Video Article

Gold Nanostar Synthesis with a Silver Seed Mediated Growth Method

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Abstract

The physical, chemical and optical properties of nano-scale colloids depend on their material composition, size and shape [1-5]. There is a great interest in using nano-colloids for photo-thermal ablation, drug delivery and many other biomedical applications [6]. Gold is particularly used because of its low toxicity [7-9]. A property of metal nano-colloids is that they can have a strong surface plasmon resonance [10]. The peak of the surface plasmon resonance mode depends on the structure and composition of the metal nano-colloids. Since the surface plasmon resonance mode is stimulated with light there is a need to have the peak absorbance in the near infrared where biological tissue transmissivity is maximal [11, 12].

We present a method to synthesize star shaped colloidal gold, also known as star shaped nanoparticles [13-15] or nanostars [16]. This method is based on a solution containing silver seeds that are used as the nucleating agent for anisotropic growth of gold colloids [17-22]. Scanning electron microscopy (SEM) analysis of the resulting gold colloid showed that 70 % of the nanostructures were nanostars. The other 30 % of the particles were amorphous clusters of decahedra and rhomboids. The absorbance peak of the nanostars was detected to be in the near infrared (840 nm). Thus, our method produces gold nanostars suitable for biomedical applications, particularly for photo-thermal ablation.

Video Link

The video component of this article can be found at https://www.jove.com/video/3570/

Protocol

1. Silver seed preparation

1. Prepare a stock solution of silver nitrate ($AgNO_3$) by taking an arbitrary mass and mixing it with 10 mL of deionized (DI) water. Calculate molarity of the solution. Keep the solution in a dark place to isolate it from light.
2. Add 14.7 mg of sodium citrate tribasic ($Na_3C_6H_5O_7$) to 10 mL of DI water to make a 5 mM solution. Shake the vial until the powder is dissolved.
3. Add 15.1 mg of sodium borohydride ($NaBH_4$) to another vial with 10 mL of DI water to make a 40 mM solution. Close the vial immediately. Gently shake the solution by hand and place it in a beaker with ice. Place the beaker in the refrigerator and start a timer (t1 = 0). The freshly made solution will be used in 15 min which is enough time to cool it down.
4. From the stock solution of silver nitrate, 1.1), prepare 10 mL at 0.25 mM. Place a stirring magnet in the vial and start stirring.
5. Add 0.25 mL of the sodium citrate tribasic solution 1.2) to 1.4).
6. At t_1 = 15 min remove the sodium borohydride solution, 1.3), from the refrigerator. Using a pipette take 0.4 mL of this solution and add it to 1.5). Note: Add the solution in a single quick stroke. The color will turn to yellow. Stir the solution for 5 min.
7. At t_1 = 20 min stop stirring, remove the magnet from the vial and keep the vial in a dark place. Do not close the vial.
8. Keep the solution in the dark at room temperature for at least 2 hours before using. Preferably use the seeds within one week from preparation.

2. Growth solution preparation

1. Prepare 80 mM of ascorbic acid ($C_6H_8O_6$) by adding 140 mg to 10 mL of DI water.
2. Prepare 10 mL of a concentrated solution of gold chloride ($HAuCl_4$). Calculate the molarity of the solution. Keep the solution isolated from light.
3. Prepare 20 mL of 50 mM of cetyltrimethylammonium bromide (CTAB - $C_{19}H_{42}BrN$) by adding 364 mg to a vial with 20 mL of DI water. Immediately place a stirring magnet into the vial and start stirring on a warm plate at 30°C. After CTAB powder is completely dissolved and the solution becomes transparent turn off the heater of the plate but keep stirring through step 2.7).

4. Add solution 1.1) to solution 2.3) to obtain a final molarity of $4.9x10^{-2}$ mM. Start a timer ($t_2 = 0$).
5. At $t_2 = 1$ min add solution 2.2) to 2.4) to obtain a final molarity of 0.25 mM.
6. At $t_2 = 2$ min add 0.1 mL of 2.1) to 2.5). The solution will turn colorless.
7. At $t_2 = 2$ min 20 sec add 0.05 mL of 1.8) (silver seeds) to 2.6). Stir the suspension for 15 min. The suspension will initially turn blue and then brown.
8. At $t_2 = 17$ min stop stirring, remove the magnet and keep the suspension at room temperature for 24 hours.

3. Separating gold nanostars from CTAB for imaging, characterization or experimentation

Note: CTAB may crystallize at room temperature. To dissolve the crystals heat up the gold colloid to 30°C or immerse the vial in hot tap-water until the crystals dissolve.

1. Sonicate the suspension for 2 min.
2. Centrifuge the suspension for 5 min at 730 rcf. Nanostars will accumulate on the wall of the tube.
3. Remove as much of the suspension with a pipette taking care not to remove the nanostars.
4. Add DI water to the tube and sonicate for 2 min.
5. Centrifuge the suspension for 3 min at 460 rcf. The suspension contains less CTAB, therefore lower centrifugal force is needed to separate the nanostars.
6. Repeat steps 3.3) and 3.4).
7. Add DI water to the suspension and centrifuge for 3 min at 380 rcf.
8. Repeat steps 3.3) and 3.4). The nanostars are ready for imaging, spectroscopy, or experimentation.

4. Representative results:

Figure 1 shows transmission electron microscope (TEM) images of the silver seeds imaged using a JEOL 2010-F TEM. The seeds have a spherical shape and an average size of 15 nm. Gold nanostars are imaged using a Hitachi S-5500 in scanning electron microscope (SEM) mode. Figure 2 shows increasing magnifications of the nanostars synthesized with our method. Star shaped particles are approximately 70 % of all the particles in the colloid. Non-formed stars appear like amorphous clusters of decahedra and rhomboids (not shown). Figure 3 shows several single gold nanostars. The size of the nanostars ranges from 200 nm to 300 nm and the number of tips vary from 7 to 10. If the gold nanoparticles synthesized by this method are left in CTAB they retain their shape for at least 1 month after synthesis.

We measured the absorption spectra of the silver seeds and nanostars using an Olis Cary-14 spectrophotometer. The peak absorption of the seeds was at 400 nm, while the peak absorption of the nanostars was between 800 nm and 850 nm (Figure 4).

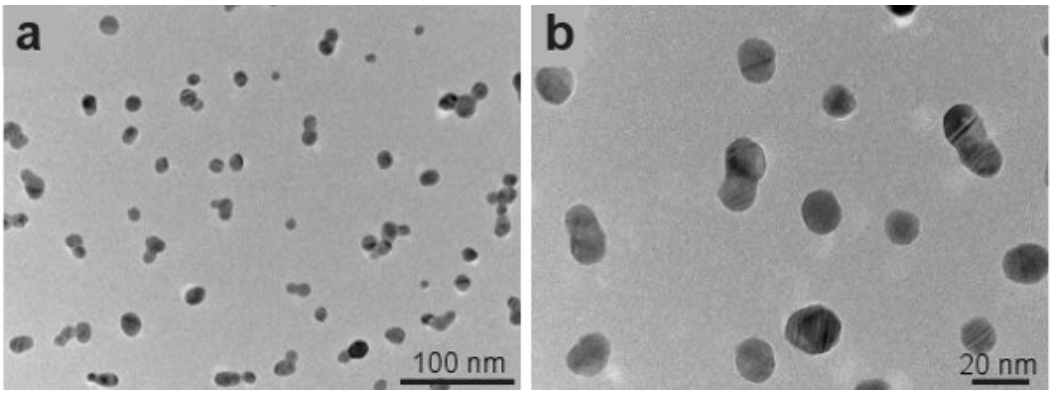

Figure 1. Transmission electron microscope images of silver seeds.

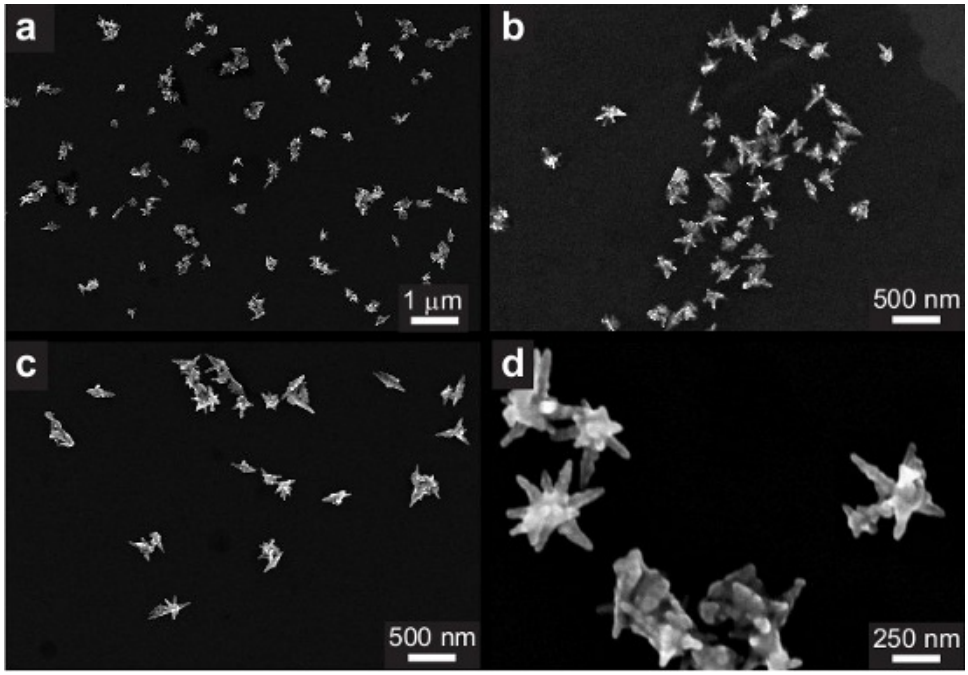

Figure 2. Scanning electron microscope images of gold nanostars.

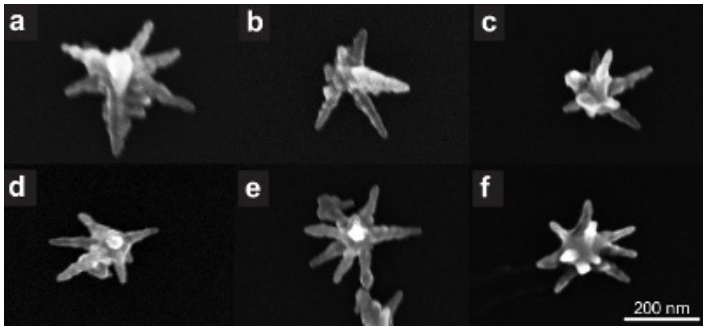

Figure 3. Scanning electron microscope images of single gold nanostars.

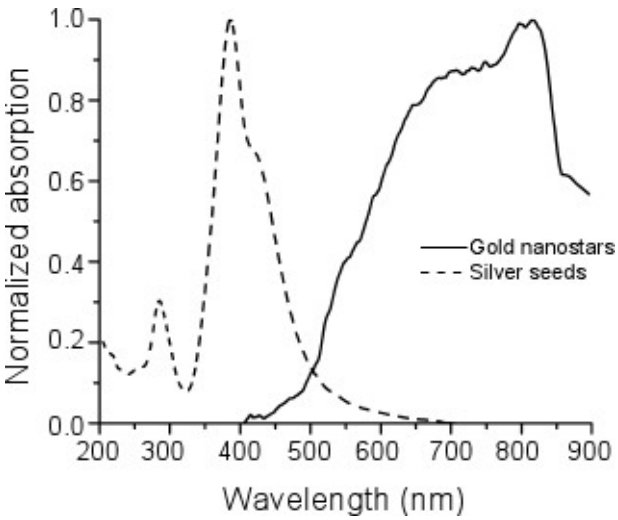

Figure 4. Normalized absorption spectra of silver seeds (dashed line) and gold nanostars (solid line).

Discussion

In this work we have presented a method to synthesize gold nanostars using silver seeds. We found that silver seeds resulted in a yield of 70 % production of nanostars. The nanostars have a near infrared absorption peak, corresponding to their surface plasmon resonance mode, centered

between 800 nm and 850 nm [7, 23]. These properties properties allow our gold nanostars to be of use for biomedical applications [24-26], such as photo-thermal ablation.

A major difference between the method explained here and other methods is the use of silver seeds instead of gold. Using silver seeds results in gold nanostars with longer tips and smaller cores. A direct comparison of yield productions between different production protocols is difficult as there are many different methods of nano-colloid synthesis. However, compared to methods that use similar seed-mediated synthesis [27] which reach a yield of 40 % - 50 % [28], our method produces the desired shapes of gold colloids with a higher yield of 70 %. Furthermore, our suspension is stable for more than one month. Although our nanostars are larger in size [16], their surface plasmon resonance mode is shifted to the near infrared which makes them more suitable for biological applications.

There are a few important points that have to be taken into consideration during nanostar synthesis. In the preparation of the seed solution, sodium citrate is used as a capping agent and sodium borohydride is used as a reducing agent. The sodium borohydride is unstable both in concentrated and diluted aqueous solutions, thus it is important to prepare it fresh every time and use it within one hour. In addition, the reaction is temperature dependent therefore the solution must be cold (step 1.6). Once the seed solution is ready it is important to allow hydrogen to escape, thus we emphasize that the container should not be closed (step 1.7). The growth solution preparation process is also time sensitive. For example, if compounds from steps 2.5) to 2.7) are mixed at different rates from the rates described in the method, the resulting particles could be spheres instead of stars.

We would like to clarify the purpose of some important steps. In the growth solution gold is reduced by adding ascorbic acid which is followed by its deposition on the silver seeds. Silver nitrate is used to provide silver ions which play a catalyzing role in the gold nanostar growth process. CTAB is believed to be responsible for anisotropic growth of gold on the surface of the silver seeds via an oriented attachment mechanism [29] where the gold crystals attach to the silver seeds bound by adsorbate molecules. The anisotropic growth process is slow which is assumed to be caused by a thermodynamic disequilibrium condition known as the kinetically controlled regime [30].

A vast majority of nanotechnology applications in biomedical research are focused on drug delivery, photo-thermal therapy, and imaging [31, 32]. The successful implementation of these applications depends on understanding the chemical, physical, and optical properties of nano-scale colloids and also on developing reproducible procedures to synthesize them. There is a need to control not only the size but also the shape of nanostructures because there is an increasing evidence that the particular shape of a nano-colloid determines its interaction with biological systems [33]. Our work advances the use of nanotechnology in biomedical applications by providing a method to produce high yields of nanostars with a surface plasmon resonance in the near infrared.

Disclosures

No conflicts of interest declared.

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