Supporting Information

Periodic Porous Alloyed Au-Ag Nanosphere Arrays and Their Highly Sensitive SERS Performance with Good Reproducibility and High Density of Hotspots

Tao Zhang,[ab] Yiqiang Sun,[ab] Lifeng Hang,[a] Huilin Li,[ab] Guangqiang Liu,[a] Xiaomin Zhang,[c] Xianjun Lyu,[d] Weiping Cai,[a] and Yue Li*[a]

a Key Lab of Materials Physics, Anhui Key Lab of Nanomaterials and Nanotechnology, Institute of Solid State Physics, Chinese Academy of Sciences, Hefei, 230031, P. R. China

b University of Science and Technology of China, Hefei, 230026, P. R. China

c College of Materials and Mineral Resources, Xi'an University of Architecture and Technology, Xi' an, 710055, P.R. China

d College of Chemical and Environmental Engineering, Shandong University of Science and Technology, Qingdao, 266590, P.R. China

*E-mail: yueli@issp.ac.cn

The enhancement factor (EF) of the porous alloyed Au-Ag NS arrays was estimated by the equation:

$$EF = \left(I_{SERS} / N_{ads}\right) / \left(I_{normal} / N_{normal}\right)$$

where I_{SERS} and I_{normal} are the characteristic peak at 1080 cm^{-1} for 10^{-7} M 4-ATP concentration and normal Raman peaks for 10^{-2} M 4-ATP concentration, respectively. N_{ads} and N_{normal} are the numbers of adsorbed molecules on the porous alloyed Au-Ag NS array substrates and Si substrates within the laser spot area. In the experiment, 5 μL of an aqueous 4-ATP solution was dropped onto the substrates.

N_{normal} and N_{ads} were estimated using the following equation:

$$N_{normal} = 5\times10^{-6} L \times 10^{-2} mol / L \times 6.02\times10^{23} mol^{-1} \times \left\{\frac{\pi\frac{d^2}{4}}{a^2}\right\} = 2.36\times10^{8}$$

$$N_{ads} = 5\times10^{-6} L \times 10^{-7} mol / L \times 6.02\times10^{23} mol^{-1} \times \left\{\frac{\pi\frac{d^2}{4}}{a^2}\right\} = 945$$

where the diameter of the laser spot (d) is about 1 um; a is the length of side of the substrates, $a = 5mm$.

Therefore,

$$EF = (I_{SERS} / N_{ads}) / (I_{normal} / N_{normal}) = 4.37\times10^{7}$$

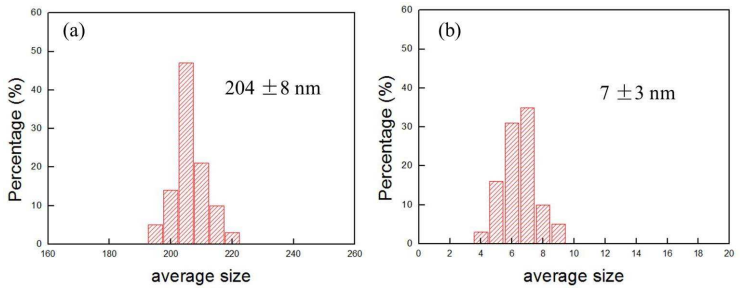

Figure S1. Particle size (a) and pore size (b) distribution of the porous alloyed Au-Ag NS arrays with a dealloying time of 60 min.

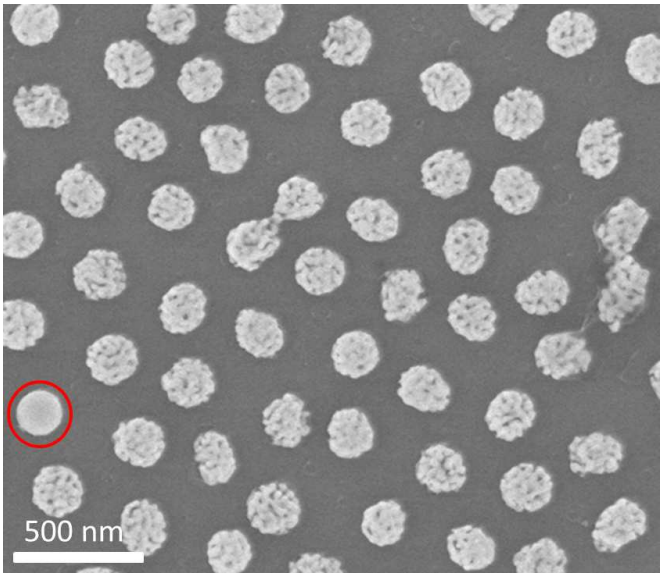

Figure S2. FESEM image of the porous alloyed Au-Ag NS arrays with a dealloying time of 60 min . Red circle indicate sparse solid alloyed Au-Ag NSs survived in the chemical dealloying process.

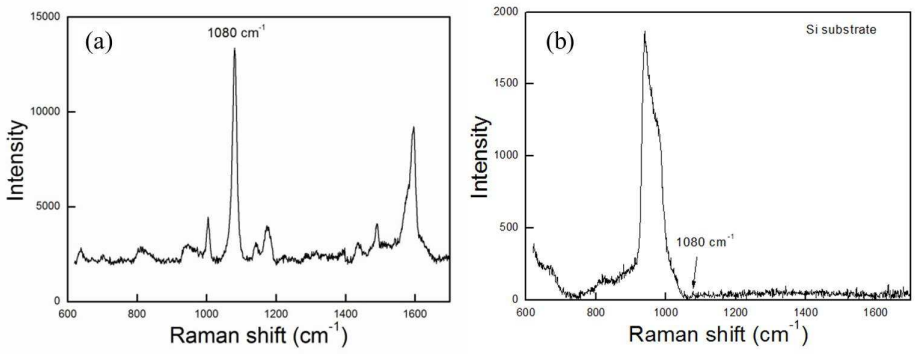

Figure S3. (a) Raman signal prepared by dropping 5 μl 4-ATP ethanol solution (10^{-7} M) on the porous alloyed Au-Ag NS arrays (area: 0.5 cm × 0.5 cm) with dealloying time of 60 min. (b) normal Raman signal obtained by depositing 5 μl of 4-ATP (10^{-2} M) ethanol solution on a silicon substrate (area: 0.5 cm × 0.5 cm). The laser power and integral time were set as 1 mW and 15 s, respectively.

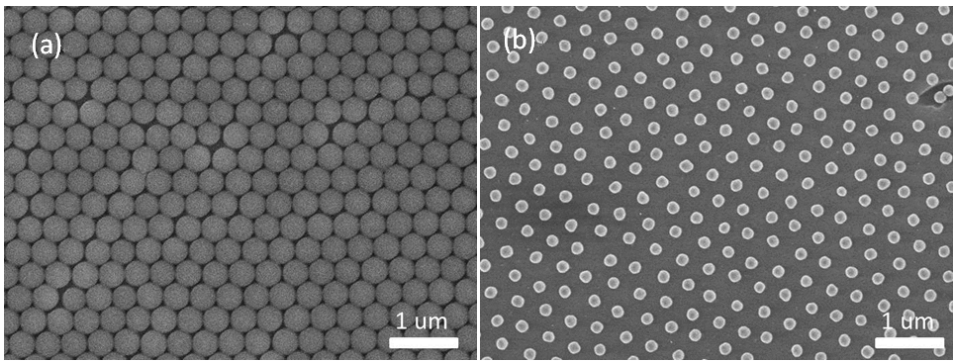

Figure S4. (a) Low-magnification FESEM images of PS monolayer colloidal crystals with diameter of 350 nm and (b) the corresponding periodic Au NS arrays.

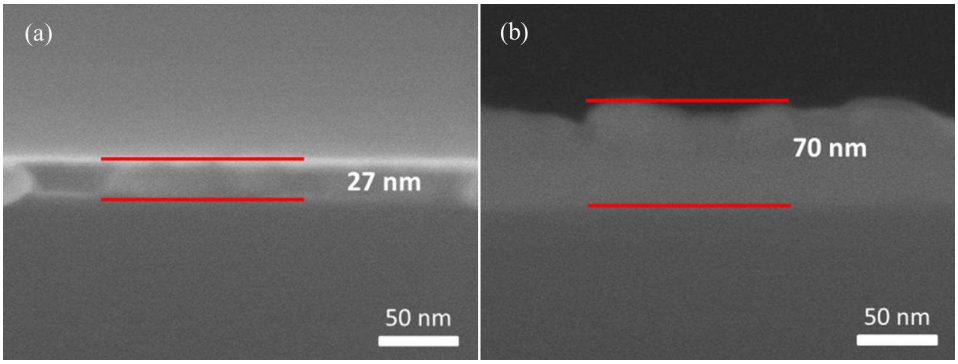

Figure S5. (a) Au film with the thickness of 27 nm obtained by the deposition process performed for 3 min. (b) Ag film with the thickness of 70 nm obtained by the deposition process performed for 10 min. FESEM observation indicates that the sputtering rate of Au and Ag was 9 and 7 nm/min, respectively. Thus, by controlling the sputtering time, we can get Au or Ag film with accurate thickness on substrates.

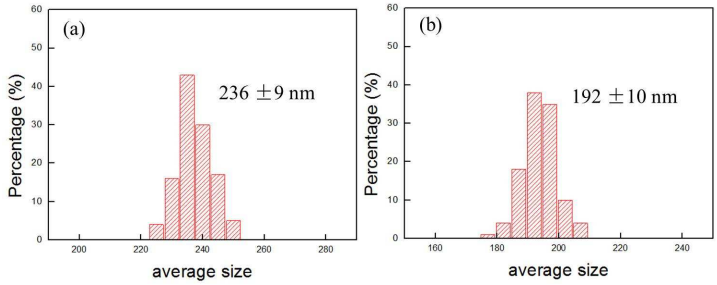

Figure S6. Particle size distribution of the porous alloyed Au-Ag NS arrays with a dealloying time of 30 min (a) and 90min (b).

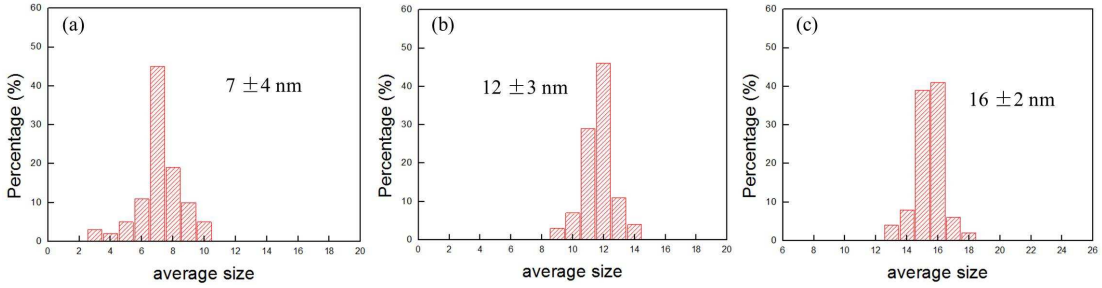

Figure S7. (a), (b) and (c): the ligament widths distribution of the porous alloyed Au-Ag NSs with a dealloying time of 30, 60, and 90 min, respectively.

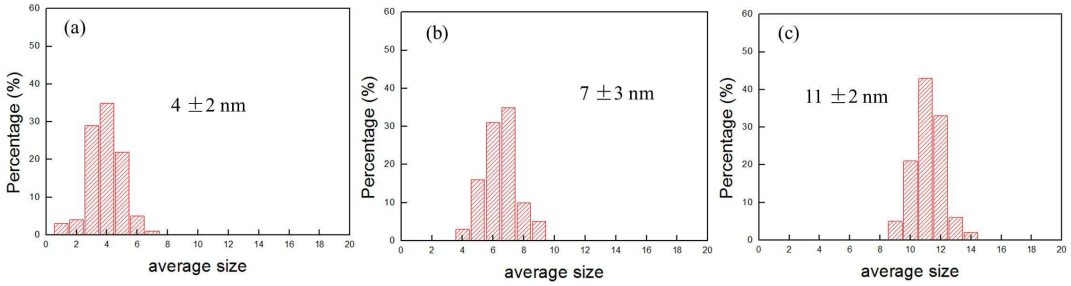

Figure S8. (a), (b) and (c): the pore size distribution of the porous alloyed Au-Ag NSs with a dealloying time of 30, 60, and 90 min, respectively.

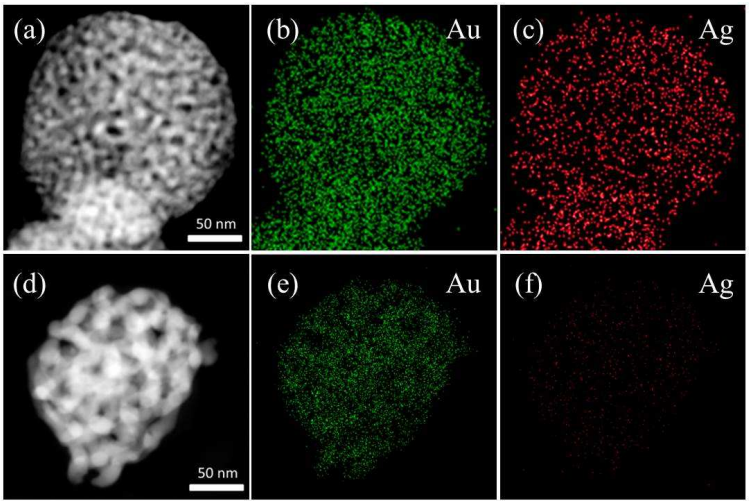

Figure S9. HAADF-STEM and EDS elemental mapping images of a single porous alloyed Au-Ag NS obtained at the dealloying time of 30 (a, b and c) and 90 min (d, e and f), respectively.

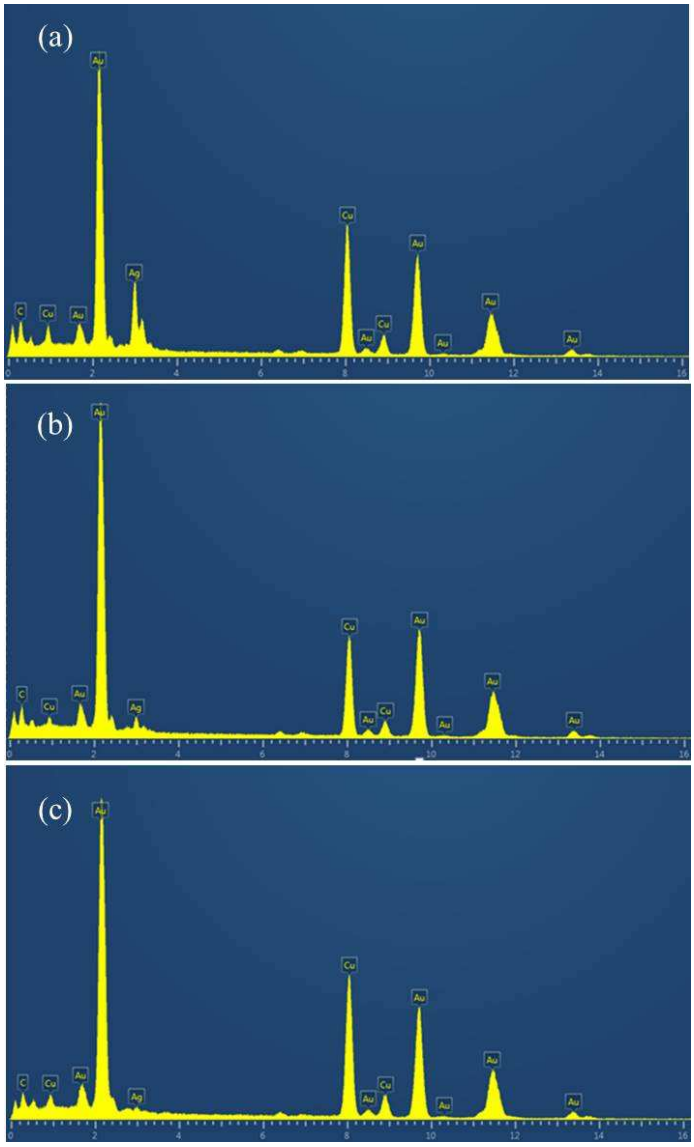

Figure S10. EDS of porous alloyed Au-Ag NS array with different dealloying time of (a) 30, (b) 60 and (c) 90 min obtained from EDS analysis. Cu and C are from carbon supported copper grid.

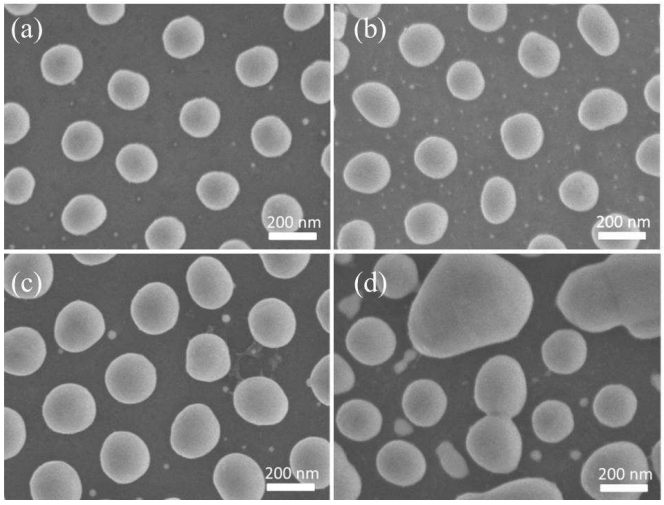

Figure S11. FESEM images of the solid alloyed Au-Ag NS arrays synthesized by annealing at 600 ℃ for 2 h after sputtering Ag for different thicknesses: (a) 42, (b) 56, (c) 70, and (d) 84 nm on Au NS arrays.

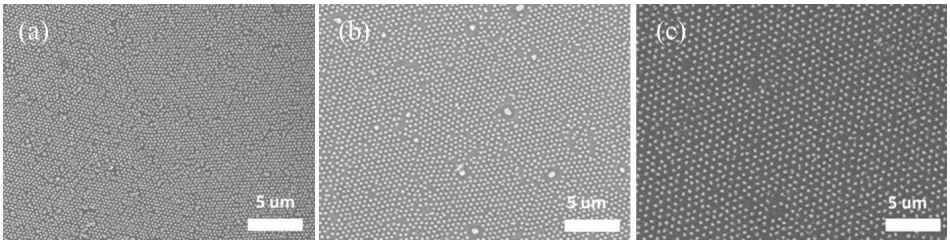

Figure S12. Low-magnification FESEM images of porous alloyed Au-Ag NS arrays with different periodic length: (a) 350, (b) 500, and (c) 750 nm.

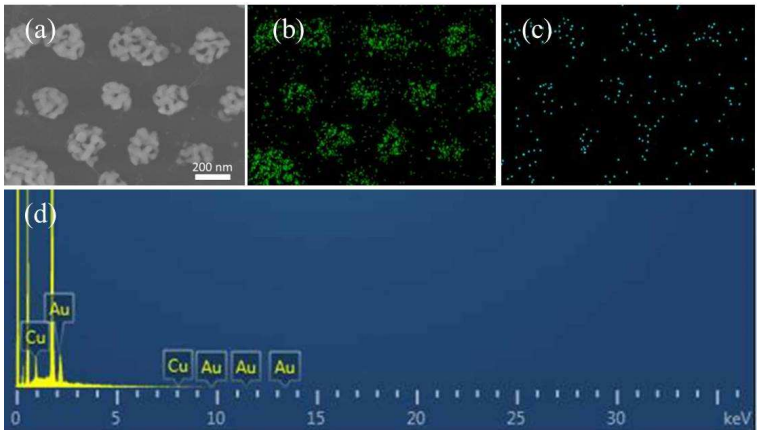

Figure S13. (a) SEM image of porous alloyed Au-Cu NSs array. EDS mapping of elementals distributions for (b) Au and (c) Cu. (d) EDS analysis obtained from (a).

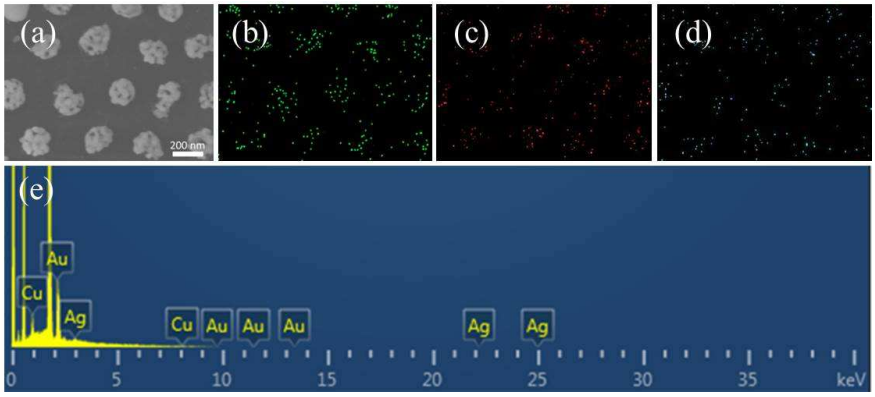

Figure S14. (a) SEM image of porous alloyed Au-Ag-Cu NSs array. EDS mapping of elementals distributions for (b) Au, (c) Ag and (d) Cu. (e) EDS analysis obtained from the porous alloyed Au-Ag-Cu NSs array.