# A Simple Large-Scale Synthesis of Nearly Monodisperse Gold and Silver Nanoparticles with Adjustable Sizes and with Exchangeable Surfactants

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## A Simple Large-Scale Synthesis of Nearly Monodisperse Gold and Silver Nanoparticles with Adjustable Sizes and with Exchangeable Surfactants

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The importance of gold and silver nanoparticles for areas ranging from electron microscopy (contrast agents),[1] analysis (chemical and biological sensors),[2–5] electronics (single-electron transistors, electrical connects),[6,7] materials (dyes, conductive coatings),[8,9] fundamental research, and even catalysis (CO oxidation on $Au/TiO_2$ composites)[10,11] is significant. These applications require nanoparticles in the 2–100-nm size range that need to be surface derivatizable with hydrophobic and hydrophilic surfactants. In the past, such nanoparticles were synthesized by either one of two methods, the citrate method introduced in 1857 by Faraday,[12] and later refined by Frens,[13] and the two-phase method originally described by Wilcoxon et al.[14] and later modified by Brust et al.[15] The citrate method produces nearly monodisperse gold nanoparticles in the size range from 2 to 100 nm.[1] Problems of the citrate method are a low gold nanoparticle content of the resulting solutions (<0.01 M) and the restriction to water as a solvent. Because the charge-stabilized particles easily undergo irreversible aggregation upon addition of electrolytes and nonpolar surfactants, particles cannot be surface-derivatized with hydrophobic surfactants. The Brust method, on the other hand, allows the introduction of hydrophobic thiols as surfactants, but it suffers from the limitation to small particle sizes (<10 nm), greater polydispersity, and higher costs for the phase transfer agents. A recently published metal atom dispersion technique solves the cost issues but it is limited to particle sizes below 6 nm and it requires special equipment for the synthesis.[16]

Here, we report an inexpensive, versatile, and very reproducible method for the large-scale synthesis of organoamine-protected gold and silver nanoparticles in the 6–21-nm (Au) and 8–32-nm (Ag) size ranges and with polydispersities as low as 6.9%. In terms of

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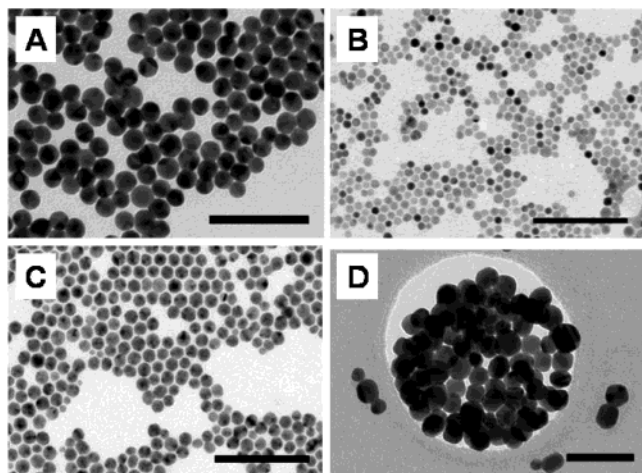(11) Pietron, J. J.; Stroud, R. M.; Rolison, D. R. *Nano Lett.* **2002**, *2*, 545–549.

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**Figure 1.** Transmission electron microscope images of Au and Ag nanoparticle samples. (A) ~21-nm Au from toluene, (B) ~9-nm Ag from toluene, (C) ~12-nm Ag nanoparticle from hexane, and (D) ~32-nm Ag from 1,2-dichlorobenzene. Scale bars are 100 nm.



**Figure 2.** Particle size distributions for samples A−D shown in Figure 1 and (E) growth dynamics for Au particles in toluene at 110 °C. Particle sizes were obtained by optical analysis of the TEMs (Supporting Information).

achievable particles sizes, polydispersites, and simplicity (only three reagents, tetrachloroauric acid or silver acetate, oleylamine, and a solvent are required) the method is superior to that of Jana et al.[17] The syntheses are fast, very reproducible, and simple (only three reagents, tetrachloroauric acid or silver acetate, oleyl-amine, and a solvent, are required). The particles are stable in dried form and they can be easily modified with hydrophobic and hydrophilic thiols to afford nanoparticles that are soluble in organic solvents or in water. Organoamine-protected gold nanoparticles (Figure 1a) of variable sizes form by refluxing a solution of tetra-chloroauric acid and oleylamine (9-octadecenylamine) in toluene over the course of 120 min. The reducing equivalents in the reaction are provided by the amine, which can undergo metal-ion-induced oxidation to ni-triles.[18,19] The carbon double bond in oleylamine does not play a significant role in this process since other aliphatic amines, for example 1-dodecylamine, work equally in the reaction. Oleylamine was chosen because it is commercially available and it is inexpensive. At the end of the reaction, the nanoparticles are isolated by precipitation with methanol and dried to yield a black powder that remains soluble in organic solvents even after prolonged storage in air. Figure 2E shows the evolution of the gold nanoparticles size as a function of time. The particle size data can be interpreted in terms of a classical nucleation/diffusional growth model.[20−22] Here, the initially formed gold atoms self-nucleate to form a fixed number of seeds during the first stage of the reaction, and particles then continue to grow by diffusion-driven deposition of gold atoms onto these existing seeds. Assuming that the rate at which gold
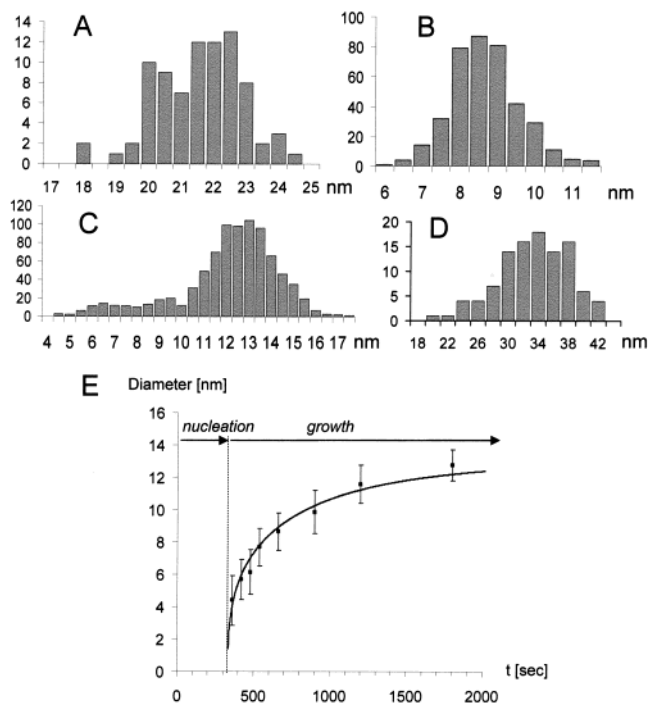
atoms are deposited onto the nuclei is linearly dependent on the concentration of gold precursor in the solution, one obtains the exponential growth curve shown in Figure 2E (details in the Supporting Information), which agrees well with the data. The intersection of the theoretical curve with the *x*-axis indicates that the end of the particle nucleation phase occurs roughly 300 s after the mixing of the reactants.

By quenching the reaction with ice cooled ethanol within 30 min after nucleation, it is possible to obtain gold nanoparticles in the 4−13-nm size regime (for images see Supporting Information). However, the yield of these particles is less than quantitative because the solution is still saturated with gold precursor. Alternatively, the gold nanoparticle sizes can be regulated with the concentrations of the gold precursor and of the amine from 15.3 nm (6.7%) to 21.3 nm (6.9%). Here, the maximum particle size is limited by the solubility of the nanoparticles. Higher concentrations of the gold precursor give smaller particles because more seed particles are formed at the beginning of the reaction. While the surfactant concentration has only a small influence on nanoparticles size, it greatly influences polydispersity of the formed colloid. Polydispersities below 10% generally require at least 65 equiv of the amine (based on gold precursor).

Micrometer-sized, multidomain colloidal crystals of 16−21-nm oleylamine-ligated Au nanoparticles (Figure 3) are routinely obtained as black solids directly from the reaction mixture upon cooling to room temperature, or by slow evaporation of the solvent from the heated solution. Crystals grown at lower temperature show a preference for the hcp lattice, whereas crystals grown at higher temperature contain an increased number of domains in the fcc structure type (see markings in Figure 3b). Sub-micrometer crystals of <10-nm amine,[23]

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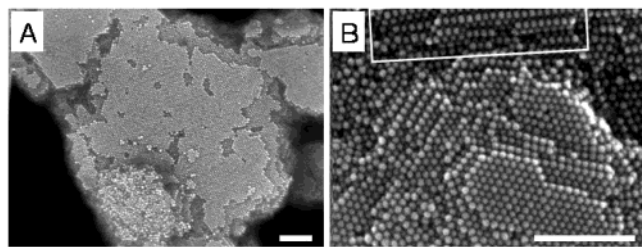


**Figure 3.** Scanning electron micrographs of colloidal crystals of oleylamine-ligated 16.6-nm Au particles. (A) Crystal grown at 110 °C with with hcp structure. (B) Crystal grown at <50 °C with hcp and fcc domains. Scale bar is 200 nm.

thiol,[16,24] and tetraalkylammonium-[25] stabilized gold nanoparticles with fcc and hcp structures have been previously reported by other groups.

Oleylamine also reduces silver acetate to silver nano-particles (Figure 1b−d). The reaction proceeds over the course of 8−24 h, and the size of the silver nanoparticles can be effectively controlled with the solvent and the growth temperature. Reflux in hexane (bp: 69 °C), toluene (bp: 110 °C), and 1,2-dichlorobenzene (bp: 181 °C) yields 8.5-nm (11.3%), 12.7-nm (10.9%), and 32.3-nm (14.3%) nanoparticles, respectively. Samples drawn after 30 min from the reaction in 1,2-dichlorobenzene reveal a bimodal particle size distribution of ∼3.0- and ∼8.9 -nm silver particles (details in Supporting Information). As the reaction proceeds, the number, size, and uniformity of the larger particles all increase, while the number of ∼3-nm particles decreases, although these particles do not disappear entirely. This indicates that the larger particles grow at the cost of the smaller ones (Ostwald ripening) and that new silver nuclei continu-ously form over the course of the entire reaction. The latter is likely due to the high temperature of the reaction in 1,2-dichlorobenzene.

The weakly absorbed oleylamine on the nanoparticles can be readily displaced with aliphatic thiols by adding a solution of the oleylamine-ligated gold nanoparticles in toluene to a boiling solution of 5−10 equiv (based
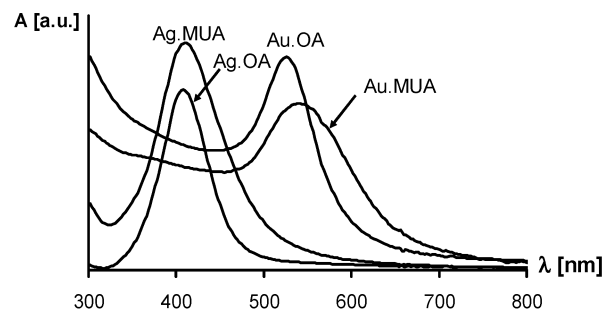


**Figure 4.** UV−vis spectra of oleylamine (OA) and 11-mercaptoundecanoic acid (MUA) ligated gold (13-nm) and silver (8.5-nm) nanoparticles in toluene (OA) and water (MUA).

on gold) of the thiol in the same solvent. Thiol-capped silver nanoparticles are obtained analogously at room temperature in chloroform. When thiols with ionizable carboxylic acid groups, such as 11-mercaptoundecanoic acid, are employed in the reaction, one obtains water-soluble nanoparticles with virtually unchanged UV/vis spectra (Figure 4) in the case of silver and with slightly red-shifted bands in the case of gold. Aliphatic thiols, on the other hand, lead to particles that are soluble in nonpolar organic solvents. Apart from the altered solubility, successful ligand exchange is also supported by the FT-IR spectra on the products (Supporting Information).

In conclusion, we have described a versatile and inexpensive method for the synthesis of gold and silver nanoparticles. The low polydispersity of the obtained colloids and the ease of surfactant exchange with aliphatic and bifunctional thiols make the synthesis attractive for most applications of gold and silver nanoparticles in both aqueous and nonaqueous media.

**Supporting Information Available:** Full synthetic de-tails, electron micrographs, IR spectra of nanoparticles, and details of the Au particle growth model. This material is available free of charge via the Internet at http://pubs.acs.org.

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