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Synthesis of Monodisperse Au, Ag, and Au−Ag Alloy Nanoparticles with Tunable Size and Surface Plasmon Resonance Frequency

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Supporting Information

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Metallic nanoparticles (NPs), especially silver and gold nanoparticles, are of great interest because of their unique optical and catalytic properties. In particular, the localized surface plasmon resonance (LSPR) of metallic NPs enables applications in many fields, including bioimaging,[1] metamaterials,[2] drug delivery,[3] cancer therapy,[4] and surface-enhanced Raman scattering.[5] The LSPR frequency is strongly dependent on the size, shape and composition of metallic NPs. Metallic NPs, especially gold and silver NPs, have been synthesized by many groups.[6] However, improved methods for the synthesis of alloy nanoparticle and for the tuning of surface plasmon resonance through composition remain of interest. Alloying is also of interest for the control of other properties, such as catalytic activity.[7] Gold and silver NPs typically have LSPR wavelength around 530 and 400 nm, respectively. These can be tuned to longer wavelengths by varying particle shape. For example, gold nanorods exhibit a longer wavelength LSPR corresponding to resonances along their longitudinal dimension. However, tuning of the LSPR frequency between 400 and 530 nm can most readily be achieved by producing Au−Ag alloy nanoparticles.

Au−Ag alloy nanoparticles have most commonly been produced in aqueous solution.[8] However, the uniformity and stability of these particles remain inferior to that which can be achieved for the pure metals. Sun's group first demonstrated synthesis of monodisperse Au−Ag NPs in organic media.[7b] The composition of the Au−Ag alloy in reported methods is controlled through the ratio of the precursors used in the synthesis. This leads to simultaneous changes in nanoparticle size and composition, and consequently a shift in the LSPR frequency that reflects both changes. Here, we present a convenient method of preparing Au−Ag alloy nanoparticles in organic solvent, with high monodispersity and controlled size from 6 to 13 nm diameter. The LSPR frequency and size of alloy nanoparticles could be controlled not only by varying the precursor ratio, but also by varying surfactant composition. Thus, the LSPR frequency could be tuned by varying composition without changing the particle size much.

Oleylamine was used as both reducing and stabilizing agent in the synthesis reported here, as detailed in the Supporting Information. The amine group can reduce gold and silver ions to produce NPs at high temperature, as previously reported.[9] Under mildly reducing conditions, the nucleation and the growth processes can be separated, because the growth phase is long, allowing production of highly monodispersed particles.[10] A broad variety of monodisperse NPs can be synthesized by such "hot colloidal" approaches.[10b,11] In this method, when precursors are injected into a solution already at the reaction temperature, the nucleation and growth processes proceed much more quickly than when precursors and surfactants are slowly heated together. This rapid injection method can often produce very monodispersed particles, because the initial nucleation burst, which occurs upon precursor injection, depletes the precursor concentration enough so that further nucleation does not occur. Slow growth of nuclei from the initial burst leads to highly uniform particles. Our results for the gold particles produced here are consistent with this expectation. Gold particles produced by rapid injection of precursors into a hot solution were much more uniform (standard deviation 5%, see Figures S1 and S2 in the Supporting Information) than those produced by heating premixed precursors and surfactants.

However, rapid injection could not be used to produce Au−Ag alloy nanoparticles, which should have a single LSPR frequency between ~400 nm (signature peak of Ag NPs) and ~530 nm (signature peak of Au NPs), depending on their composition. The absorption spectrum of particles produced by rapid precursor injection (in a ratio corresponding to 75 atomic % Ag) show two different absorption peaks at 420 nm and 500 nm separately (Figure 1a). The peak at 420 nm is attributed to silver NPs or silver-rich alloy NPs, and the peak at 500 nm is attributed to Au-rich alloy nanoparticles. This is similar to core−shell gold−silver nanoparticles, which usually show two plasmonic peaks either between the signature peaks of Au and Ag or outside this region depending on the structure of the particles.[12] A possible mechanism here for generating both silver and alloy NPs is shown schematically in Figure S3 in the Supporting Information. When gold and silver precursors are injected simultaneously, the driving force for particle formation is large for both precursors, and both Au and Ag nanoparticles may nucleate simultaneously. In this method, the initial nucleation and growth process is complete after several seconds, as evidenced by the color change of the colloid. During the growth phase, gold monomers may preferentially deposit on the gold

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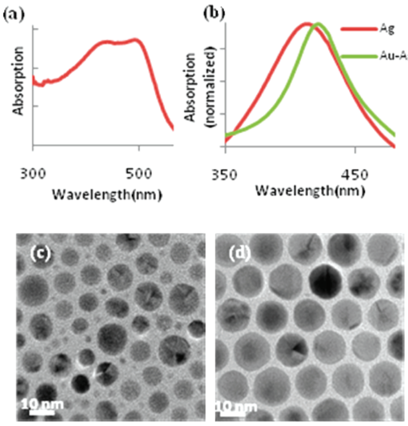

Figure 1. UV−vis spectrum of Au−Ag mixtures (a) synthesized with "fast syringe" method and (b) silver and $Au_{0.25}$−$Ag_{0.75}$; TEM images of (c) Ag and (d) $Au_{0.25}$−$Ag_{0.75}$ alloy NPs .

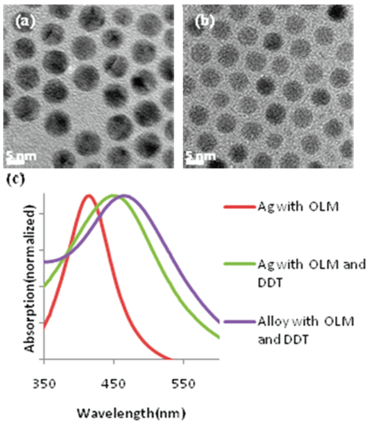

Figure 2. TEM images of (a) $Au_{0.25}$−$Ag_{0.75}$ and (b) Ag NPs synthesized with OLM and DDT together; (c) the UV−vis spectrum of silver and $Au_{0.25}$−$Ag_{0.75}$ NPs with different surfactants.

nuclei, and silver monomers may preferentially deposit on the silver nuclei. The result is a mix of silver-rich particles with LSPR frequency near that of pure silver particles, and gold-rich particles with LSPR frequency near that of pure gold particles. On the other hand, if Au and Ag precursors are heated together, then the more reactive precursor will decompose first, producing nuclei of that material. Subsequent growth will occur by monomer deposition of both species on those nuclei, and particles of uniform composition will result. The results shown below support this mechanism. When chloroauric acid and silver acetate were heated together from room temperature to 150 °C, monodispersed Au−Ag alloy nanoparticles were produced, with LSPR absorption peaks at wavelengths between 400 and 530 nm. Effects of surfactants and the ratio of Au/Ag precursors are discussed below.

In one series of experiments, the Au^{3+}/Ag^{+} ratio was fixed at 1:3 to determine the effect of added surfactants on LSPR and size. Initially, OLM was used alone as surfactant (as well as reducing agent) and the alloy nanoparticles had an LSPR absorption peak at 425 nm, which is red-shifted by ∼20 nm relative to the peak for pure silver nanoparticles (Figure 1b). The alloy nanoparticles were about 13 nm in diameter, as shown in Figure 1d. Under the same conditions, pure silver nanoparticles were also synthesized for comparison (Figure 1c). The alloy nanoparticles were much more monodispersed, with a standard deviation of 7% (see Figure S4 in the Supporting Information). Gold nanoparticles are usually more easily synthesized with a narrow size distribution and shorter reaction time[9] compared to silver nanoparticles. Thus, we suggest that the gold nuclei form from Au^{3+}, and then Au^{3+} and Ag^{+} deposit upon the uniform gold nuclei without generating any new silver-rich nuclei. This results in more uniform alloy particles.

The addition of dodecanethiol (DDT) along with OLM shifts the LSPR absorbance of the alloy NPs from 425 to 465 nm, using the same precursor ratio (Figure 2c). The average size was reduced from 13 to 8 nm, but the monodispersity was maintained, as shown in Figure 2a, with a standard deviation of 8% (see Figure S5 in the Supporting Information). It is not surprising that the size decreases when an additional strongly binding surfactant is added. The red-shift of the LSPR peak suggests a composition change. Addition of DDT, which binds gold very strongly, might change the particle composition. However, energy-dispersive X-ray spectroscopy (EDX) shows that the particles produced with and without DDT have similar composition (see Table S1 in the Supporting Information). For comparison, pure silver NPs were also synthesized with both OLM and DDT as surfactants. In this case, the peak was also red-shifted from the signature peak at around 400 to 440 nm (Figure 2c), accompanied by a decrease of the average size from 13 nm (with OLM alone) to 6 nm (Figure 2b) and a marked decrease in polydispersity (see Figure S6 in the Supporting Information). Hence, the addition of DDT has a similar effect of red-shifting the LSPR absorbance and decreasing the average size for both pure Ag and the alloy nanoparticles. The addition of 25% Au precursor only shifted the LSPR absorbance from 440 to 460 nm which is the same 20 nm shift observed in going from pure Ag to alloy particles with OLM alone.

The nanoparticle size can also be used for tuning the LSPR absorbance, but in this size range (5−15 nm), it does not have a strong effect on the LSPR frequency. To further vary the size, we added 1-hexadecylamine (HDA), along with OLM and DDT. The LSPR absorption peak remained at 460 nm (Figure 3a). However, the average particle size decreased from 8 to 6 nm, as shown in Figure 3d (size distribution is shown in Figure S7 in the Supporting Information). Thus, HDA addition changed the nanoparticle size without changing the LSPR frequency. OLM and HDA were also used without DDT. In that case, the LSPR peak was at 425 nm and particles were around 5 nm in diameter (see Figure S8 in the Supporting Information). Thus, DDT can change both the LSPR frequency and the size of the alloy NPs and can therefore play a more important role in LSPR tuning than other surfactants, such as HDA and OLM. On the other hand, HDA can be used to tune the size of the alloy nanoparticles from 13 to 6 nm diameter, without changing the LSPR frequency. To find out the role of DDT, we added excess DDT to the $Au_{0.25}$−$Ag_{0.75}$ NPs, initially synthesized with OLM and HDA, to exchange some of the OLM and HDA ligands for DDT. After 4 h of stirring, the color of the solution changed from reddish brown to brownish red, and the absorption peak shifted from 425 nm to about 465 nm (see Figure S9 in the Supporting Information). The experiment demonstrates that the shift in LSPR frequency results from DDT binding to the NP surface, rather than from the effects of DDT on NP growth. This shift is rather large to be rationalized in terms of a change in local dielectric environment due to the change in surface ligand.

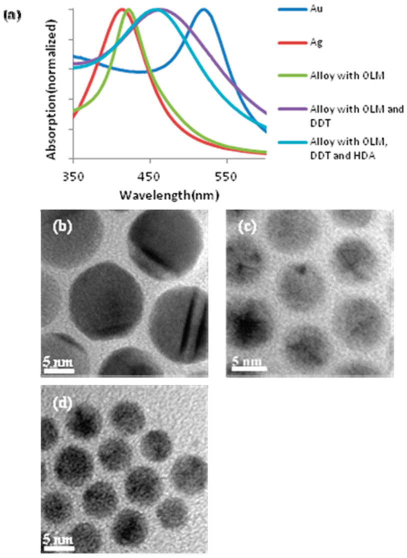

Figure 3. (a) UV−vis spectra of Ag, Au and $Au_{0.25}$−$Ag_{0.75}$ nanoparticles with different surfactants. TEM images of $Au_{0.25}$−$Ag_{0.75}$ nanoparticles synthesized with surfactants of (b) OLM, (c) OLM and DDT, and (d) OLM, DDT and HDA.

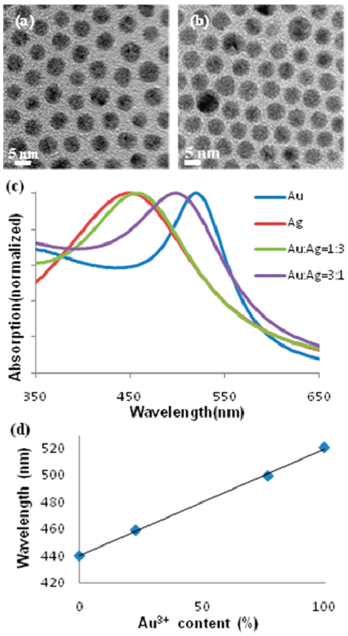

Figure 4. TEM images of (a) $Au_{0.25}$−$Ag_{0.75}$ and (b) $Au_{0.75}$−$Ag_{0.25}$ nanoparticles synthesized with the same surfactants; (c) UV−vis spectra of the alloy nanoparticles synthesized with different ratios of precursors and fixed surfactants; (d) linear relation between the Au precursor mole fraction and the absorption peak of alloys.

However, it could be accounted for by the formation of a very thin interfacial layer of silver sulfide (Ag_2S). Figure S10 in the Supporting Information shows spectra computed from extended Mie theory[12,13] for Ag core/Ag_2S shell particles with an overall diameter of 9 nm and shell thicknesses of 0 to 0.5 nm. The computed LSPR peak shifts from 400 to 441 nm almost linearly as the shell thickness increases from 0 to 0.5 nm, and simultaneously becomes much broader.

Along with the surfactants and size, the composition of the alloys can also change the LSPR frequency.[8a] Here, the size of the alloy nanoparticles was fixed at ∼6 nm (Figure 4a,b) by adding both DDT and HDA. Upon increasing the fraction of Au precursors, the LSPR peak shifted from 440 to 530 nm, as shown in Figure 4c. The relationship between the composition of alloy nanoparticles and LSPR peak position was approximately linear (Figure 4d).

In conclusion, we have synthesized monodispersed Au, Ag, and Au−Ag alloy nanoparticles with a simple and reproducible hot-colloidal method (the methods and properties of nanoparticles are summarized in Table S2 in the Supporting Information). Although a rapid injection method produced more uniform gold nanoparticles, it could not be used to produce alloy nanoparticles. However, when mixed metal precursors and surfactants were heated together, monodispersed alloy nanoparticles with controlled LSPR peak could be produced. The size of synthesized alloy nanoparticles is uniform and could be controlled from 6 to 13 nm in diameter. The LSPR absorption peak of alloy nanoparticles could be tuned by varying the precursor composition or the added surfactants.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed materials and methods; TEM of Au NPs; size distributions of Au, Ag, and alloy NPs; additional TEM and UV−vis spectra of alloy NPs; NP composition measurements by energy-dispersive X-ray spectroscopy, computed absorbance spectra for Ag/Ag_2S core/shell particles. This material is available free of charge via the Internet at http://pubs.acs.org/.

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