

Wet chemical synthesis of gold nanoparticles using silver seeds: a shape control from nanorods to hollow spherical nanoparticles

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Abstract

A seed-mediated method was employed here for CTAB-assisted gold nanoparticle growth. 3–4 nm silver aqueous colloid was stabilized by sodium citrate and used as seed solution to initial gold particle growth. The concentration of seed solution was calculated based on its relationship with silver atom concentration and seed particle statistical mean volume. It was found that there is a maximum seed concentration of 8.57×10^{-12} M ($\sim 25 \mu\text{l}$ 0.343×10^{-8} M seed solution added) in 10 ml 2.5×10^{-4} M HAuCl₄ growth solution for growth of rodlike particles. Below this seed amount, the aspect ratio of nanorods could be controlled by varying the silver seed amount, i.e. nanorods with aspect ratio ~ 18.9 were obtained when the seed concentration in the growth solution was 0.343×10^{-12} M by adding 1 μl 0.343×10^{-8} M silver seed solution and nanorods with aspect ratio ~ 9.69 were obtained when the seed concentration in the growth solution was 1.715×10^{-12} M by adding 5 μl 0.343×10^{-8} M silver seed solution. As the seed concentration in the growth solution was more than 8.58×10^{-12} M (25 μl 0.343×10^{-8} M silver seed solution was added), there were no rodlike particles formed but spherical ones instead. These spheres were further studied by TEM and found to all be hollow structures. It was suggested that there were probably two different nucleation processes for growth of nanorods and spheres. For hollow spheres, the reaction between Ag seeds and Au ions formed hollow structures based on the Ag particle template effect. Then further growth of Au on these hollow structures produced hollow gold nanospheres. For nanorods, due to the very low concentration of silver seed (molar ratio of Ag seed: Au = 3.426×10^{-8}), the growth process here probably was started by silver-induced Au nucleation, in which reduction of gold ions by silver resulted in small gold clusters. These gold clusters further grew up into nanoparticles and nanorods in the presence of CTAB.

 Supplementary data are available from stacks.iop.org/Nano/18/115608

1. Introduction

Controlled synthesis of nanoparticles (NPs) in terms of size and shape is a technological scaffold for their further

practical and fundamental studies because the properties of nanoparticles are greatly size- and shape-dependent. Important progress has been made over the past few years in the preparation of monodispersed metal and semiconductor nanocrystals with various sizes and shapes [1, 2]. For example,

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Table 1. The shape details of as-prepared gold nanoparticles and corresponding silver seeding amounts.

Structure	Solid NRs					Hollow NPs	
Silver seeds (μl)	1	2.5	5	10	25	50	100
Seed concentration (10^{-12} M)	0.343	0.857	1.715	3.43	8.57	17.15	34.3
Diameter (nm)	~ 20	~ 15	~ 13	~ 14	~ 13	~ 20	~ 20
Length (nm)	~ 376	~ 226	~ 126	~ 86	~ 46		
Aspect ratio	~ 18.9	~ 15.1	~ 9.69	~ 6.14	~ 3.54		

some metal nanoparticles with controllable shapes, such as rods [3], wires [4], prisms [5], cubes [6], discs [7] and polyhedrons [8], etc, have been synthesized by using a variety of different methodologies. Among these methodologies, a seed-mediated growth procedure developed by Murphy *et al* [3] has attracted a great deal of attention since it provides an easy way to obtain well-controlled gold nanorods (NRs) as compared to electrochemical [9] and photochemical [10] methods. The method involves surfactant directed growth of nanorods from spherical seeds [11–13] and allows people to directly investigate the growth process with the UV–visible spectrum of a gold nanorod solution right after seed addition [14]. Although the exact growth mechanism of this method remains unclear, it has been demonstrated as a versatile method for synthesis of multiple shaped gold particles [15], silver rods and wires [16], as well as Cu_2O cubes [17] at nanoscale. To date, varying the Au seeding amount is one of the successful ways to control the aspect ratio of gold nanorods [3, 18]. Generally, with the increase of the seeding amount, the aspect ratio decreases and finally reaches ~ 1 (spherical particles). Gole *et al* recently carried out a systemic study on the role of the size and nature of the seed [19]. It reveals that both size and charge play roles in determining the nanorod aspect ratio. Increasing the seed size results in lowering of the gold nanorod aspect ratios for a constant concentration of reagents. For positively charged seeds variation in the aspect ratio is not as pronounced as that for negatively charged seeds.

The seed-mediated method for synthesis of gold nanorods has been well studied in recent years. However, to the best of our knowledge, most studies and reports employ a gold seed colloid to initiate nanorod growth. A question for experimental chemists is whether other metal seed colloids can be used to initiate nanocrystal growth. Here, we report a shape evolution from nanorods to hollow spherical nanoparticles. The gold nanorods were synthesized via the seed-mediated growth method, in which as an alternative to gold seeds, trace silver seeds are used to initiate crystal growth. The advantage in using Ag seeds instead of Au seeds is that tuning the Ag seed amount leads to a shape control of the product nanoparticles. Using Au seeds only controls the aspect ratio of nanorods, but not the shape evolution to hollow nanoparticles.

2. Experimental section

Table 1 shows the structural details of gold nanoparticles and corresponding silver seeding amounts. Silver seeds are prepared by reduction of NaBH_4 in the presence of trisodium citrate [16]. The growth of gold nanoparticles involves the addition of silver seed solutions into the aqueous growth solutions containing cetyltrimethylammonium bromide

(CTAB), HAuCl_4 and ascorbic acid [3]. A one-step procedure is employed here for growth of both nanorods and hollow spherical particles. Typically, a 20 ml aqueous solution containing 2.5×10^{-4} M AgNO_3 and 2.5×10^{-4} M trisodium citrate was prepared in a clean flask. Then, 0.5 ml freshly prepared 0.1 M NaBH_4 was added to the solution under stirring. The solution colour turned yellow immediately due to the formation of a silver colloid. The as-prepared silver seeds in 3–4 nm were used within 3–8 h of preparation. For gold nanoparticle growth, the one-step procedure is employed here. Eight conical flasks, each containing 10 ml growth solution consisting of 2.5×10^{-4} M HAuCl_4 and 0.1 M cetyltrimethylammonium bromide (CTAB), were mixed with 0.06 ml 0.1 M freshly prepared ascorbic acid aqueous solution. The colour of the reaction solution changed from brown-yellow to colourless when ascorbic acid was added to the growth solution. This is because ascorbic acid as a mild reducing agent reduced Au^{3+} to Au^+ [20]. Next, a series of silver seed solutions in different volumes, 1, 2.5, 5, 10, 25, 50, 100 μl , were added to the eight growth solutions, respectively. That the colour of the solutions changed slowly to light red at the beginning indicates Au nanoparticles began to grow. The further growth of Au nanoparticles led to a wine red colour. The less seeds added, the more slowly colour changed. After 2–3 h, all the solutions were a dark wine red and no obvious colour change observed later on indicates that the growth of Au nanoparticles was nearly finished after 3 h. The solutions were centrifuged several times at 6000 rpm for 10 min to remove excess surfactant.

The samples were dropped onto a silicon wafer and investigated by a field emission type scanning electron microscope (XL30 S-FEG, FEI Corp.) at 10 kV. TEM and HRTEM were performed on a JEOL-200CX operating at 120 kV and a Philips CM200FEG operating at 200 kV, respectively. UV–visible absorption spectra were recorded by a Cary IE UV–visible spectrometer.

3. Results and discussion

Figure 1 shows the TEM image of as-prepared silver seeds. The histogram of size distribution (see inset) indicates the silver seeds' average diameter is 3.5 ± 1.5 nm and its statistical mean diameter is 3.33 nm. The mole concentration of as-prepared Ag seeds in seed solution (M_s) can be assessed based on its relationship with silver atom concentration and seed particle statistical mean volume as follows:

$$M_s = \frac{M_{\text{Ag}} V_{\text{fcc}}}{\frac{4}{3} \pi R^3 n_{\text{fcc}}}$$

where M_{Ag} is mole concentration of Ag atoms of seed solution (2.5×10^{-4} M); V_{fcc} is silver unit cell volume (fcc, $a = b =$

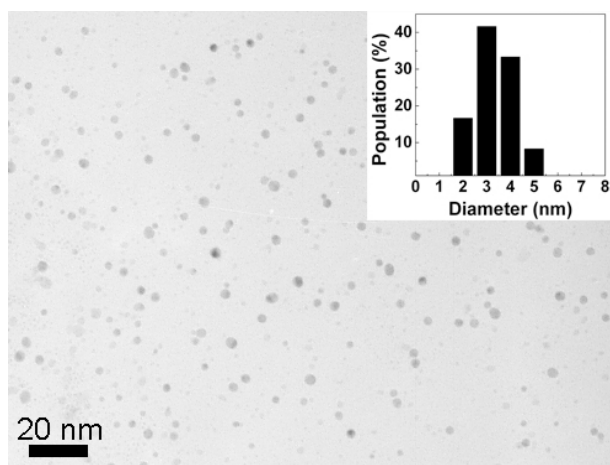


Figure 1. The TEM image of as-prepared silver seeds. The inset is a histogram of size distribution.

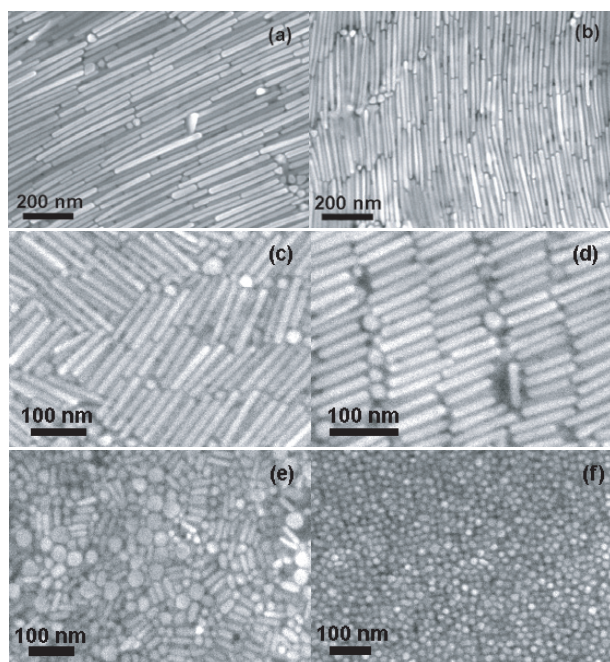


Figure 2. SEM images of gold particles obtained at different silver seed concentrations: (a) 0.343×10^{-12} M; (b) 0.857×10^{-12} M; (c) 1.715×10^{-12} M; (d) 3.43×10^{-12} M; (e) 8.57×10^{-12} M and (f) 1.715×10^{-11} M.

$c = 0.4078$ nm, $V_{\text{fcc}} = 0.0678$ nm³); R is the statistical mean radius of as-prepared silver seeds (1.665 nm, obtained from TEM study); n_{fcc} is the atomic number of each unit cell (4 for fcc). The calculated M_s is $\sim 0.343 \times 10^{-8}$ M. Therefore, on adding 1, 2.5, 5, 10, 25, 50 and 100 μ l seed solution into 10 ml HAuCl₄ growth solution, the corresponding molar concentrations of silver seed in growth solution are 0.343×10^{-12} M, 0.857×10^{-12} M, 1.715×10^{-12} M, 3.43×10^{-12} M, 8.57×10^{-12} M, 1.715×10^{-11} M and 3.43×10^{-11} M.

Figure 2 shows the SEM images of as-prepared gold particles. The assemblies of nanorods were fabricated by a shape self-selective effect induced by capillary force [21]. The

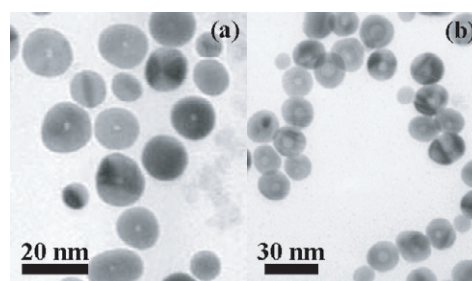
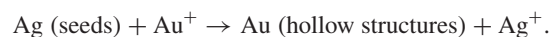


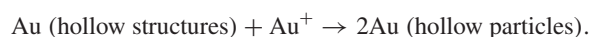
Figure 3. TEM images of hollow spherical particles obtained above CSA: (a) 1.715×10^{-11} M and (b) 3.43×10^{-11} M.

gold nanorods shown in 1(a)–(d) are obtained by adding small amounts of silver seeds (concentration below 8.57×10^{-12} M). The aspect ratios of gold nanorods can be controlled by varying the seeding amounts. On adding 1, 2.5, 5 and 10 μ l silver seed solutions into the growth solution, the seed concentrations in growth solution are 0.343×10^{-12} M, 0.857×10^{-12} M, 1.715×10^{-12} M and 3.43×10^{-12} M, respectively. The aspect ratio of gold nanorods is controlled at ~ 18.9 , ~ 15.1 , ~ 9.69 and ~ 6.14 , respectively. This is similar to the typical method for controlling the aspect ratio using different Au seeding amounts [3, 19]. It is noted that the concentration of silver seeds for growth of gold nanorods could not be more than 8.57×10^{-12} M; otherwise most of the final products are spherical. A shape transformation of products from rodlike to spherical is observed as the seed concentration is 8.57×10^{-12} M (figure 2(e)). We called this concentration (8.57×10^{-12} M) the critical seeding amount (CSA), below which nanorods formed and above which spherical particles formed. Figure 2(f) shows a SEM image of the spherical particles obtained as the seed concentration reaches 1.715×10^{-11} M.

The spherical particles obtained above CSA were characterized by TEM. Figure 3 shows the TEM images of the nanoparticles obtained as the seed concentrations are 1.715×10^{-11} M and 3.43×10^{-11} M, respectively. These nanoparticles show hollow structures. In figure 3, nanoparticles prepared with high concentrations of silver seeds show a clear contrast changing from the particle edge to the centre area, which is believed to arise from the evident hollow nature [22]. These Au hollow nanospheres are uniform and have dimensions of ~ 20 nm at different amount of Ag seeds. It is known that silver particles can be used as sacrificial templates to generate gold nanoparticles with a well-defined shape and hollow structure [2]. Here the silver seeds undoubtedly play the role of sacrificial template⁴.



Further reduction of Au^+ by ascorbic acid deposit Au on Au (hollow structures) to form hollow particles,



In figure 3, the diameter of Au hollow spherical nanoparticles prepared at different Ag seeds is about 20 nm,

⁴ Before adding silver seeds, Au^{3+} is initially reduced to Au^+ with the addition of ascorbic acid (see [20]).

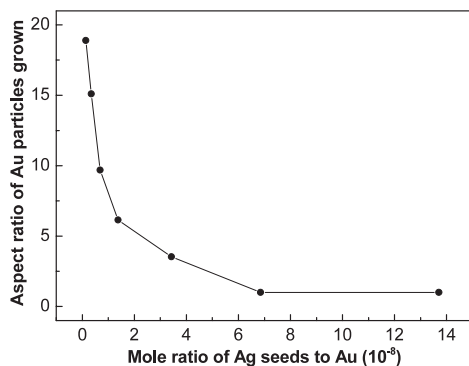


Figure 4. The dependence of the aspect ratio of Au particles on the mole ratio of Ag seeds to Au in the growth solution.

but their core sizes are different. This suggests that changing the amount of silver seeds may control the core size of gold hollow spheres, for example, the silver seed concentrations of 1.715×10^{-11} M and 3.43×10^{-11} M result in a mean pore size of gold hollow spheres of ~ 2 nm and ~ 7 nm, respectively. The reason for this is still unclear and further detailed study on this is underway. Based on the role of sacrificial template, the pores may be also found on the nanorods as a trace of silver seeds, which is probably helpful for revealing the growth mechanism of nanorods. However, the TEM study of the nanorods obtained below CSA did not give any evidence supporting that hypothesis. It shows that there are no pores found in nanorods as well as the by-product of spherical particles. Further HRTEM studies also find that there is no hollow structure in nanorods. This fact gives an indication that the silver seeds at a very low concentration probably serve as an inducement of nucleation of Au crystals, which further grow to Au rodlike particles under the direction of surfactants. When the added amount of silver seeds exceeds CSA, this nucleation effect does not prevail and the reaction between Au^+ and Ag seeds is significant due to the increase of Ag. The typical HRTEM image of the nanorod was shown in figure S1 (supplementary data file available at stacks.iop.org/Nano/18/115608). The image shows well-defined continuous {111} fringes ($d = 0.236$ nm) running parallel to the direction of elongation on both sides of the rod. It confirmed the fact that the growth of the rod is along the [100] direction with (111) lattice planes parallel to the twin boundaries [20]. The HRTEM image of the hollow spherical particles obtained above CSA is shown in figure S2 (available at stacks.iop.org/Nano/18/115608). The inset is the corresponding Fourier transform pattern. They both show the hollow spherical particle is single crystalline. Figure S3 (available at stacks.iop.org/Nano/18/115608) shows the representative energy-dispersive x-ray spectroscopy (EDX) spectra of the nanorods (obtained at 8.57×10^{-12} M silver seeds) and the hollow spherical particles (obtained at 3.43×10^{-11} M silver seeds). The copper is from the TEM grid. The remarkable Au peaks indicate that the as-prepared nanoparticles are gold ones. The absence of an Ag characteristic peak implies that there is no silver or the silver content is less than $\sim 0.1\%$ (EDX detection limit). This is quite different from the core/shell bimetallic (Au/Ag) nanoparticles obtained from bigger Ag nanoparticles. They showed remarkable silver signals in EDX spectra [22, 23].

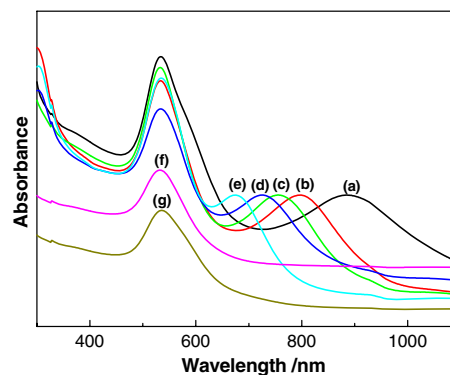


Figure 5. The UV-visible spectra of as-prepared gold nanoparticles obtained at different silver seeding amounts: (a) 0.343×10^{-12} M; (b) 0.857×10^{-12} M; (c) 1.715×10^{-12} M; (d) 3.43×10^{-12} M; (e) 8.57×10^{-12} M; (f) 1.715×10^{-11} M; (g) 3.43×10^{-11} M.

(This figure is in colour only in the electronic version)

For a more detailed relationship between the silver seeding amount and the Au particles' shape, the mole ratio of Ag seeds to Au in growth solution for each sample is studied. The mole ratio of Ag seeds to Au (x_{mr}) is calculated as follows:

$$x_{\text{mr}} = \frac{M_{\text{S}} V_{\text{S}}}{M_{\text{Au}} V_{\text{G}}}$$

where M_{S} is the mole concentration of as-prepared Ag seeds; V_{S} is the volume of silver seed solution added; M_{Au} is the mole concentration of Au in growth solution (2.5×10^{-4} M); V_{G} is the volume of growth solution (10 ml). The calculated M_{S} is $\sim 0.343 \times 10^{-8}$ M, therefore the mole ratios (10^{-8}) of Ag seeds to Au in each sample are 0.137, 0.343, 0.685, 1.371, 3.426, 6.853 and 13.705 corresponding to the volume of silver seed solution added: 1, 2.5, 5, 10, 25, 50 and 100 μl . Figure 4 shows the dependence of the aspect ratio of Au particles on the mole ratio of Ag seeds to Au in the growth solution. From the curve, one can estimate the mole number of silver seeds for the growth of Au nanoparticles with desired shape and structure.

Figure 5 shows the UV-vis spectra of different structures of gold nanoparticles obtained by adding different amounts of silver seeds. For rod samples, their longitudinal absorption bands are normalized to 1 for peak position comparison and their higher transverse absorption bands are due to the presence of spherical by-products. It is well known that the optical absorption spectra of gold nanorods are different from spheres. They usually show two absorption bands, one around 520–530 nm due to the electron oscillation at the transverse direction of the nanorods and the other at the high wavelength region due to the electron oscillation at the longitudinal direction [24]. It was found that the longitudinal plasma band greatly depends on the aspect ratio of nanorods. With the increase of aspect ratio, the longitudinal plasma band red-shifts to a higher wavelength region [3, 12, 18, 24]. This size dependence is also found in our experiments. The longitudinal plasma bands of as-prepared nanorods red-shift from ~ 674 to ~ 888 nm as their aspect ratios increase from ~ 3.54 to ~ 18.9 . It can be noticed that there are some tails presented in the spectra below 400 nm. This should be ascribed to the interband transitions in Au [25]. The

hollow spherical particles obtained above the CSA exhibit their absorption band at ~ 531 nm and ~ 534 nm corresponding to 1.715×10^{-11} M and 3.43×10^{-11} M seeding amounts, respectively. It is generally believed that the hollow structures exhibit very different optical properties compared to the solid counterparts, which are caused by their relatively lower density and higher surface areas [22]. But the optical properties of hollow particles synthesized here seem very similar to that of solid ones. (The spectrum of solid Au nanoparticles at similar diameter ~ 20 nm is shown in figure S4 (available at stacks.iop.org/Nano/18/115608).) This is probably due to the small size of pores, which has little influence on the density and surface area of whole particles. The attempt to get hollow particles with bigger pores via increasing the seeding amount is not successful. When > 150 μ l silver seed solution was used (seed concentration 5.145×10^{-11} M), the particles obtained were no longer spherical, but amorphous (figure S5; available at stacks.iop.org/Nano/18/115608). Most of them present a cone-like shape. This is a typical shape often found when using Au seeds to grow Au particles in the presence of proper Ag^+ ions [15]. It indicates a concentration increase of Ag^+ resulted from Au oxidation and gives evidence for the presence of Ag^+ ions.

4. Conclusion

In summary, we have synthesized gold nanorods and hollow spherical particles via a seed-mediated method involving silver seeds and a one-step growth procedure. By changing only one experimental parameter, a novel structure and shape control from nanorods to hollow spherical particles is successfully achieved in one synthesis methodology.

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