Supplementary information

AuAg alloy nanomolecules with 38 metal atoms

Chanaka Kumara and Amala Dass*

Department of Chemistry and Biochemistry, University of Mississippi, 352 Coulter Hall, University, 38677 Mississippi, USA. Fax: +1 662 915 7300; Tel: +1 662 915 1826; E-mail: amal@olemiss.edu

Experimental details

*Synthesis: S*ynthesis of the $Au_{38-n}Ag_n(SR)_{24}$ involves two steps. The first step is the synthesis of crude product that contains polydisperse AuAg clusters using the method reported by Negishi et al.[1] The second step is the thermo-chemical treatment of the crude product with excess thiol resulting in mixtures with $Au_{38-n}Ag_n(SR)_{24}$ alloy nanomolecules.

Step 1. Aqueous solution (30 mL) containing $HAuCl_4$ and $AgNO_3$ (total metal concentration was set to 15 mM) was mixed with toluene solution (30 mL) of tetraoctylammonium bromide, TOABr (0.55 mmol). The initial mole ratios of Au:Ag precursors were set to 1:0, 1:0.05, 1:0.10, 1:0.15,1:0.20,1:0.30, 1:0.35 and 1:0.40 in different synthetic batches. After stirring for 30 min, the turbid organic phase was separated and phenylethane thiol (5 mmol) was added. The stirring was continued for 30 min at room temperature. The reaction mixture was then cooled to 0 ^{0}C in ice bath for 30 min. An aqueous solution of $NaBH_4$ (10 mmol, 20 mL) cooled to 0^{o}C, was rapidly added to the reaction mixture under vigorous stirring and reaction carried out at 0 ^{o}C. After 3 hours, the organic layer was separated from aqueous layer and evaporated to dryness. The product was washed with methanol to remove excess thiols and other byproducts. The residual mixture was extracted with toluene. Smaller clusters less than 10 kDa range [$(AuAg)_n(SR)_m$ clusters] were removed by following solvent fractionation.

Crude product was dissolved in acetonitrile (25 mL) and soluble and insoluble part was separated. $(AuAg)_n(SR)_m$ clusters less than 10 kDa further removed by the following procedure. Crude product was dissolved in toluene (0.3 mL) and acetone (1 mL) was added slowly. Then acetonitrile (~10 mL) was added very slowly and the soluble, insoluble portions were separated. Soluble portion contains $(AuAg)_n(SR)_m$ clusters that less than 10 kDa. Then the remaining product (~10-40 kDa mass range) was subjected to second step.

Step 2: 20 mg of ~10-40 kDa portions was dissolved in 0.50 mL of toluene and subjected to thermochemical treatment with excess phenylethane thiol (0.50 mL) at 80^{o}C under stirring. Aliquots from the reaction were monitored using MALDI MS at different time intervals. When pure $Au_{38-n}Ag_n(SR)_{24}$ nanoalloy was observed in MALDI ~12h, the reaction was stopped and washed with methanol. Then product was subjected to solvent fractionation to isolate pure $Au_{38-n}Ag_n(SR)_{24}$ nanoalloy removing other species such as $(AuAg)_{144}$ nanoalloys.

Then product was subjected to following solvent fractionation steps to isolate pure $Au_{38-n}Ag_n(SR)_{24}$ nanomolecules. First step is to remove clusters larger than ~10 kDa from the product. Product obtained from thermo-chemical treatment was dissolved in toluene (0.2 ml) and 0.5 mL of acetone was added slowly. Then acetonitrile was added very slowly (in 0.25 mL increments), allowing precipitates to form, which was monitored with MALDI. When $Au_{38-n}Ag_n(SR)_{24}$ nanomolecules start to precipitate, soluble part was separated and solvent evaporated. In second step clusters less than ~10 kDa were removed from the mixture. The soluble part was re-dissolved in acetone (0.5 ml) and acetonitrile was added very slowly (as a fraction of 0.05 to 0.1 mL) while monitoring with MALDI. When most of the $Au_{38-n}Ag_n(SR)_{24}$ nanomolecules were seen in the insoluble portion, process was stop. This insoluble portion contain pure $Au_{38-n}Ag_n(SR)_{24}$ nanomolecules.

Fig. S1 MALDI TOF mass spectra (positive mode, wide mass range (4 – 40 kDa)) of $Au_{38-n}Ag_n(SR)_{24}$ nanomolecules (isolate as pure fraction) for Au : Ag precursor ratios of 1 : 0 (black), 1 : 0.05 (red), 1 : 0.10 (blue), 1 : 0.15 (olive) and 1 : 0.20 (orange) and 1 : 0.30 (purple) in the starting material.

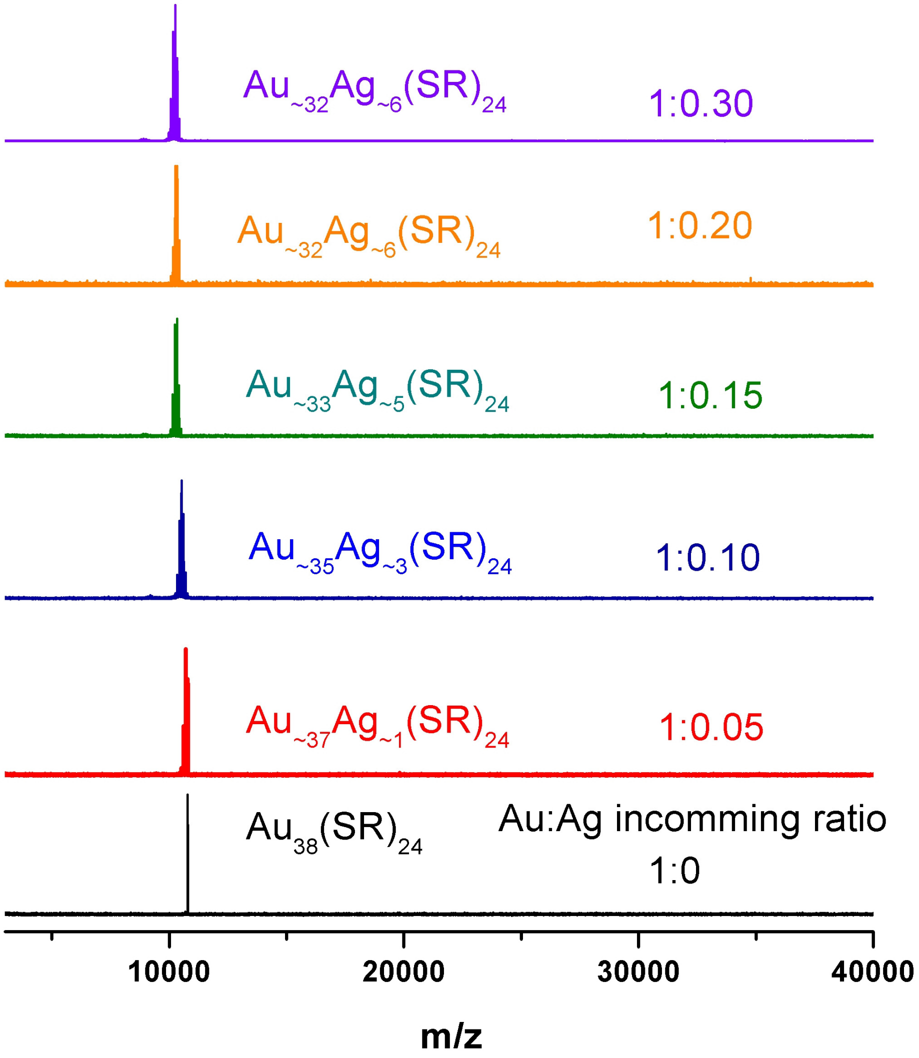


Fig. S2 *(Expansion of Figure 1 in the main article)* MALDI TOF mass spectra (positive mode) of $Au_{38-n}Ag_n(SR)_{24}$ nanomolecules for Au : Ag precursor ratios of 1 : 0(black), 1 : 0.05 (red), 1 : 0.10 (blue), 1 : 0.15 (olive) and 1 : 0.20 (orange), 1 : 0.30 (purple), 1 : 0.35 (dark yellow) and 1 : 0.40 (brown) in the starting material.. The mass difference between the peaks in nanoalloys corresponds to the Au (196.97 Da) and Ag (107.87 Da) mass difference, Δm=89.10 Da. The number of Au and Ag atoms of most dominant peak is denoted above each distribution of peaks

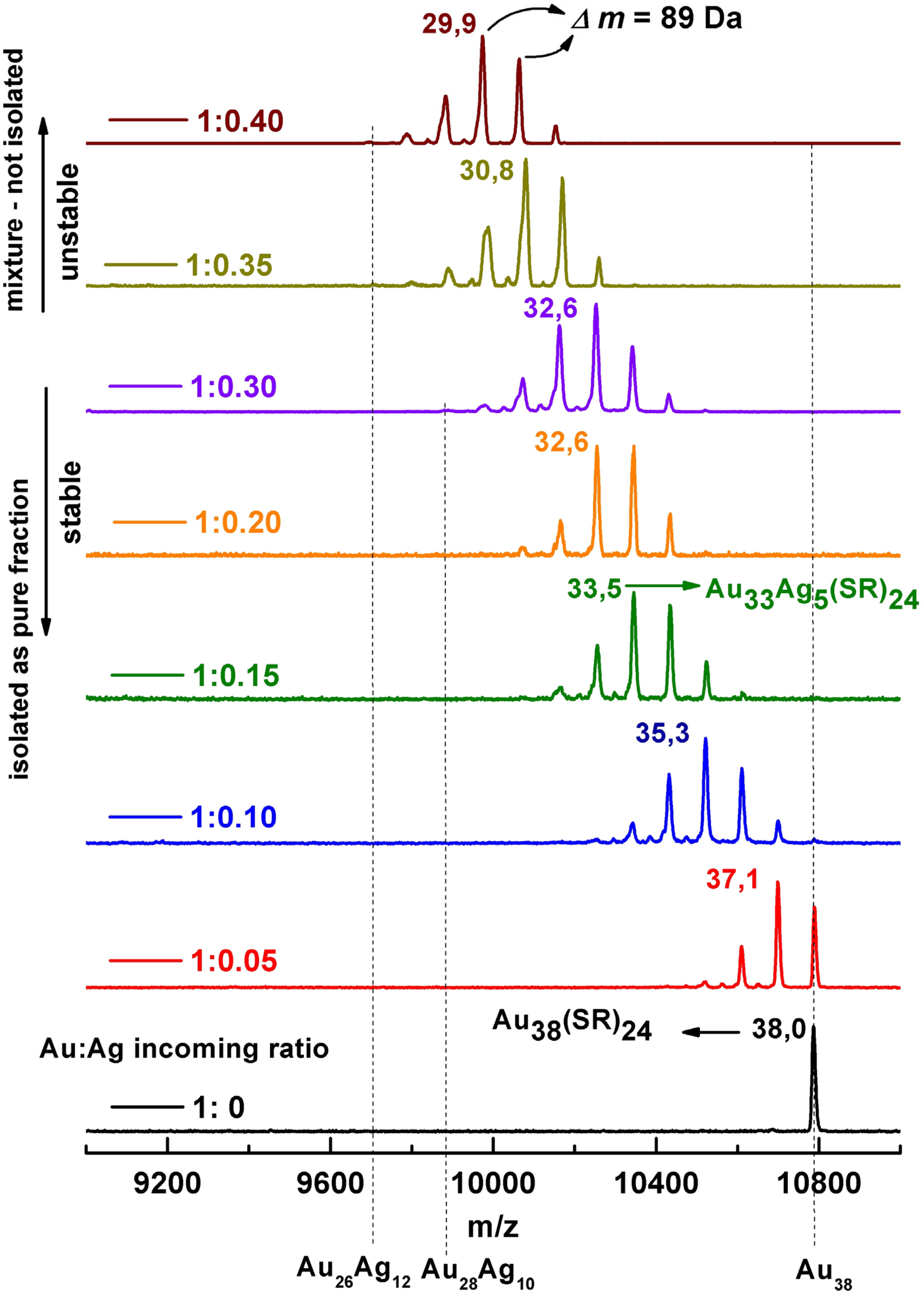
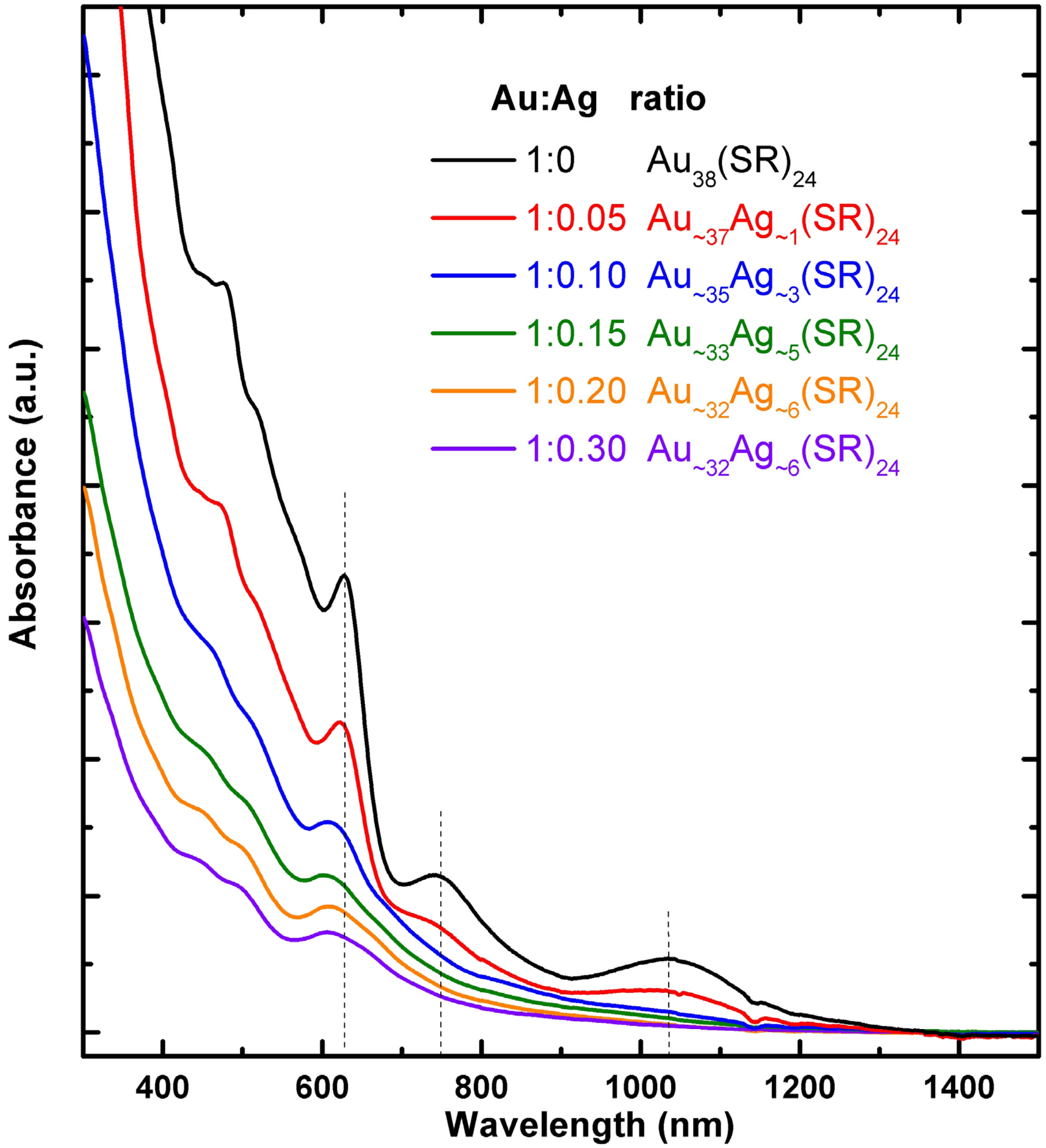


Fig. 3 *(Expansion of Figure 2 in the main article)* UV-vis spectra of $Au_{38-n}Ag_n(SR)_{24}$ nanomolecules in toluene with Au : Ag precursor ratios of 1 : 0 (black), 1 : 0.05 (red), 1 : 0.10 (blue), 1 : 0.15 (olive) and 1 : 0.20 (orange), 1 : 0.30 (purple) in the starting material



1. Y. Negishi, T. Iwai and M. Ide, *Chemical Communications*, 2010, **46**, 4713-4715.