

Size controlled synthesis of gold nanoparticles using photochemically prepared seed particles

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Abstract

Gold nanoparticles having prechosen size ranging from 5 to 110 nm have been prepared in two steps. Firstly, small spherical particles (seed) of average diameters between 5 and 20 nm were prepared by varying the ratio of gold ion concentration to stabilizer/reductant, TX-100 concentration and using UV irradiation. Secondly, 20–110 nm particles were formed by a non-iterative seed-mediated growth where small particles produced by the above irradiation technique were exploited as seeds and fresh Au(III) ions were reduced onto the surface on the seed particles by ascorbic acid. The kinetics of particle formation has also been reported. These methods were fast and showed improved monodispersity sphericity and excellent reproducibility.

Introduction

Nanoparticles have potentially useful size- and shape-dependent properties (Ahmadi et al., 1996; Belloni, 1996; Henglein, 1993; Pal et al., 1997; Jana et al., 1999; Schmid, 1994; Whitten et al., 1999). The synthesis of nanoparticles with desired size/shape has, therefore, enormous importance, especially in the emerging field of nanotechnology (Collier et al., 1998; Rao, 1999; Schmid et al., 1999). However, it is a fact that the reproducible preparation of stable particles with controlled/prechosen size is a very difficult task using the popular colloid-chemical approach (Schmid, 1994). This, in fact, demands development of a new general method as well as improvement over the existing ones. Among the known colloidal nanoparticle systems, gold is one of the most widely studied ones. And a few systematic approaches already exist to obtain particles of prechosen size via its controlled formation (Brown et al., 2000, 1998; Frens, 1973; Goia & Matijevec, 1998, 1999; Henglein, 1999; Henglein & Meisel, 1998;

Leff et al., 1995; Schmid, 1992; Schmid et al., 1996). For example, Frens (1973) proposed a method where reducing/stabilizing agent, citrate to gold ratio was varied. This results in particles with a broad size range (diameters between 10 and 150 nm). But for more than 30 nm diameter particles the monodispersity was observed to be poor. Leff et al. (1995) synthesized gold particles with diameters ranging from 1.5 to 20 nm by varying the Au(III) ion to stabilizer thiol molar ratio. This approach requires long time, 12 h or so to allow the reaction products to attain equilibrium. Another methodology, known since 1906, is 'seed'- or 'germ'-mediated growth which promises to obtain particles of desired size (Schmid et al., 1996). Here, appropriate amounts of precursor ions are reduced over the preformed 'seed' or 'germ', i.e., small particles by suitable reducing agents. The reducing agent used in the second stage of 'seed'-mediated growth is generally a weaker one, viz., H₂NOH, ascorbate ion, etc. (Brown et al., 2000; Goia et al., 1998). They should reduce only the precursor ions which are adsorbed onto the

'seed' surface without creating any new nucleation center.

The final size of the particles would depend on the size of the 'seed' and the amount of the precursor ions to be reduced on them (Schmid, 1992). Therefore, in principle, the smaller is the starting seed, the lower will be the desired size limit of the particles. It allows preparing particles over a broad size range. Smaller particles are generally produced by using stronger reducing agents, viz., NaBH_4 , phosphorus, tetrakis (hydroxymethyl) phosphonium chloride, etc., or radiolytic method (Belloni, 1996; Grunwaldt et al., 1999; Henglein, 1999; Henglein et al., 1998; Sarathy et al., 1997; Schneider et al., 1994; Slot & Geuze, 1981). Furthermore, nature of the particle stabilizer, solvent, reaction condition, viz., pH, temperature, etc., plays crucial role in determining the final size of the particles.

Recently, a radiolytic and a chemical size control with improved monodispersity via seed-mediated growth of colloidal gold nanoparticles were reported by Henglein and Meisel (Henglein, 1999; Henglein & Meisel, 1998) and Natan's group (Brown & Natan, 1998; Brown et al., 2000), respectively. They have followed iterative growth method, i.e., particles were grown in the immediately previous step were used as seeds in the next growth step. In the present study, we examine the applicability of a combination of photochemical approach with a non-iterative growth method to develop a simple and fast technique of size control. Here, particles of various size ranging from average diameter 5 to 20 nm could be obtained within few minutes by UV irradiation at room temperature (28°C) in presence of air. Furthermore, larger size particles (diameter 25–110 nm) were produced directly from the original seed particles by varying the ratio of original [seed] to [Au(III)] and using ascorbic acid as reductant. It should be noted that ascorbate ion is frequently used as reducing agent for reduction of Au(III) or Ag(I) ions. Goia and Matijevic (Goia et al., 1999) recently used isoascorbic acid at various pH conditions to synthesize relatively large spherical gold particles (ranging in modal diameter from 80 nm to 5 μm) directly from Au(III) ions.

Experimental section

Reagents

All the reagents were used of AR grade. Double distilled water was used for the preparation of all solutions.

A stock solution of gold (III) chloride was prepared by dissolving 1 g chloroauric acid (Johnson Matthey, Royston, Hertfordshire, UK) in 500 ml distilled water and it was standardized by quinol method (Vogel, 1973). TX-100, i.e., Triton X-100 (Aldrich) chemically named as poly(oxyethylene)iso-octylphenyl ether solution was prepared by dissolving appropriate volume in distilled water to obtain the required concentration. Freshly prepared aqueous solution of ascorbic acid (Aldrich) solution was used regularly.

Procedure

UV radiation was carried out with an ordinary germicidal lamp (Philips, Holland G15T8Uvc, 15 W). Appropriate amounts of chloroauric acid and TX-100 solutions were taken in 4×1 cm stoppered quartz cuvettes for photo-irradiation. The cuvettes were placed at a distance of 3 cm from the light source and were irradiated for 25 min. The photoactivation produced pink colored Au(0) particles. These particles were used as 'seeds' for further growth. Then various amounts of 'seed' particles and the Au(III) ions were taken in such a way that the total amount of gold remains constant whereas gradually [Au(III)]/[seed] ratio increases. The ratio was varied from 2 to 100. In the next step, ascorbic acid was added slowly to the unstirred mixture of 'seed' and Au(III) ions. The particles develop within a few minutes.

The kinetics of particle development was followed at $\lambda = 532$ nm at $28 \pm 1^\circ\text{C}$. UV-visible spectroscopy using 1 cm quartz cuvette with Shimadzu UV-160 (Kyoto, Japan) spectrophotometer. Transmission electron microscopy (TEM) were used to characterize the particles. Sample was prepared by placing a drop of solution containing nanoparticles on a carbon-coated Cu grid. TEM measurement was carried at 400 kV using JEOL 4000 EX instrument.

Results and discussion

Photochemical control of particle size

In the present study, almost monodispersed gold particles were obtained by UV irradiation of a solution of HAuCl_4 in aq. TX-100. The procedure showed excellent reproducibility. UV irradiation technique was used by Zhou et al. (1999) for shape control of gold particles in the presence of a capping polymer. In the present case, TX-100 serves the purpose of stabilizer as well as reductant which has been reported elsewhere by

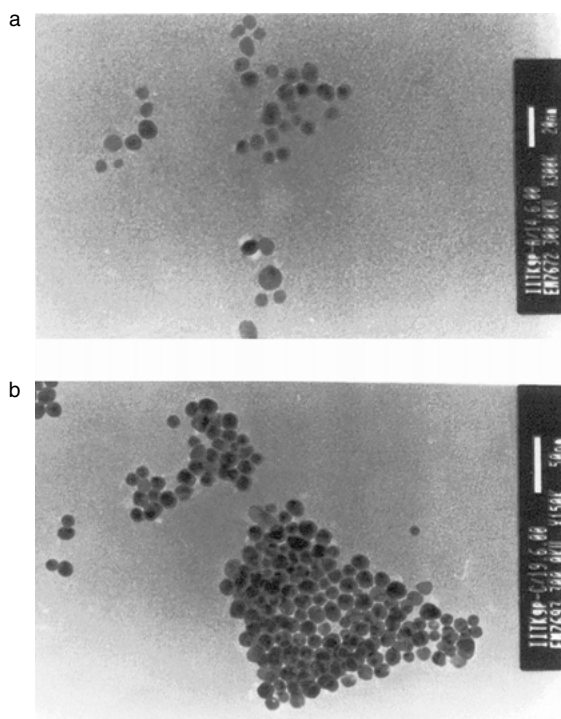


Figure 1. Transmission electron micrographs of Au particles prepared from (a) 3.9×10^{-5} M Au(III) ions and 0.992×10^{-2} M TX-100 and (b) 3.9×10^{-5} M Au(III) ions and 7.93×10^{-6} M TX-100 after 25 min irradiation.

us (Pal, 1998a,b). TEM study (Figure 1) showed that spherical particles were formed in all the cases and the size of the particles increases (authenticated from the red shift of the plasmon band as shown in Figure 2) with the increase in the ratio of [Au(III)] to [TX-100]. For example, 0.4×10^{-4} and 5×10^{-4} M Au(III) solutions in 10^{-2} M TX-100 produce particles of average diameter 5.6 nm (Figure 1(a)) and 23 nm (Figure 3(S)), respectively. Again, 0.4×10^{-4} M Au(III) solution in 7.93×10^{-6} M TX-100 gives particles of average diameter 9 nm (Figure 1(b)) (compare this with Figure 1(a)). The particle distribution was found to be very sharp in all the cases.

Non-iterative seed-mediated growth

Here, particles of any desired size was prepared in a single step from the original seed by adding and reducing appropriate amounts of Au(III) ions to various amounts of seed particles. Ascorbic acid was used as the reductant. Though ascorbate ion (or a combination of ascorbic acid and NaOH) is generally used for the reduction

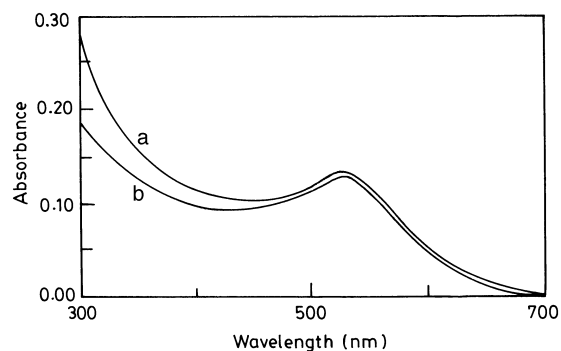


Figure 2. UV-visible spectra of colloidal Au nanoparticles. Conditions for (a) and (b) as in Figure 1(a) and (b) respectively.

of Au(III) ions, ascorbic acid itself could not produce gold particles from Au(III) ions in TX-100 medium. But when a small amount of seed particles was added to the Au(III) ion system, ascorbic acid immediately started forming gold particles. This showed very weak reducing character of ascorbic acid as well as particle catalyzed reduction of Au(III) ions. In principle, in the synthesis of particles of prechosen size by seed-mediated growth, nucleation and growth steps should be separated from each other and new nucleation and coagulation during the growth stage should be stopped. Therefore, Au(III) ions should be reduced only on the existing seed particles in the growth period. It requires a weak reducing agent like ascorbic acid, which would not create any new nucleation center except reducing the ions on the surface of the existing seed particles. The calculated sizes, assuming equal distribution per seed particle, and only surface reduction, of Au(III) ions, agree fairly well with the experimentally (TEM) determined ones. The size of the particle could be calculated (Schmid, 1992) using the following equation:

$$d_{\text{final}} = d_{\text{seed}} \left\{ \frac{[\text{Au(III)}]}{[\text{Au(0)}]} + 1 \right\}^{1/3},$$

where d stands for diameter of the particle. In a typical batch the total amount of gold was kept constant at 5×10^{-4} M in each case, whereas the ratio of [Au(III)] to [Au(0)] in seed was varied between 2 and 100. For the given conditions in Figure 3, the calculated sizes were 33, 50, 72 and 107 nm, respectively. From the TEM study (Figure 3), the respective average sizes were determined to be 31, 51, 82 and 112 nm, which are in very good agreement with the calculated ones. This suggests that ascorbic acid reduces only the surface adsorbed Au(III) ions creating hardly any new

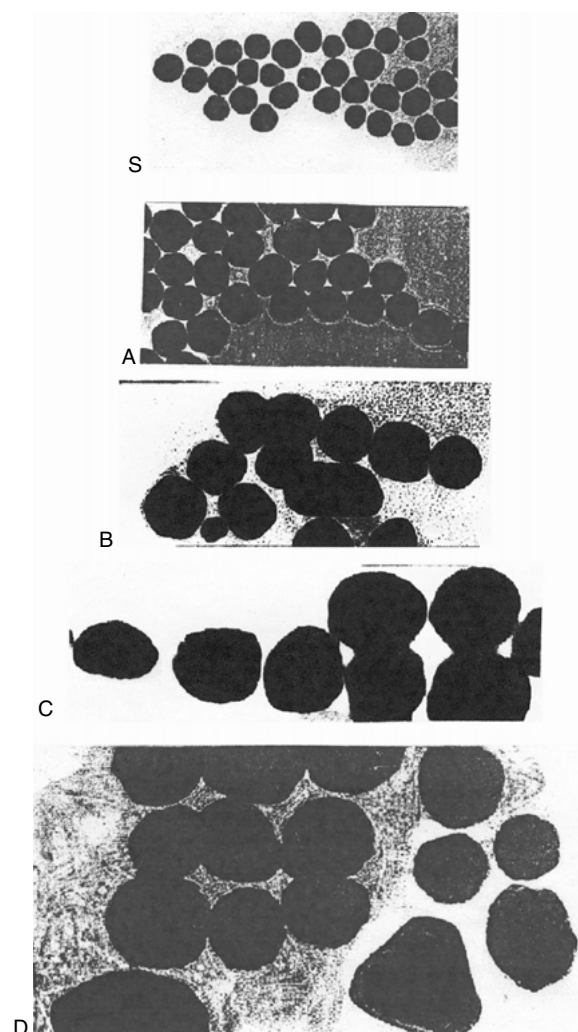


Figure 3. Transmission electron micrographs of seed (s) and other gold nanoparticles grown by seed mediation from the above seed. Conditions: S: 5×10^{-4} M Au(III) ions; and $[\text{Au(III)}]/[\text{Au(0)}] = 2$ (for A); 9 (for B), 29 (for C) and 100 (for D). Total gold concentration was 5×10^{-4} M in all cases. $[\text{TX-100}] = 1 \times 10^{-2}$ M and $[\text{ascorbic acid}] = 6 \times 10^{-4}$ M.

nucleation center. Further support for the surface catalytic reduction of Au(III) ions comes from the study of kinetics of the seed-mediated particle growth (Figure 4(a), Aiken III & Finke, 1998). The growth kinetics followed an autocatalytic behavior for sets B, C and D for first parts of their development. However, the length of the autocatalytic step shrinks from B to D. And in the same order there is a fall in the autocatalytic rate constant values ($k_{\text{obs}} = 4.67 \times 10^{-3}$, 4.16×10^{-3} and $3.2 \times 10^{-3} \text{ s}^{-1}$, respectively) which were determined

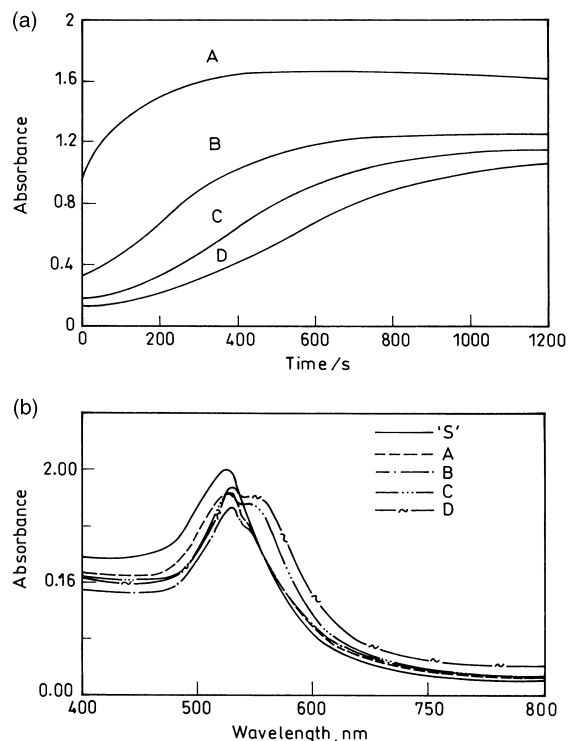


Figure 4. (a) Kinetics of Au nanoparticle development by seed mediation. Condition: as in Figure 3. (b) UV-visible spectra of Au nanoparticles grown via non-iterative seed mediation. Condition: as in Figure 3.

from the slope of the $\ln A_t / (A_\alpha - A_t)$ versus time plot. (Here A_t stands for absorbance at any time t and A_α that for time $t \rightarrow \alpha$). First order behavior was observed for set A from the beginning of the particle development and for other sets. After the autocatalysis steps. Figure 4(b) gives the UV-visible spectra of the finally developed particles for the above sets along with the seed particles. There was always a clear trend in red shift with the increase in particle size. But the shift was small 8 nm for a size variation from 23 to 112 nm. Shoulders appeared in the longer wavelength region (550 nm) for higher ratio of $[\text{Au(III)}]$ to $[\text{TX-100}]$, and became prominent gradually with the increase in Au(III) ions. Presence of similar weak shoulder was reported by Henglein, 1993. This might be because of a small aggregation effect of the particles.

Conclusion

Size control in the small size range by UV irradiation is a simple, clean, reproducible and fast technique with

very few control parameters. Experimental manipulation is easy for the photoirradiation process and unlike the chemical reduction technique for seed preparation. Again these small particles can be used as seeds for seed-mediated growth of nanoparticles to vary their size over a broad range. It is observed that the size control both by UV irradiation and by non-iterative seed mediation results in good results in terms of both improved monodispersity and sphericity to a fairly high concentration of Au(III) ions. But for higher [Au(III)], the size distribution becomes wide and faceted particles are formed.

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