b>
<b>Acknowledgments</b>	<b>vi</b>
<b>1. Introduction and Background</b>	<b>1</b>
<b>2. Experiment and Calculations</b>	<b>3</b>
2.1 Materials .....	3
2.2 Preparation of Gold Seeds .....	4
2.3 Growth of Gold Nanoparticles .....	4
2.4 Purification .....	6
<b>3. Results and Discussion</b>	<b>6</b>
<b>4. Summary and Conclusions</b>	<b>10</b>
<b>5. References</b>	<b>11</b>
<b>List of Symbols, Abbreviations, and Acronyms</b>	<b>14</b>
<b>Distribution List</b>	<b>15</b>

---

## List of Figures

---

Figure 1. Schematic for Au seed preparation. Average size was confirmed to be about 4 nm through TEM.....	4
Figure 2. Schematic for Au nanoparticle growth: (a) nanorod, (b) nanoprism, and (c) nanosphere. Only the first two seeding steps are shown. Subsequential seeding can be continued for growth of larger particles.....	5
Figure 3. Au seeds (about 4 nm in diameter). Scale bars are 5 nm (left) and 50 nm (right). .....	7
Figure 4. Au nanospheres: (a) solution A (about 5 nm in diameter) and (b) solution B (about 8 nm in diameter). Scale bars are 5 nm.....	7
Figure 5. Au (a) nanorods (aspect ratio 10) and (b) nanoprisms (about 150-nm edge length). Scale bars are 50 nm (top) and 200 nm (bottom).....	7
Figure 6. Energy dispersive spectroscopy of Au nanosphere A sample. EDS for all other samples were similar.....	8
Figure 7. Visible absorption spectra for Au seeds, nanorods, nanoprisms, nanosphere A, and nanosphere B.....	9

---

## List of Tables

---

Table 1. Zeta potential (surface charge) for shape-controlled Au nanoparticles. ....	9
--	---

---

## **Acknowledgments**

---

The authors wish to acknowledge the help of Dr. Aaron Jackson for his interest and support on this project. Hailey Cramer is especially grateful to Drs. James McCauley, Brad Forch, Melanie Cole, and Rose-Pesce Rodriguez for educating her in the various aspects of materials science, chemistry, tunneling effects, and a whole lot more in science. This research was supported by an appointment to the Student Research Participation Program at the U.S. Army Research Laboratory (ARL) administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and ARL.

---

## 1. Introduction and Background

---

Due to their small dimensions, nanoparticles obey the laws of quantum mechanics and, therefore, have the ability to participate in quantum tunneling. A recent paper published in *Nature* by Mebrahtu et al. (1) has examined this effect by showing that an electron can successfully hop on a carbon nanotube as it travels between two electrical leads. In a similar fashion, our research aims to fundamentally understand and describe the quantum tunneling effect in shape-controlled metal nanoparticles, specifically gold (Au) nanorods, nanoprisms, and nanospheres. While the effect of size on the properties of isotropic nanoparticles has been extensively studied in the past two decades, similar studies on the shape of nanoparticles have received little or no attention. In fact, it is not only the composition and size of nanoparticles that affect their unique optical, chemical, and electrical properties but also the shape. An increased understanding of the structure-property relationships of shape-controlled nanomaterials will allow for their future integration into advanced materials such as optoelectronics, photonics, biosensors, and drug carriers.

Recently, multiple methods have been explored for growing nanorods (2–12), triangular prisms (5, 13–17), nanospheres (18, 19), and other platonic (20–22), branched (12), and anisotropic (12, 23, 24) morphologies. Although synthesis can be achieved through photochemical and electrochemical methods, colloidal wet-chemistry synthesis has proved to be the most advantageous, as little equipment is necessary and procedures can be scaled up to produce larger quantities of shape-controlled nanoparticles. The majority of the literature (24, 25) relies on a two-step, “seed-mediated” growth method. In the first step, small spherical seed particles, often less than 5 nm in diameter, are created under conditions that allow for rapid growth of all crystal facets. This step involves the use of a metal salt, a capping agent, and a strong reducing agent. In the second step, a growth solution containing more metal salt in the presence of a shape-directing molecule or surfactant is used in addition to a weak reducing agent. The seeds are added to this solution to serve as nucleation sites and facilitate the reduction of metal ions onto their surface in a seed-overgrowth fashion. In opposition to the one-pot homogeneous nucleation we have done previously in our laboratory for synthesis of various nanoparticle shapes (26), this heterogeneous, seed-mediated growth lowers the activation energy needed for metal reduction and allows for more fine-tuned control over growth conditions using weaker reducing agents and temperatures. This control is favorable, as aqueous, shape-controlled crystal growth requires precise tuning of the thermodynamic and kinetic parameters of the reaction, including reaction rate, capping agent, reactant concentration, temperature, and pH. The difficulty in controlling these uniquely linked parameters has made it difficult to fully understand the mechanisms behind shape-controlled colloidal synthesis. Therefore, recently there has been greater focus in the literature (27, 28) on developing an explanation for the shape-controlled growth mechanism than on investigating the unique properties of these materials.

Sau and Murphy (12) found, through a seed-mediated growth method, that various shapes such as rods, wires, cubes, and prisms can be grown through careful control over the growth step. Gold seeds of about 3–5 nm in diameter were grown through a quick nucleation step using sodium citrate as a capping agent. They were added to a solution containing Au salt, the surfactant cetyltrimethylammonium bromide (CTAB), and ascorbic acid. In this case, ascorbic acid can reduce the Au only in the presence of the seeds. In the case of nanorods (7), it was found that through controlling the ratios of reactants, several different aspect ratios ranging from 4.6 to 18 could be obtained, although multiple centrifugation steps were necessary to separate them from spherical particles. Others in Murphy's group (3, 4) also found that employing a surfactant with a longer tail yielded longer nanorods, and that Au seeds of different sizes and charged surface functionalities resulted in rods with different aspect ratios. In addition, by changing the pH of the growth solution from 2.8 to 3.5, nanorods with a drastically improved yield were produced with minimal centrifugation (2).

Using a chemical process similar to that used by Murphy's group, Ha et al. (5) found that Au nanoprisms could be synthesized by adding trace amounts of halide ions into a growth solution initially designed for the growth of nanorods. The size and yield of the nanoprisms were manipulated through control over pH and temperature. There are issues, however, with the degree to which these shaped nanoparticles can be reproduced. Ha's work, in particular, contrasts with Shankar et al. (15, 16), who reported that iodide ions suppress the formation of nanoprisms. Millstone et al. (27) suggest that these conflicting results can be due to the fact that, depending on the supplier, CTAB may contain iodide contaminants that cause the production of different shapes. This research shows that identical seed particles and growth solutions could be used to form rods, triangular prisms, and spheres simply by controlling the iodide ion concentration and using purified CTAB.

In contrast to the foregoing research methods, Nikoobakht and El-Sayed (10) synthesized Au seeds using CTAB instead of sodium citrate as the capping agent. These CTAB-capped seeds were used in the presence of silver nitrate ( $\text{AgNO}_3$ ) and produced nanorods in 99% yield, making it the most popular chemical synthesis method for Au nanorods. By changing the amount of  $\text{AgNO}_3$  added to the growth solution, nanorods with aspect ratios ranging from 1.5 to 5 were synthesized. Murphy's group (6) followed up this research by using their citrate-capped seeds and adding  $\text{AgNO}_3$  to the growth solution. They found that instead of producing nanorods, as expected, spheroidal-shaped nanoparticles were produced. Liu and Guyot-Sionnest (9) showed through high-resolution transmission electron microscopy (TEM) that citrate-capped seeds have a multiply twinned structure, as opposed to the CTAB-capped seeds that were single crystals with 1.5-nm diameters, and thus explained the importance of the seed in shape-controlled nanoparticle synthesis. Interestingly, the composition of the seed particle does not have to be the same as the metal chosen for overgrowth (24). Seed particles made of a metal with a weaker reduction potential metal have been used to grow hollow shell nanostructures. In addition,

shape-specific nanoparticles of one metal have been used as seeds to allow for overgrowth of another metal, producing various bimetallic anisotropic and polyhedral shapes.

In contrast to the typical CTAB method used in the literature, Kim et al. (20) used a polyol reaction method involving the use of poly(vinylpyrrolidone) as a reducing agent to produce various platonic Au nanoparticles. In a very different method, Xie et al. (17) synthesized Au nanospheres and triangular nanoplates using bovine serum albumin as the reductant and found that  $\text{AgNO}_3$  could be used to control the size of the particles. Shankar et al. (15) synthesized Au nanoplates using lemongrass leaf extract as a reducing agent and a shape-directing molecule.

The objective of this research was to precisely synthesize shape-controlled Au nanoparticles. We have successfully synthesized Au nanoparticles of cylindrical (nanorods), prismatic (nanoprisms), and spherical (nanospheres) shapes using seed-mediated aqueous methods. Our approach combined previously used approaches (5, 19) and differed in using the same seed for all shapes, identifying and utilizing the effect of relative concentration of the starting materials on the yield of the nanoparticles. Transmission electron microscopy, energy-dispersive spectroscopy (EDS), UV-Vis spectroscopy, and dynamic light scattering (DLS) measurements were performed to characterize, respectively, the shape, structure, chemical composition, absorption spectrum, and surface charge of the synthesized nanoparticles. The quantum tunneling effect studies on synthesized shape-controlled nanoparticles are underway and will be reported in future communications.

---

## 2. Experiment and Calculations

---

### 2.1 Materials

Hydrogen tetrachloraurate (III) trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), CTAB, trisodium citrate dihydrate, sodium borohydride ( $\text{NaBH}_4$ ), L-ascorbic acid, and potassium iodide (KI) were purchased from Sigma-Aldrich. All chemicals were used as received. Distilled deionized water was used for all solution preparations. All glassware was cleaned in the following order: tap water and dish detergent, purified water, ethanol, and nitrogen gas to dry. The growth stock solution was used within 6 h of preparation. If surfactant fell out of the growth solution, it was heated at 50 °C to redissolve the precipitate and then cooled to room temperature. Stock solutions of  $\text{NaBH}_4$  and L-ascorbic acid were prepared fresh before every synthesis. All other solutions were stable for up to several months.

## 2.2 Preparation of Gold Seeds

An Au seed solution was prepared by mixing 10 mL of a  $5.0 \times 10^{-4}$ -M hydrogen tetrachloroaurate ( $\text{HAuCl}_4$ ) stock solution with 10 mL of a  $5.0 \times 10^{-4}$ -M trisodium citrate dihydrate stock solution in a 40-mL vial. While vigorously stirring, 600  $\mu\text{L}$  of ice-cold 0.1-M  $\text{NaBH}_4$  was added to the vial, which turned the solution light pink in color. Stirring continued for 2 min, at which point the solution became red in color. The solution was aged at room temperature for 3 h and then used directly. The aging period is necessary to allow the remaining sodium borohydride to react with water, but periods of time longer than 10 h cause the particles to aggregate, which is undesirable for their use in further shape-controlled growth. Measured with TEM, the particles averaged about 4 nm in diameter. The solution was fairly monodisperse, with very few particles with shapes other than spheres. A diagram illustrating this procedure is shown in figure 1.

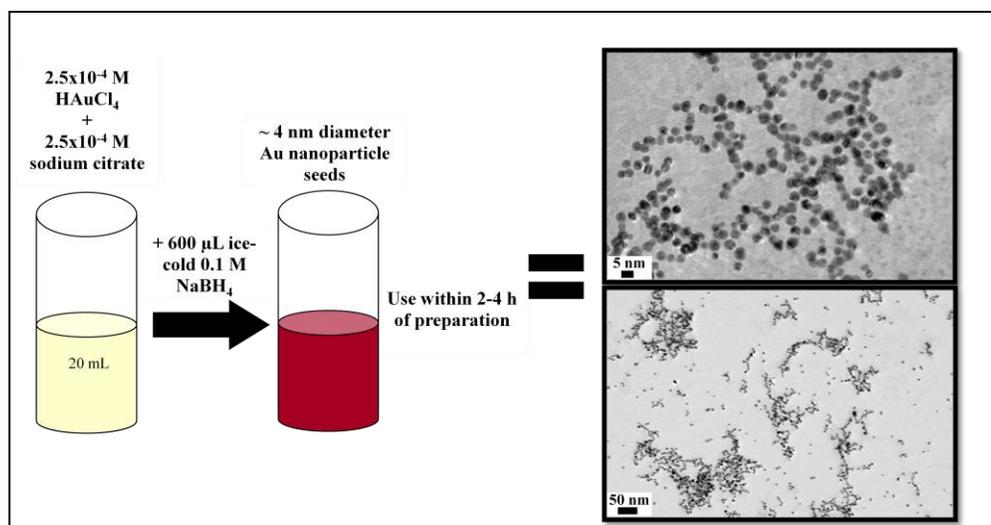


Figure 1. Schematic for Au seed preparation. Average size was confirmed to be about 4 nm through TEM.

## 2.3 Growth of Gold Nanoparticles

A 200-mL stock growth solution containing  $2.5 \times 10^{-4}$ -M  $\text{HAuCl}_4$  and 0.1-M CTAB was prepared in a beaker. This solution was then heated at 50  $^\circ\text{C}$  with occasional stirring to dissolve the CTAB. After about 10 min, the solution turned a clear orange color, and was removed from the hot plate and allowed to cool to room temperature. The color change indicates the formation of the complex ion  $\text{CTA}^+\text{AuCl}_4^-$ . This growth stock solution and the Au seeds were then used to synthesize Au nanorods, nanospheres, and triangular nanoprisms through manipulating reaction parameters, as shown in figure 2.

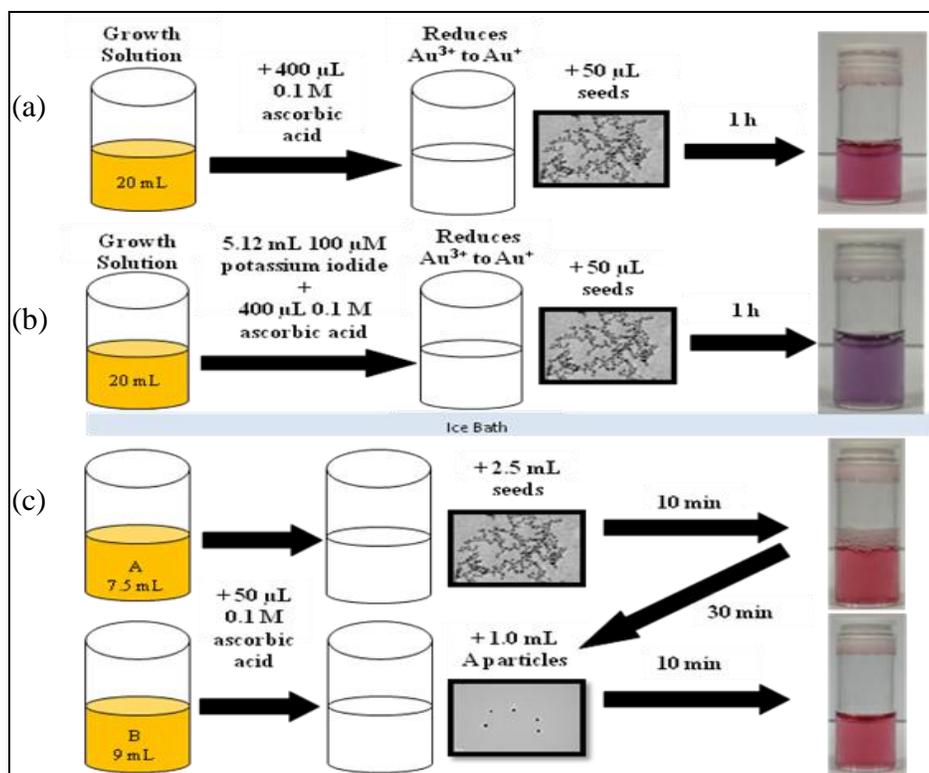


Figure 2. Schematic for Au nanoparticle growth: (a) nanorod, (b) nanoprism, and (c) nanosphere. Only the first two seeding steps are shown. Subsequent seeding can be continued for growth of larger particles.

The synthesis of Au nanorods was achieved by adding 20 mL of the stock growth solution into a 40-mL vial and mixing in 400 µL of a freshly prepared 0.1-M ascorbic acid solution by inverting the vial three times. The addition of ascorbic acid causes the solution to change from yellow in color to clear, indicating the reduction of the Au<sup>3+</sup> ions in solution to Au<sup>+</sup>. Ascorbic acid is too weak to fully reduce the Au salt without the addition of Au seeds, so 50 µL of the seed solution was added to the vial and the tube was inverted 10 times to mix. The entire reaction was performed at 25 to 30 °C. No further mixing was done for the next 5–10 min, as the solution became magenta in color, indicating particle growth. After 1 hr, the solution was red-purple in color.

For the growth of nanoprisms, a similar procedure for the growth of Au nanorods was used; however, KI was mixed with the initial growth solution and the reaction occurred at a lower temperature. In a 40-mL vial, 5.12 mL of a 100-µM solution of KI was mixed with 20 mL of the stock growth solution. The vial was then placed in a water bath maintained at 15 °C during the rest of the reaction, as lower temperature has been found to increase the yield of nanoprisms. To the vial, 400 µL of a freshly prepared 0.1-M ascorbic acid solution was added, and the vial was inverted three times to mix. To begin nucleation, 50 µL of the seed solution was then added and the vial was inverted 10 times to mix. No further mixing was done for the next 10–20 min, as the solution became purple in color, indicating particle growth.

It was noted that the addition of KI slowed the reaction rate, and color change occurred after a longer period of time than observed for nanorod growth. After 2 hr, the solution was purple in color. Some of the surfactant precipitated out of solution, so the solution was heated at 50 °C to redissolve.

A multistep seeding growth procedure was used to produce increasingly larger nanospheres. Three flasks were labeled A, B, and C, respectively. In flask A, 7.5 mL of growth solution was added, while 9 mL of growth solution was added to B and C. The entire reaction was performed at 25 to 30 °C. In each flask, 50 µL of 0.1-M ascorbic acid solution was added while vigorously stirring with a stir bar. In flask A, 2.5 mL of the seed solution was quickly added and vigorously stirred. Stirring continued for the next 10 min, as the solution turned to a deep red color, indicating particle formation. After 30 min, 1.0 mL of the solution A was quickly added to vial B and vigorously stirred for 10 min. Sequentially, after allowing 30 min for particles B to form, 1.0 mL of solution B was quickly added to flask C while vigorously stirring. Stirring was again continued for 10 min. It was noted that the solutions became increasingly purple in color from A to C, as shown in figure 2.

## **2.4 Purification**

Directly after synthesis, all solutions were placed into 10-mL centrifuge tubes for purification. For nanorods and nanoprisms, centrifugation was performed at 1000 rpm for 10 min. For nanospheres, centrifugation was done at 5600 rpm for 30 min. The light pink supernatant, containing smaller spherical particles and other shaped impurities, was removed from each tube with a pipette, and the pellet was redispersed in 10 mL of deionized water. The solutions were then recentrifuged at the previously stated speeds and times. This was repeated until bubbles were no longer visible in the tubes after shaking, indicating that the majority of the surfactant was removed. After the last centrifugation step, the pellet for each sample was redispersed in 100 µL of distilled deionized water.

---

## **3. Results and Discussion**

---

The particles were characterized through UV-Vis spectroscopy, TEM, EDS, and DLS. For TEM and EDS analysis, the purified solutions were sonicated for 15 min and deposited onto copper grids. Purified solutions were used as-made for UV-Vis spectroscopy and DLS.

Figures 3–5 show the TEM images of the shape-controlled nanoparticle solutions and confirm that nanospheres, nanorods, and nanoprisms were successfully synthesized. The spherical seed particle solution shown in figure 3 was very monodisperse, with average particle diameters of about 4 nm and very few impurities of undesired shapes.

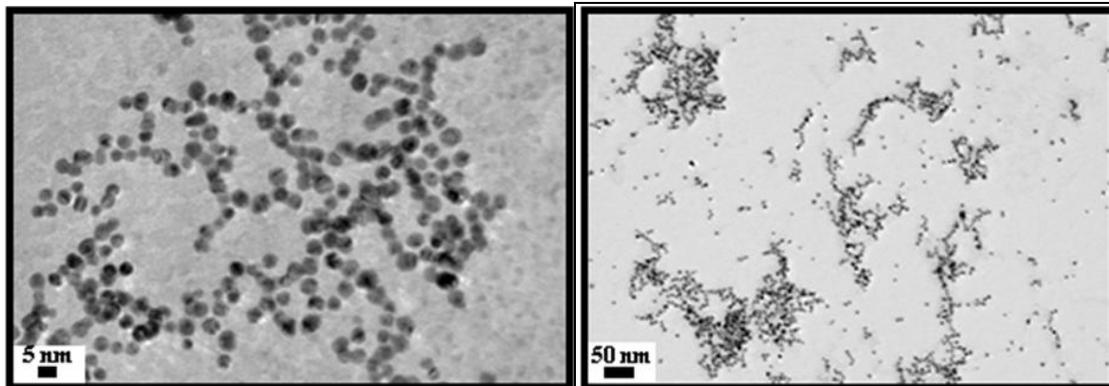


Figure 3. Au seeds (about 4 nm in diameter). Scale bars are 5 nm (left) and 50 nm (right).

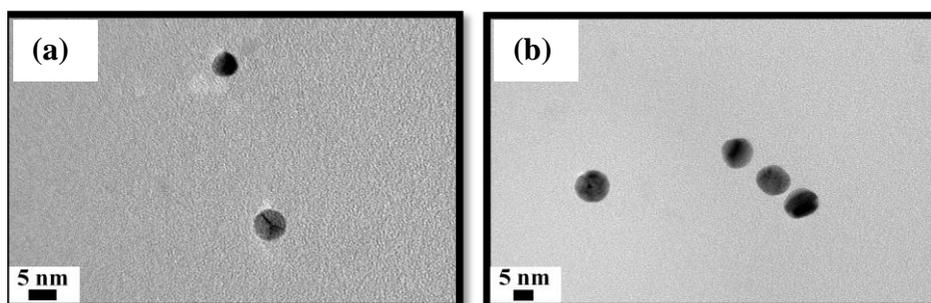


Figure 4. Au nanospheres: (a) solution A (about 5 nm in diameter) and (b) solution B (about 8 nm in diameter). Scale bars are 5 nm.

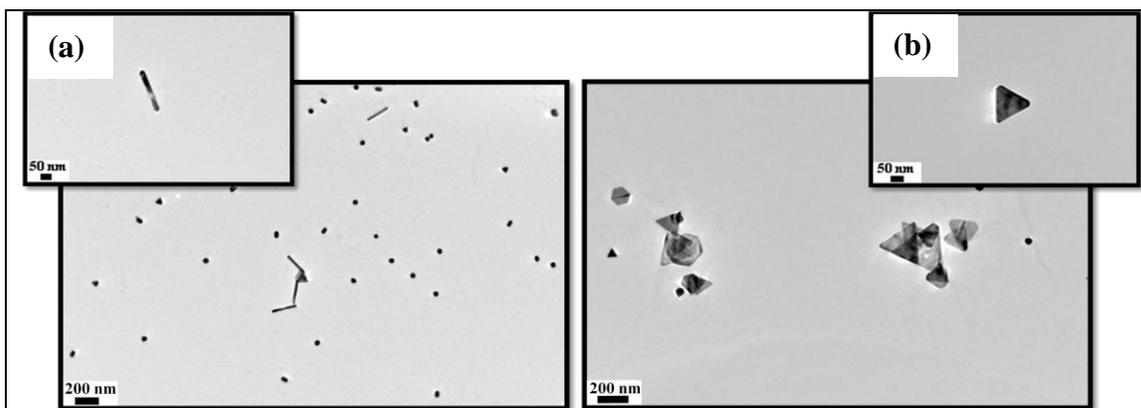


Figure 5. Au (a) nanorods (aspect ratio 10) and (b) nanoprisms (about 150-nm edge length). Scale bars are 50 nm (top) and 200 nm (bottom).

The nanospheres shown in figure 4 increased in size through the multiple-seeding growth method, with particles in solution A averaging about 5 nm in diameter and particles in solution B about 8 nm in diameter, respectively. These nanosphere solutions were also fairly monodisperse, with few impurities of undesired shapes. For nanoprisms, shown in figure 5b, a majority of particles had an edge length of about 150 nm, although a variety of smaller and larger nanoprisms was seen. Note that in figure 5b the crystal lattices of two nanoprisms are overlapping, indicating that these particles are only a few nanometers thick. Lastly, the Au nanorod sample, shown in figure 5a, contained very monodisperse nanorods of about 200 nm length and 20 nm width, giving an aspect ratio of 10. However, the yield for these nanorods was low, and large quantities of spherical-shaped impurities were seen. These impurities could have been further centrifuged out from the nanorods, although this would not improve the number of rods seen through TEM.

The EDS, shown in figure 6, confirms the presence of Au in solution. Peaks indicating copper can be rejected due to the copper grid on which the samples were characterized.

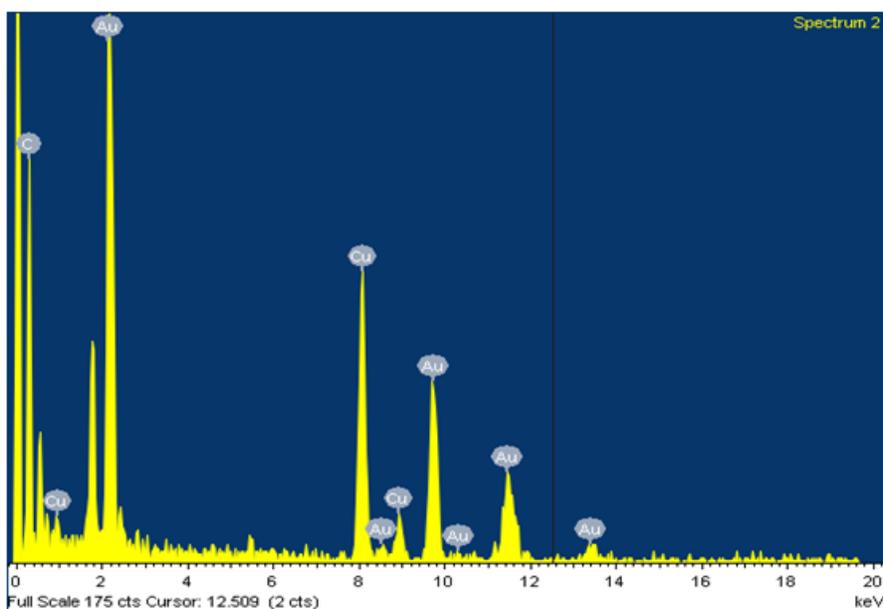


Figure 6. Energy dispersive spectroscopy of Au nanosphere A sample. EDS for all other samples were similar.

Figure 7 shows the visible absorption spectra of the shape-controlled particles. As expected, a small red-shift in the absorbance peaks was noted, as the size of the shape-controlled nanoparticles increased, with seeds being the smallest and nanoprisms the largest. No red-shift was seen from the spheres A to spheres B solution because the size change of these particles was only a few nanometers. The second extended peak seen on the nanoprism spectra can be attributed to the larger nanoprisms in solution.

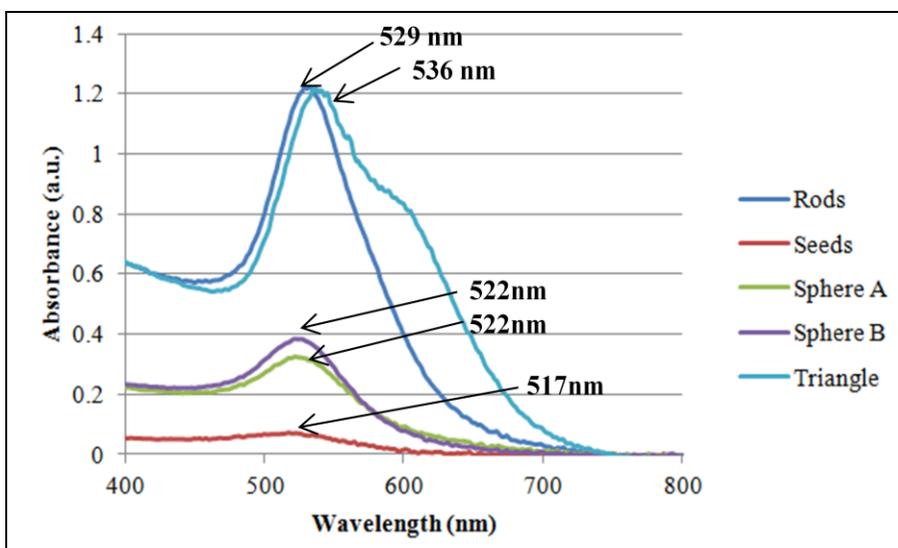


Figure 7. Visible absorption spectra for Au seeds, nanorods, nanoprisms, nanosphere A, and nanosphere B.

Dynamic light scattering was used to determine the zeta potential, or surface charge, of the shape-controlled particles. As can be seen in table 1, all particles exhibited a positive surface charge that increased with increasing particle size. The cationic surfactant, CTAB, used in the growth of these particles as a capping agent, attributes to the positive charge. This confirms that as the particle size increases, more CTAB will bind to the Au crystal faces. If crystal growth occurs through the binding of CTAB bilayers to certain Au crystal faces, as stated in literature (28), these results suggest that the bilayer elongates as nanoparticle size increases. However, these surface charges are much greater than those usually observed for nanoparticles. Residual surfactant that was not completely purified out could have influenced these results, though centrifugation was repeated multiple times to remove excess surfactant.

Table 1. Zeta potential (surface charge) for shape-controlled Au nanoparticles.

<b>Sphere A</b>	<b>Sphere B</b>	<b>Rods</b>	<b>Triangles</b>
57.87 mV	65.6 mV	98.46 mV	123.4 mV

---

## 4. Summary and Conclusions

---

Three different Au nanoparticle shapes—nanorod, nanoprism, and nanosphere—were successfully synthesized through a seed-mediated chemical method. The nanoparticle shape can be completely changed from rod to triangular prism through simple addition of a trace amount of halide ion. It was also possible to control the yields of the nanoparticles by controlling relative concentration of the starting materials. Future work will aim at improving the yield of the shape-controlled nanoparticles, address removal of the positive surface charge of the particles through a ligand exchange, and investigate the effect of the shape and the size on quantum tunneling effect through scanning tunneling microscopy. In addition, nanolithography will be used to position these shape-controlled nanoparticles between two electrical leads to measure tunneling current. The results of the quantum tunneling effect will be reported in a subsequent communication.

---

## 5. References

---

1. Mebrahtu, H. T.; Borzenets, I. V.; Liu, D. E.; Zheng, H.; Bomze, Y. V.; Smirnov, A. I.; Baranger, H. U.; Finkelstein, G. Quantum Phase Transition in a Resonant Level Coupled to Interacting Leads. *Nature* **2012**, *488*, 61–64.
2. Busbee, B. D.; Obare, S. O.; Murphy, C. J. An Improved Synthesis of High-Aspect-Ratio Gold Nanorods. *Advanced Materials* **2003**, *15*, 414–416.
3. Gao, J.; Bender, C. M.; Murphy, C. J. Dependence of the Gold Nanorod Aspect Ratio on the Nature of the Directing Surfactant in Aqueous Solution. *Langmuir* **2003**, *19*, 9065–9070.
4. Gole, A.; Murphy, C. J. Seed-Mediated Synthesis of Gold Nanorods: Role of the Size and Nature of the Seed. *Chemistry of Materials* **2004**, *16*, 3633–3640.
5. Ha, T. H.; Koo, H. J.; Chung, B. H. Shape-Controlled Syntheses of Gold Nanoprisms and Nanorods Influenced by Specific Adsorption of Halide Ions. *The Journal of Physical Chemistry C* **2007**, *111*, 1123–1130.
6. Jana, N. R.; Gearheart, L.; Murphy, C. Seed-Mediated Growth Approach for Shape-Controlled Synthesis Of Spheroidal and Rod-Like Gold Nanoparticles Using a Surfactant Template. *Advanced Materials* **2001**, *13*, 1389–1393.
7. Jana, N. R.; Gearheart, L.; Murphy, C. J. Wet Chemical Synthesis of High Aspect Ratio Cylindrical Gold Nanorods. *The Journal of Physical Chemistry B* **2001**, *105*, 4065–4067.
8. Kim, F.; Song, J. H.; Yang, P. Photochemical Synthesis of Gold Nanorods. *Journal of the American Chemical Society* **2002**, *124*, 14316–14317.
9. Liu, M.; Guyot-Sionnest, P. Mechanism of Silver (I)-Assisted Growth of Gold Nanorods and Bipyramids. *The Journal of Physical Chemistry B* **2005**, *109*, 22192–22200.
10. Nikoobakht, B.; El-Sayed, M. A. Preparation and Growth Mechanism of Gold Nanorods (NRs) Using Seed-Mediated Growth Method. *Chemistry of Materials* **2003**, *15*, 1957–1962.
11. Sau, T. K.; Murphy, C. J. Seeded High Yield Synthesis of Short Au Nanorods in Aqueous Solution. *Langmuir* **2004**, *20*, 6414–6420.
12. Sau, T. K.; Murphy, C. J. Room Temperature, High-Yield Synthesis of Multiple Shapes of Gold Nanoparticles in Aqueous Solution. *Journal of the American Chemical Society* **2004**, *126*, 8648–8649.

13. Millstone, J. E.; Métraux, G. S.; Mirkin, C. A. Controlling the Edge Length of Gold Nanoprisms via a Seed-Mediated Approach. *Advanced Functional Materials* **2006**, *16*, 1209–1214.
14. Millstone, J. E.; Hurst, S. J.; Métraux, G. S.; Cutler, J. I.; Mirkin, C. A. Colloidal Gold and Silver Triangular Nanoprisms. *Small* **2009**, *5*, 646–664.
15. Shankar, S. S.; Rai, A.; Ankamwar, B.; Singh, A.; Ahmad, A.; Sastry, M. Biological Synthesis of Triangular Gold Nanoprisms. *Nat Mater* **2004**, *3*, 482–488.
16. Shankar, S. S.; Bhargava, S.; Sastry, M. Synthesis of Gold Nanospheres and Nanotriangles by the Turkevich Approach. *Journal of Nanoscience and Nanotechnology* **2005**, *5*, 1721–1727.
17. Xie, J.; Lee, J. Y.; Wang, D. I. C. Synthesis of Single-Crystalline Gold Nanoplates in Aqueous Solutions Through Biomineralization by Serum Albumin Protein. *Journal of Physical Chemistry C* **2007**, *111*, 10226–10232.
18. Jana, N. R.; Gearheart, L.; Murphy, C. J. Evidence for Seed-Mediated Nucleation in the Chemical Reduction of Gold Salts to Gold Nanoparticles. *Chemistry of Materials* **2001**, *13*, 2313–2322.
19. Jana, N. R.; Gearheart, L.; Murphy, C. J. Seeding Growth for Size Control of 5–40 nm Diameter Gold Nanoparticles. *Langmuir* **2001**, *17*, 6782–6786.
20. Kim, F.; Connor, S.; Song, H.; Kuykendall, T.; Yang, P. Platonic Gold Nanocrystals. *Angewandte Chemie International Edition* **2004**, *43*, 3673–3677.
21. Skrabalak, S. E.; Chen, J.; Sun, Y.; Lu, X.; Au, L.; Copley, C. M.; Xia, Y. Gold Nanocages: Synthesis, Properties, and Applications. *Accounts of Chemical Research* **2008**, *41*, 1587–1595.
22. Sun, Y.; Xia, Y. Shape-Controlled Synthesis of Gold And Silver Nanoparticles. *Science* **2002**, *298*, 2176–2179.
23. Murphy, C. J.; Sau, T. K.; Gole, A. M.; Orendorff, C. J.; Gau, J.; Gou, L.; Hunyadi, S. E.; Tan, L. Anisotropic Metal Nanoparticles: Synthesis, Assembly, and Optical Applications. *The Journal of Physical Chemistry B* **2005**, *109*, 13857–13870.
24. Tao, A. R.; Habas, S.; Yang, P. Shape Control of Colloidal Metal Nanocrystals. *Small* **2008**, *4*, 310–325.
25. Grzelczak, M.; Pérez-Juste, J.; Mulvaney, P.; Liz-Marzán, L. M. Shape Control in Gold Nanoparticle Synthesis. *Chemical Society Reviews* **2008**, *37*, 1783–1791.

26. Dandekar, V. V.; Cramer, H. E.; Lee, E. N.; Griep, M. H.; and Karna, S. P. Chemical vs. Sonochemical Synthesis and Characterization of Silver, Gold, and Hybrid Nanoparticles; ARL-TR-5764; U.S. Army Research Laboratory: Aberdeen, MD, 2011.
27. Millstone, J. E.; Wei, W.; Jones, M. R.; Yoo, H.; Mirkin, C. A. Iodide Ions Control Seed-Mediated Growth of Anisotropic Gold Nanoparticles. *Nano Letters* **2008**, *8*, 2526–2529.
28. Lofton, C.; Sigmund, W. Mechanisms Controlling Crystal Habits of Gold and Silver Colloids. *Advanced Functional Materials* **2005**, 1197–1208.

---

## List of Symbols, Abbreviations, and Acronyms

---

Au	gold
CTAB	cetyltrimethylammonium bromide
DLS	dynamic light scattering
EDS	energy dispersive spectroscopy
KI	potassium iodide
NaBH <sub>4</sub>	sodium borohydride
TEM	transmission electron microscopy

NO. OF  
COPIES ORGANIZATION

1 DEFENSE TECHNICAL  
(PDF) INFORMATION CTR  
DTIC OCA

1 DIRECTOR  
(PDF) US ARMY RESEARCH LAB  
IMAL HRA

1 DIRECTOR  
(PDF) US ARMY RESEARCH LAB  
RDRL CIO LL

1 GOVT PRINTG OFC  
(PDF) A MALHOTRA

ABERDEEN PROVING GROUND

5 DIR USARL  
(HC) RDRL WM  
S KARNA

6 RDRL WMM A  
(5 HC M GRIEP (HC)  
1 PDF) J SANDS

INTENTIONALLY LEFT BLANK.