Supplementary information for:

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

Sha Liu[†], Guanying Chen[‡], Paras N. Prasad[‡,§] and Mark T. Swihart[*,†,‡]

[†]Department of Chemical and Biological Engineering, [‡]Institute for Lasers, Photonics and Biophotonics, and [§]Department of Chemistry, The University at Buffalo (SUNY), Buffalo, New York, USA

[*]Corresponding author, swihart@buffalo.edu

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Detailed Materials and Methods:

Materials

Gold (III) chloride trihydrate ($HAuCl_4 \cdot 3H_2O$, Aldrich, 99.9+%), silver acetate (Aldrich, 99.99%), oleylamine (Aldrich, technical grade), 1-dodecanethiol (Aldrich, >=98%), 1-hexadecylamine (Aldrich, 98%), phenyl ether (Sigma, 99%), ethanol (Decon Labs, Inc.), and hexane (EMD, GR ACS) were used as received without further purification.

Synthesis of gold nanoparticles

We used two different methods to synthesize gold nanoparticles: (1) rapidly injecting gold precursors into a pre-heated surfactant solution; or (2) heating the precursor and surfactants together from room temperature to the reaction temperature (Heating rate is around ~8°C/min in all the experiments).

Method 1: 5 mL oleylamine (OLM) was refluxed at 150 °C in a 100 mL flask under argon. A mixture of 0.3 mmol of $HAuCl_4 \cdot 3H_2O$ in 1 mL OLM was rapidly injected into the hot solution and heating was continued for 1.5 hours.

Method 2: A total of 0.3 mmol of $HAuCl_4 \cdot 3H_2O$, 2 mL oleylamine, 1mL oleic acid and 10 mL phenyl ether were mixed in a 100 mL flask. Under an argon atmosphere, the mixture was heated to 150°C with magnetic stirring. The solution was kept at this temperature for 2.

Synthesis of silver nanoparticles

A total of 0.3 mmol of silver acetate, 2 mL oleylamine, 1mL oleic acid and 10 mL phenyl ether were mixed in a 100 mL flask. Under an argon atmosphere, the mixture was heated to 150 °C with magnetic stirring. The solution was kept at this temperature for 5 hours then cooled to room temperature. To produce 5 nm silver nanoparticles, 0.5 mL dodecanethiol was added to the initial mixture.

Synthesis of Au-Ag alloys

A total of 0.225 mmol of silver acetate, 0.075 mmol $HAuCl_4 \cdot 3H_2O$, 2 mL oleylamine, 1mL oleic acid and 10 mL phenyl ether were mixed in a 100 mL flask. Under an argon atmosphere, the mixture was heated to 150 °C with magnetic stirring. The solution was kept at this temperature for 5 h. 0.5 mL dodecanthiol and 2 g 1-hexadecylamine were added to control the surface plasmon resonance frequency and the size of alloy nanoparticles. When the ratio of Au and Ag precursors was varied to produce alloys with different composition and surface plasmon resonance frequency, the total quantity of metal salts was maintained at 0.3 mmol.

Nanoparticle recovery

In each of the above approaches, after cooling the flask to room temperature, ethanol was added to precipitate the particles and the suspension was centrifuged at 11000 rpm for 5 min. The supernatant was discarded. The nanoparticles were re-dispersed in hexane.

Nanoparticle Characterization

The size and morphology of nanoparticles were characterized by transmission electron microscopy (TEM) using a JEOL JEM-2010 microscope at an acceleration voltage of 200 KV. Absorption spectra were acquired using a Shimadzu 3600 UV–Visible-NIR scanning spectrophotometer.

Supplementary Figures and Table:

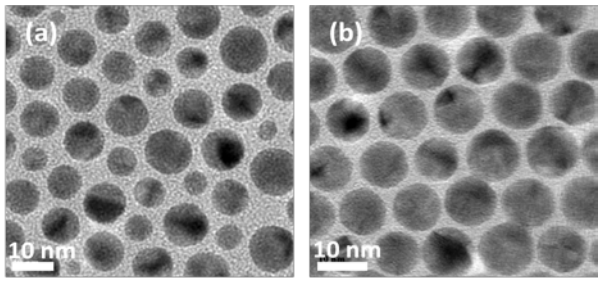


Figure S1. Au nanoparticles synthesized by (a) heating precursors and surfactants together; and (b) by rapid injection of precursor into a pre-heated surfactant solution.

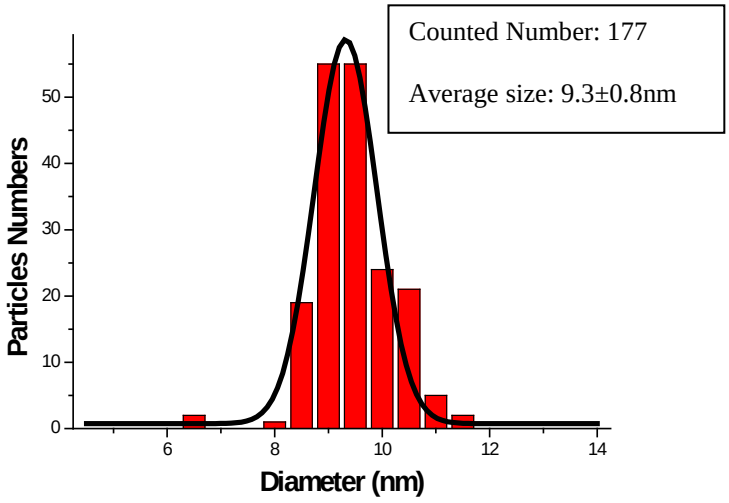


Figure S2. Size distribution of Au NPs synthesized with rapid injection of precursors.

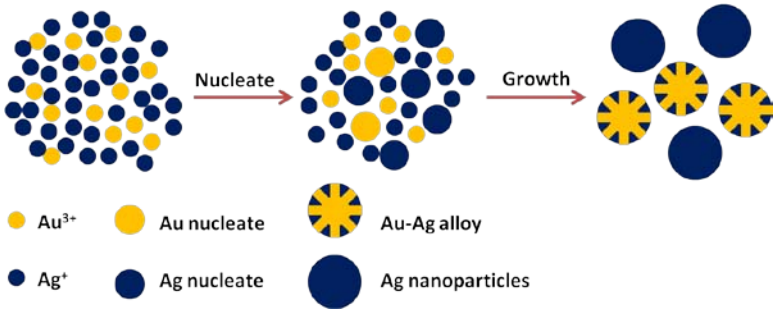


Figure S3. Drawing of possible mechanism of producing Au-Ag mixtures using the rapid injection method.

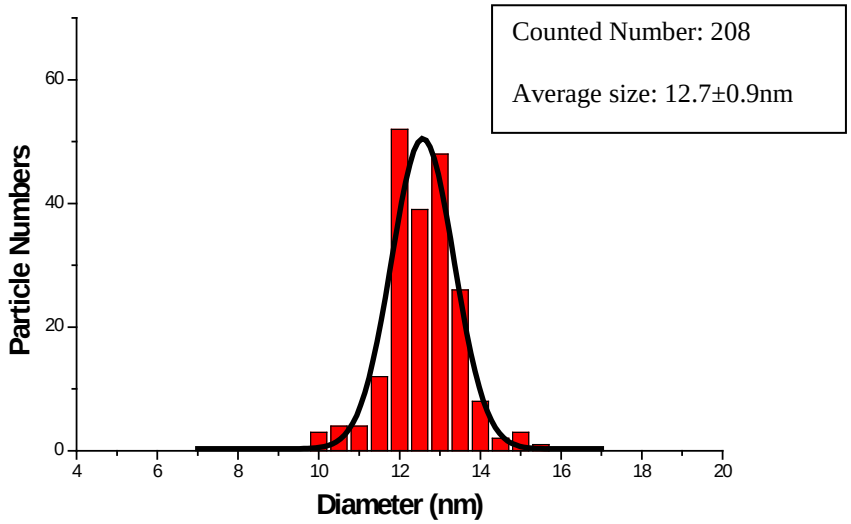


Figure S4. Size distribution of $Au_{0.25}$-$Ag_{0.75}$ NPs synthesized with OLM alone.

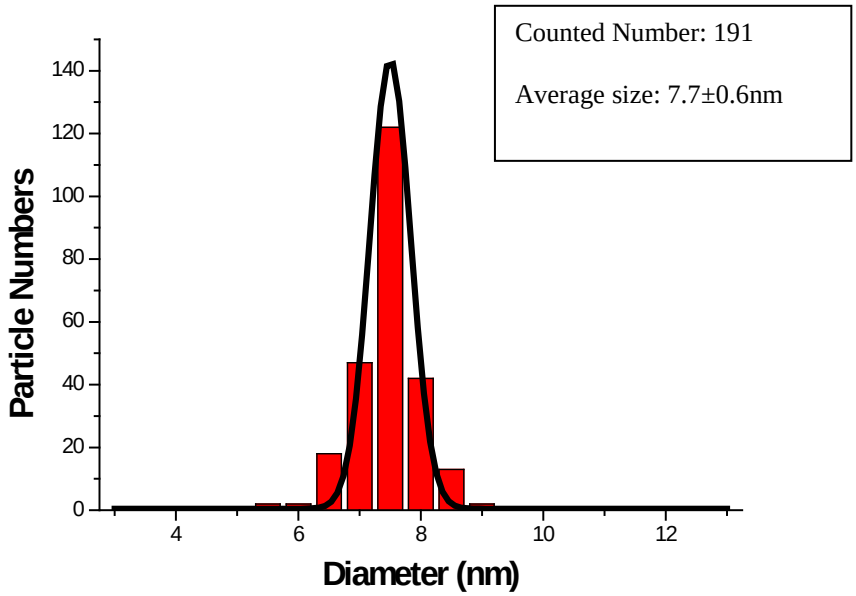


Figure S5. Size distribution of $Au_{0.25}$-$Ag_{0.75}$ NPs synthesized with OLM and DDT together.

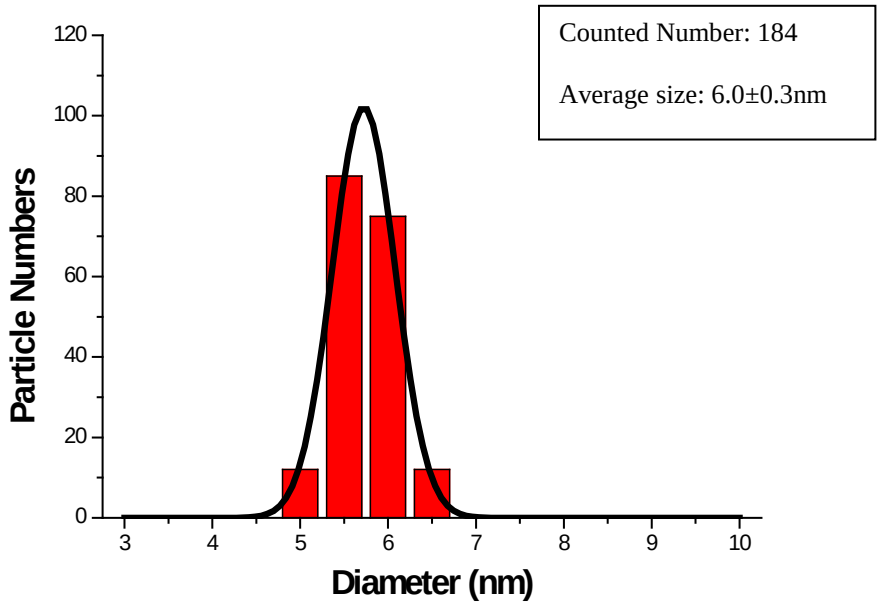


Figure S6. Size distribution of Ag NPs synthesized with OLM and DDT together.

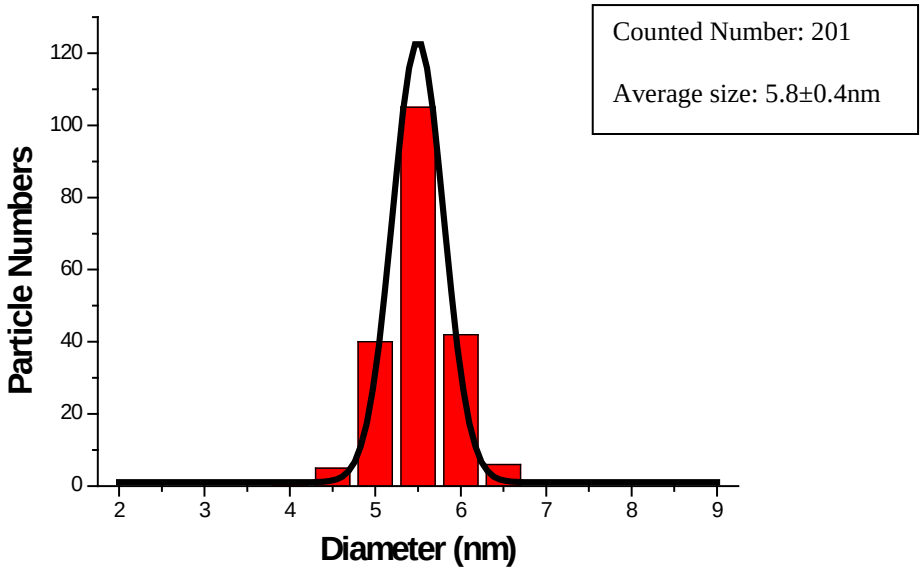
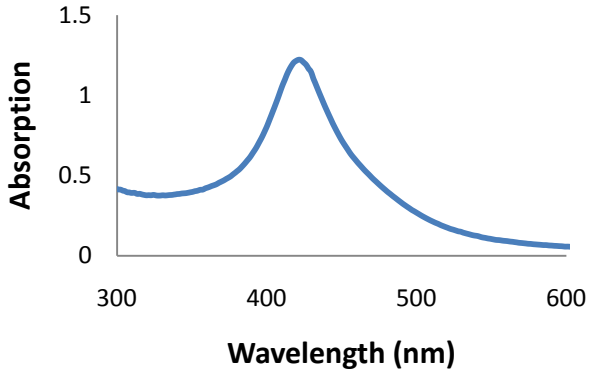


Figure S7. Size distribution of $Au_{0.25}$-$Ag_{0.75}$ NPs synthesized with OLM, DDT and HDA.



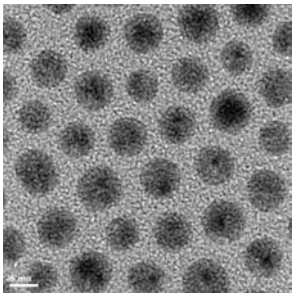


Figure S8. (a) UV-Vis absorption and (b) TEM image of $Au_{0.25}$-$Ag_{0.75}$ NPs synthesized with OLM and DDT.

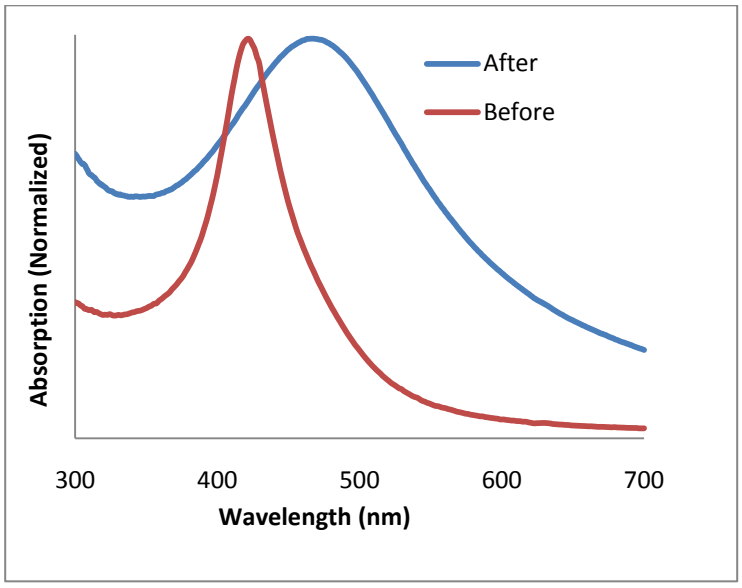


Figure S9. UV-Vis spectra of $Au_{0.25}$-$Ag_{0.75}$ nanoparticles with OLM, before and after ligand exchange with DDT.

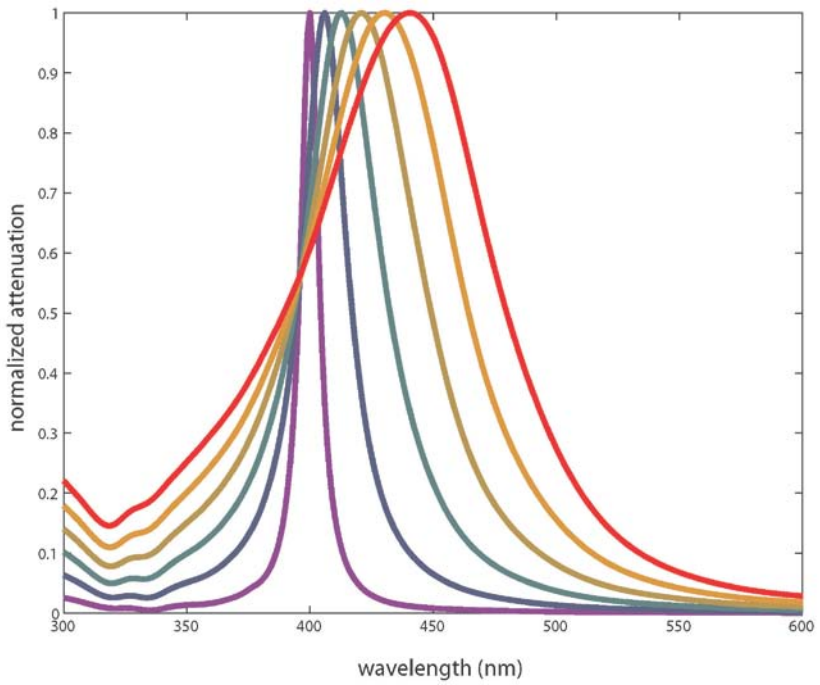


Figure S10. Computed normalized attenuation (absorption plus scattering) spectra for 9 nm Ag particles in which a thin surface layer of Ag is replaced by Ag_2S. As the thickness of the Ag_2S layer increases from 0 to 0.5 nm in 0.1 nm increments the spectrum broadens and red-shifts by about 41 nm. The refractive index of the solvent is taken as 1.45. Properties of Ag and Ag_2S are from the CRC Handbook of Chemistry and Physics and from Bennett et al., J. Opt. Soc. Am., **60**, 224-232 (1970), respectively.

Table S1. Summary of results of energy-dispersive x-ray spectroscopy analysis of $Au_{0.25}$-$Ag_{0.75}$ NPs synthesized with different surfactants.

Surfactants Added		**OLM**	**OLM, DDT**	**OLM, HDA**	**OLM, DDT & HDA**
Precursors	**Au%**	25	25	25	25
	Ag%	75	75	75	75
Synthesized Particles	**Au%**	27.7	19.0	24.9	23.0
	Ag%	72.3	81.0	75.1	77.0

Table S2. Summary of the conditions used for synthesizing all samples discussed in the manuscript and the resulting average size and LSPR absorption peak

Particles	**Au atomic %**	**Ag atomic %**	**Slow Heating Method**	**OLM (mL)**	**DDT (mL)**	**HDA (g)**	**PE (mL)**	**Average Size(nm)**	**Absorption peak(nm)**
Au	100%	0%	Yes	2	0	0	10	9	530
$Au_{0.25}$-$Ag_{0.75}$	25%	75%	No	2	0	0	10	12	420/500
$Au_{0.25}$-$Ag_{0.75}$	25%	75%	Yes	2	0	0	10	12.9	420
$Au_{0.25}$-$Ag_{0.75}$	25%	75%	Yes	2	0.5	0	10	7.6	460
$Au_{0.25}$-$Ag_{0.75}$	25%	75%	Yes	2	0.5	2	10	5.6	460
$Au_{0.75}$-$Ag_{0.25}$	75%	25%	Yes	2	0.5	2	10	5.9	500
Ag	0%	100%	Yes	2	0	0	10	9	400
Ag	0%	100%	Yes	2	0.5	0	10	5.9	440