Electronic Supplementary Material (ESI) for RSC Advances.

Highly Sensitive and Reliable SERS Probes based on Nanogap Control of Au-Ag Alloy on Silica Nanoparticle

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Enhancement factor:

1. Raman band : 1096 cm^{-1}

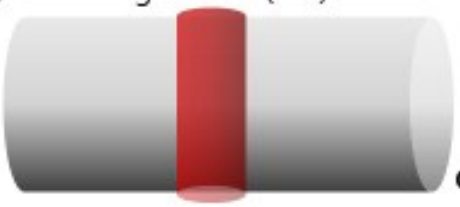
I_{SERS} = 1099.9 cps (all), 1818 cps (I>1000)

I_{NR} = 111.3 cps

cps = counts per second

2. N_{NR} / N_{SERS}

1) Scattering volume(S.V.) of normal Raman measurement



$$V = \pi r^2 \times h = 13.62\ um^3$$

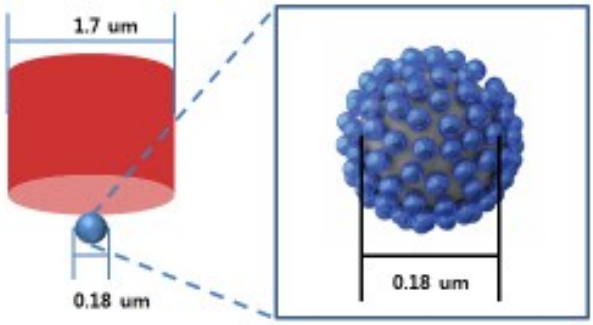
r = 0.85 um / h = 6 um

2) N_{NR} (molecules) : M.W. = 128.16 g/mole, Density(D) = 1.203 g/cm^3

$$N_{NR} = \frac{S.V. \times D}{M.W} \times N.A. = \frac{13.62\ um^3 \times 1.203\ g/cm^3}{128.16\ g/mole} \times 6.02 \times 10^{23} mol^{-1} = 7.7 \times 10^{10}$$

2) N_{SERS} = $\frac{Exposed\ surface\ area\ of\ Nanoprobe}{Area\ occupied\ by\ one\ molecule}$

2-1) exposed surface area of Au/Ag HSA



$$exposed\ surface\ area\ of\ Au/Ag\ \ HSA = \frac{1}{2} \times 4\pi(90\ nm)^2 \times 1.37 = 6.9 \times 10^4\ nm^2$$

(Roughness factor =1.37 Langmuir, 2006, 22, 8083)

Area occupied by one molecule = 0.383 nm^2/molecule (Langmuir, 2009, 25, 5012)

$$N_{SERS} = \frac{6.9 \times 10^4\ nm^2}{0.383\ nm^2/molecule} = 1.8 \times 10^5\ molecules$$

Enhancement Factor = $\left(\frac{I_{SERS}}{N_{SERS}} \div \frac{I_{NR}}{N_{NR}}\right)$

I_{SERS} = 1099.9 cps (all), 1818 cps (I>1000)

N_{SERS} = 1.8×10^5 molecules

I_{NR} = 111.3 cps

N_{NR} = 7.7×10^{10} molecules

For enhancement factor:

$$\frac{1099.9\ cps}{1.8 \times 10^5\ molecules} \div \frac{111.3\ cps}{7.7 \times 10^{10}\ molecules} = 4.2 \times 10^6$$

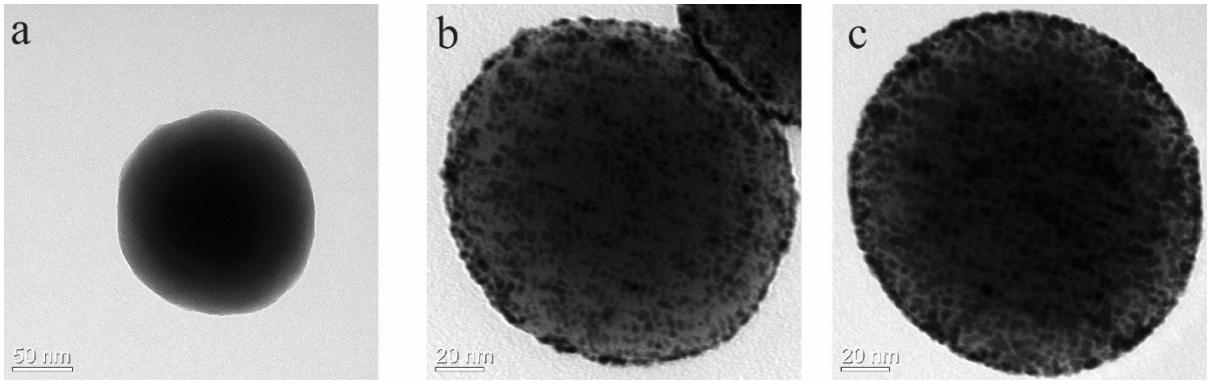


Figure S1. Transmission electron microscopic images of (a) SiO_2 NP and SiO_2@Au NP with SiO_2 modified with (b) NH_2 groups (APTS) and (c) SH groups (MPTS).

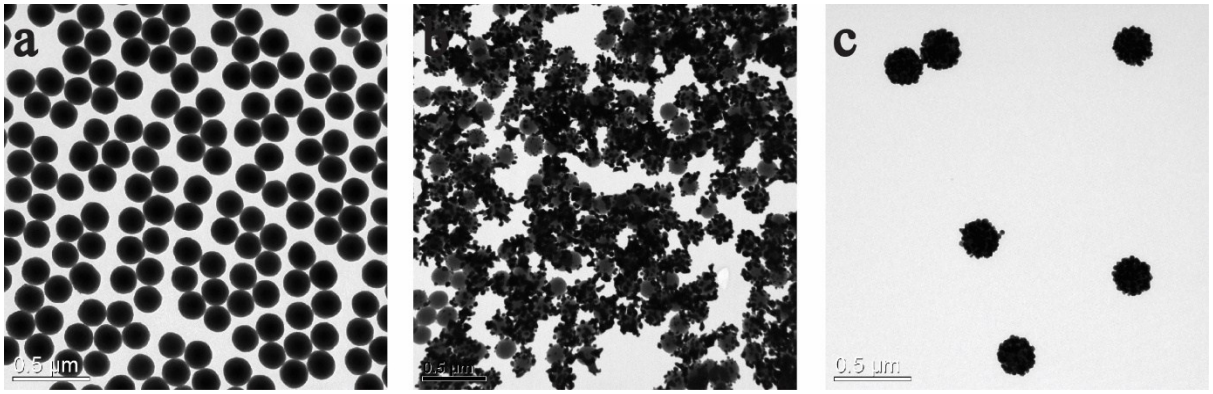


Figure S2. Transmission electron microscopic images of Au-SiO_2 NPs and Ag-Au alloy-based SiO_2 NPs with using (a) 1.0 mg mL^{-1} PVP, and (b) without using PVP, (c) Distribution of the SiO_2@Au@Ag NPs synthesized at 300 µM $AgNO_3$.

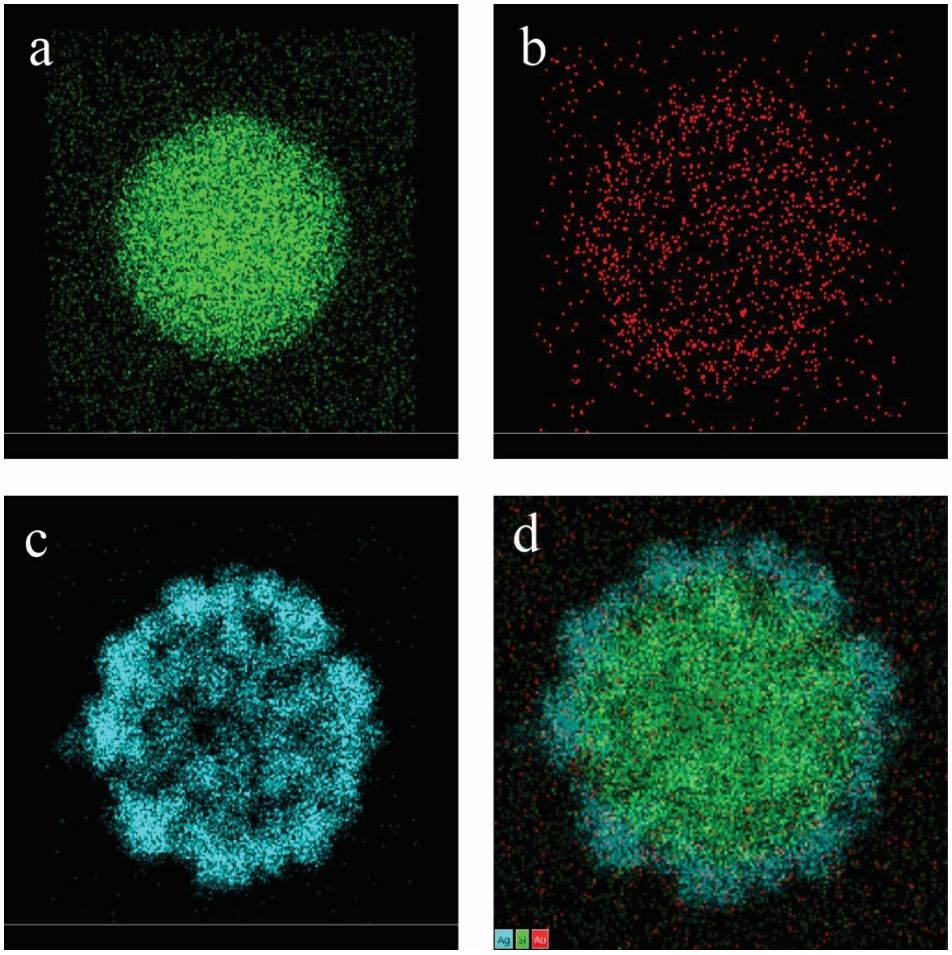


Figure S3. Energy-dispersive X-ray spectroscopy mapping images of (a) Si, (b) Au, (c) Ag, and (D) merged images of the Ag-Au alloy on SiO_2 NP.

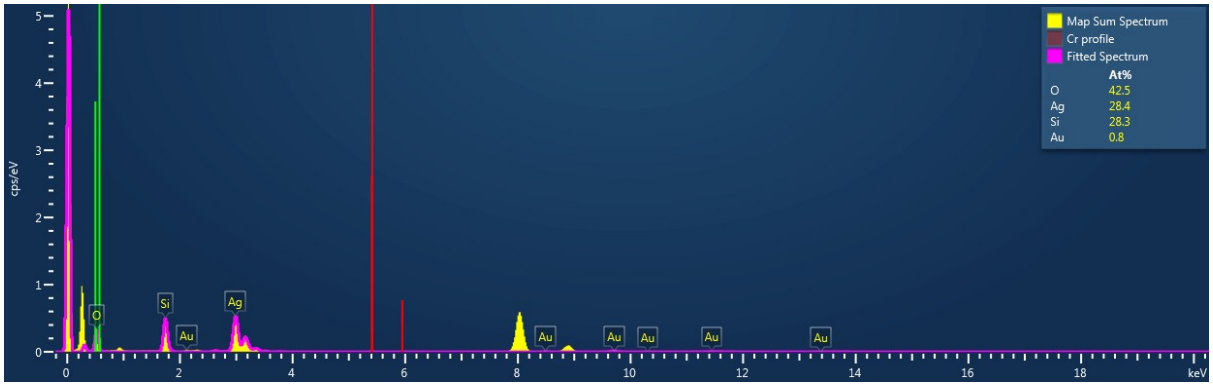


Figure S4. Atomic element components of the SiO_2@Au@Ag NPs synthesized at 300 μM $AgNO_3$.

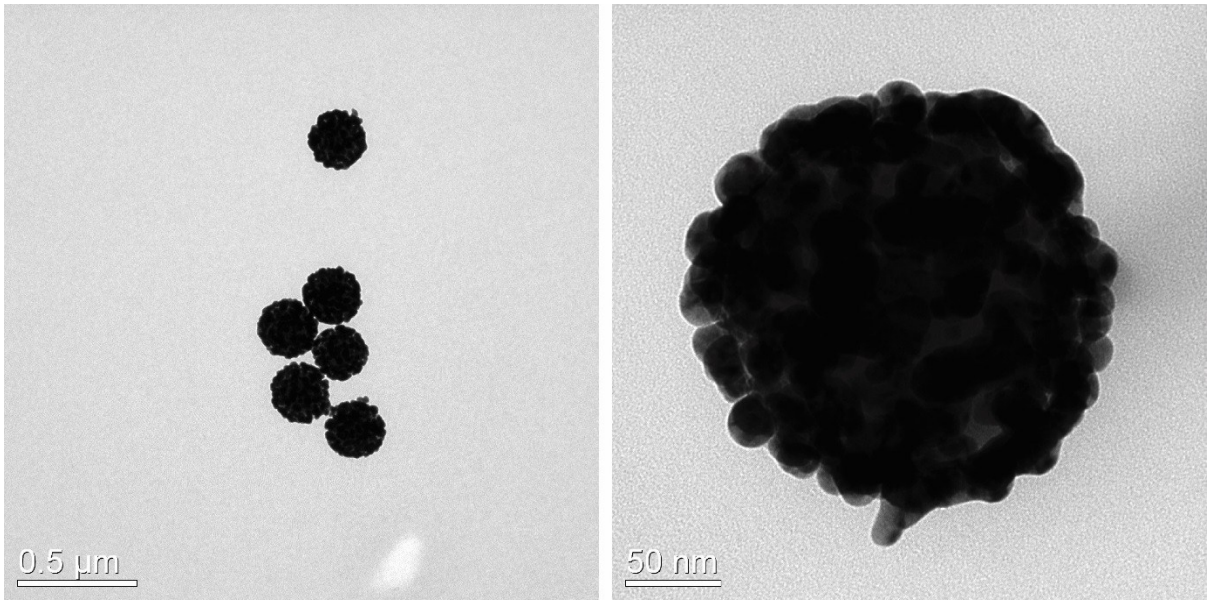


Figure S5. TEM images of SiO_2@Ag NPs with nanogaps.

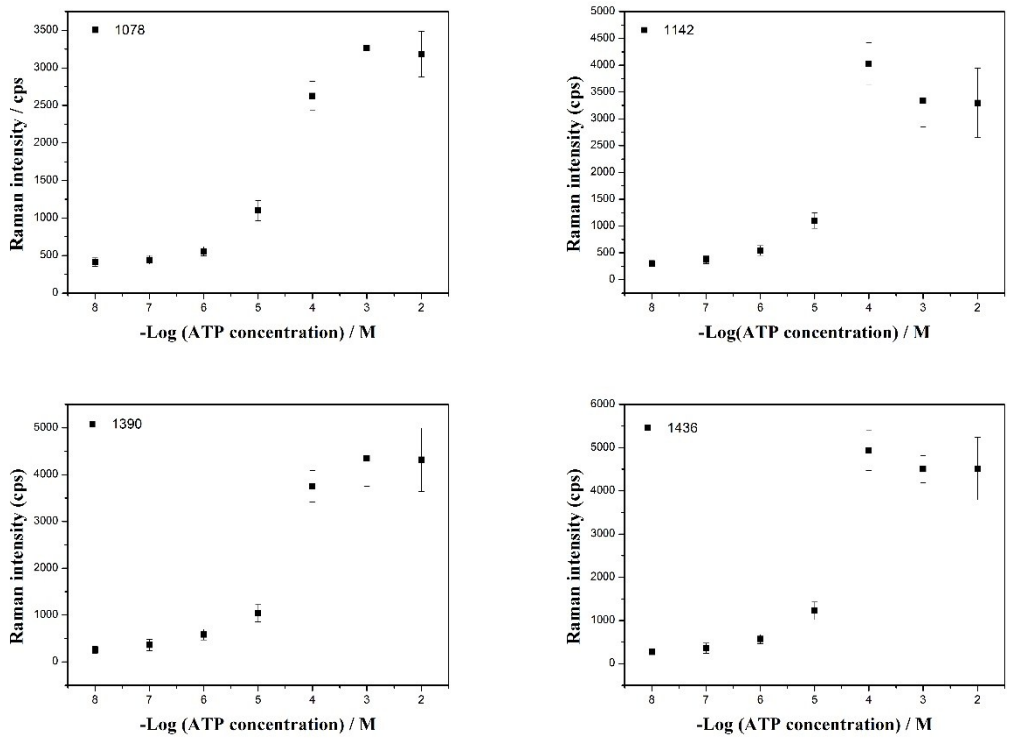


Figure S6. Calibration curves for the SiO_2@Au@Ag NPs at different ATP concentrations of 10^{-8}–10^{-2} M at 1,078, 1,142, 1,390, and 1,436 cm^{-1}, respectively. SERS spectra of 10 mM ATP were obtained using a 532 nm laser with 10 mW power for 5 s.

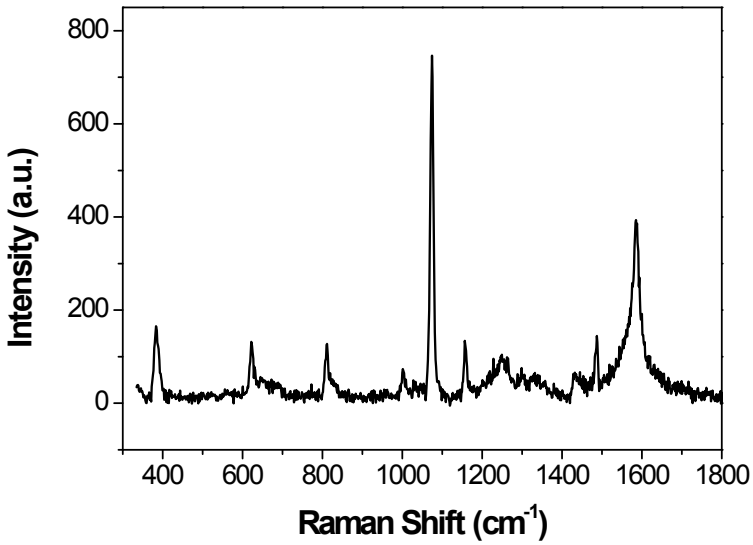


Figure S7. Typical SERS signal of single SiO_2@Au@Ag NPs bearing 4-FBT.

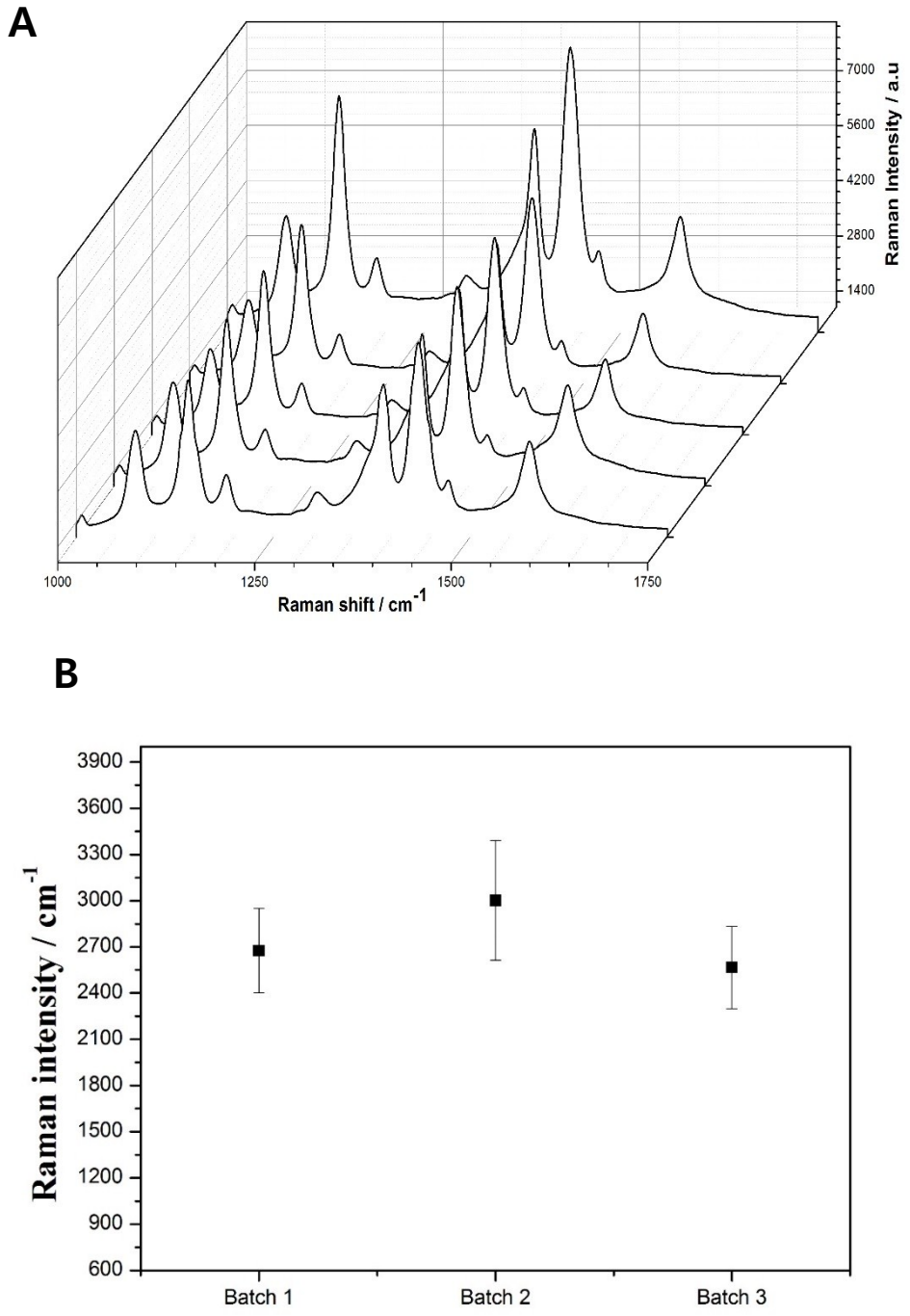


Figure S8. (A) Reproducibility curves and (B) plot of Raman signals of the SiO_2@Au@Ag NPs at 1,575 cm^{-1} for ATP. SERS spectra of 10 mM ATP were obtained using a 532 nm laser with 10 mW power for 5 s.

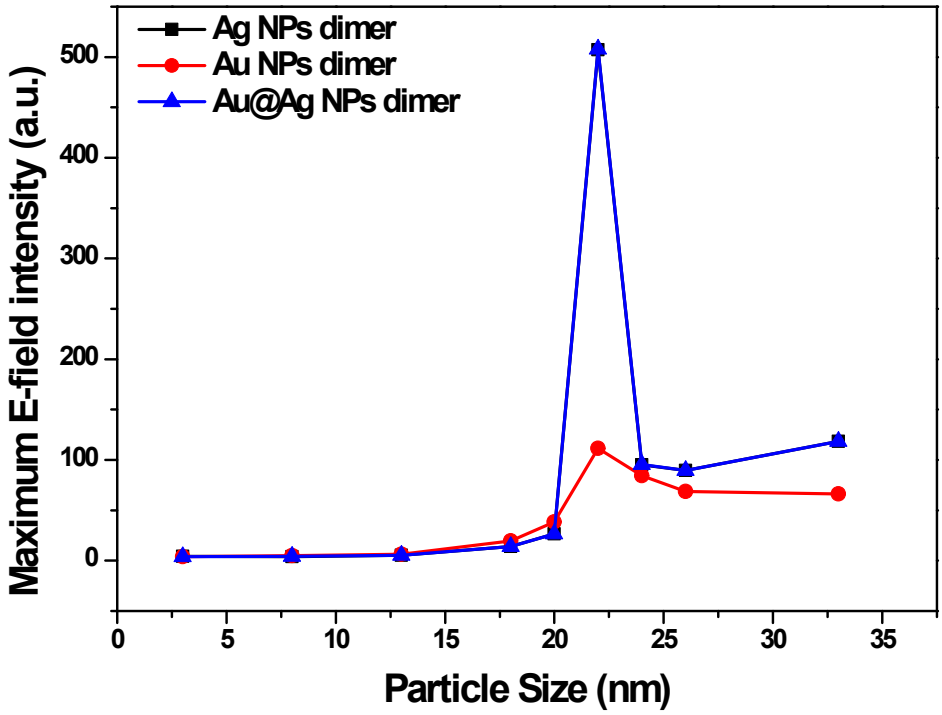


Figure S9. Theoretically calculated maximum E-field intensity of Ag, Au and Au@Ag NPs dimer with different particle sizes. Core Au NP size of calculated Au@Ag NPs dimer was 3 nm and Ag shell was grown as the particle size was increased. Black line means maximum E-field intensity of Ag NPs dimer and red and blue line mean those of Au and Au@Ag NPs dimer.