Electronic Supplementary Information

Fluorescent Au-Ag Alloy Cluster Synthesis and SERS Applications

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Chemicals

Tetrachloro auric acid ($HAuCl_4$. $3H_2O$), silver nitrate ($AgNO_3$), 11-mercaptoundecanoic acid (MUA), tereakis(hydroxymethyl)phosphonium chloride (THPC), hexachloro platinate, cupric nitrate, glutathione reduced (GSH), L-cysteine (CYS), 2,5-dihydroxybenzoic acid (DHB) and methylene blue (MB) were purchased from Sigma-Aldrich. Sodium borohyrdied ($NaBH_4$), sodium hydroxide granules (NaOH) and sodium tetra borate were obtained from Merck India. Throughout the experiment high purity water (≈ 18.2 MΩ) was used. Dialysis tube (molecular cut off < 5 KDa) was purchased from Fischer-Chemicals. All the chemicals of highest purity grade were used without further purification.

One pot synthesis of gold nanocluster (AuNC)

In our modified method, different amounts (5 µL to 120 µL) of 1 wt % Au^{3+} were mixed with 3.75 mL water. Then, 500 µL of 50 mM borax or 50 µL (1M) NaOH was added without stirring. In this alkaline solution, 1.25 mL of 40 mM MUA in ethanol was added. Samples were kept for incubation at dark without stirring for 5-6 hours. To remove excess MUA, all samples were centrifuged at 5000 rpm for 5 min. Then, the supernatant was dialyzed for 6 hours to remove the unreacted Au^{3+}. These purified solutions were used throughout the experiment and stored in refrigerator. Solution having highest fluorescent intensity was used for further experiments.

Synthesis of gold nanoparticle or silver nanoparticle (AuNP or AgNP)

For synthesis of AuNP or AgNP, 0.25 mL of 1(M) NaOH was added to 0.50 mL of 80 % THPC solution in 22.5 mL water under stirring. 0.75 mL of 1 wt % Au^{3+} or Ag^{+} was added under vigorous stirring. Deep brown color solution indicates the reduction of Au^{3+} to Au^{0} or Ag^{+} to Ag^{0}. Vigorous stirring was continued for 30 min to confirm the complete reduction. Finally, these solutions are diluted and stored at 4^{0}C for further use.

Sample preparation for Stability of the alloy NC and SERS enhancement

To observed the stability of the AuAgNC, very high concentration (30 %) H_2O_2 and 220 mM of $NaBH_4$ was directly added. 10 µL of the AuNC or AuAgNC are drop casted on different glass slides then allowed to dry in ambient condition. 10 µL solution of MB of 0.1 mM was then allowed to adsorb on the NC surface and dried. One blank MB solution (without any NC) having same concentration was also prepared. All dried films of the analytes were used for SERS study.

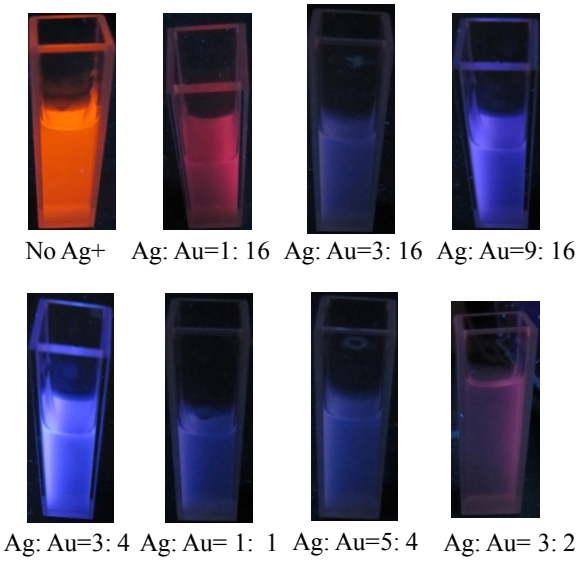

Figure S1. Digital photographs of the clusters with increasing Ag: Au ratio under excitation at 365 nm by UV torch.

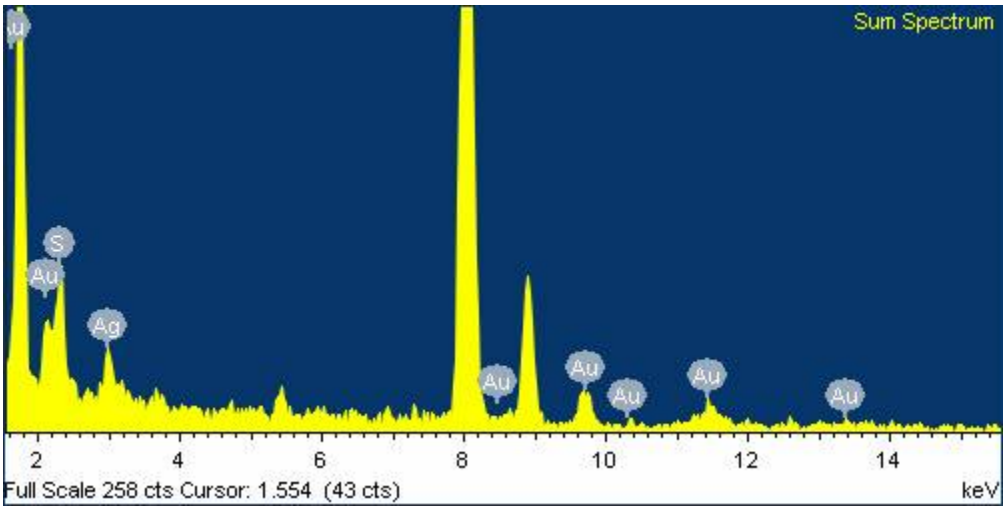

Figure S2. EDS of AuAg bimetallic cluster.

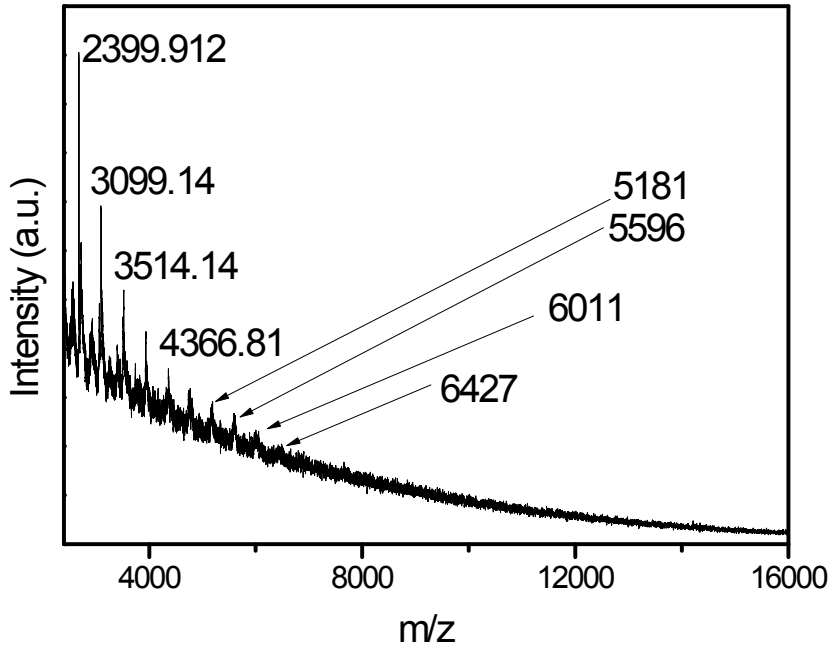

Figure S3. MALDI-TOF spectrum of Au cluster.

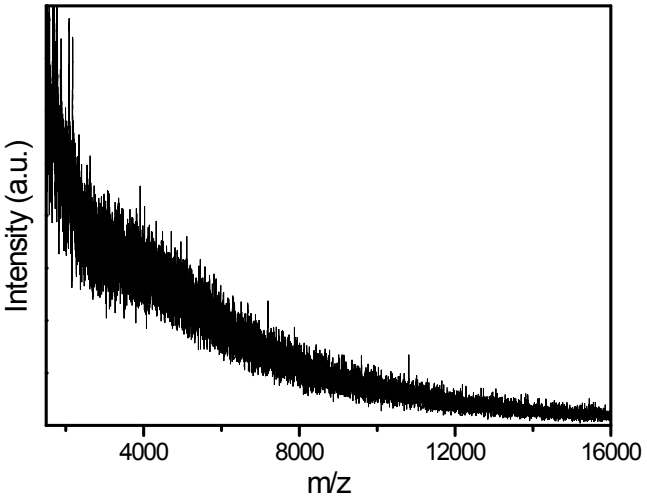

Figure S4. MALDI-TOF spectrum of AuAg alloy cluster.

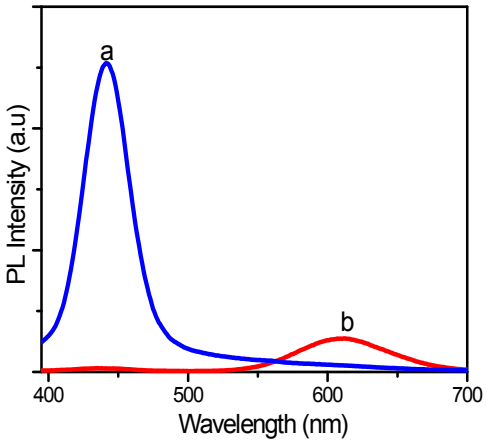

Figure S5. PL spectra of a mixture of AuNP and Ag^{+} (a for 48 hrs incubation and b for 6 hrs incubation)

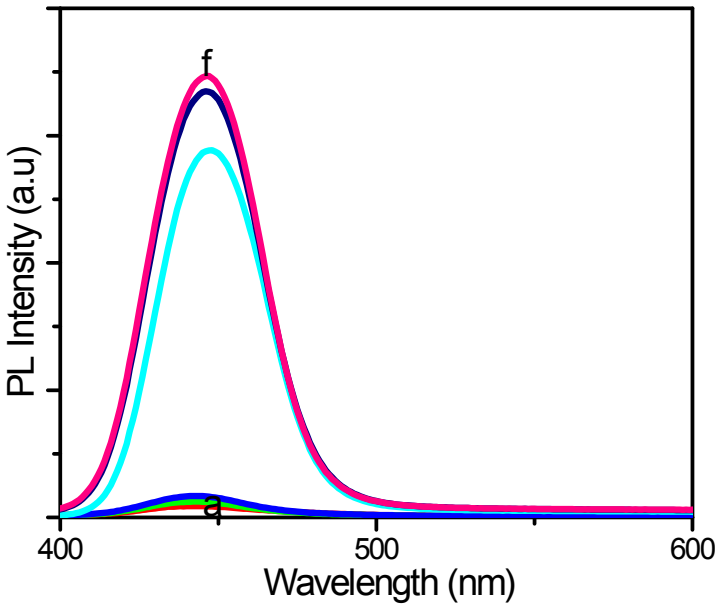

Figure S6. Photoluminescence spectra of the mixture of AgNP and Au^{3+} (a to f for 30 min to 2 days).