Supporting Information

Simply Controllable Growth of Single Crystal Plasmonic Au-Ag Nano-spines with Anisotropic Multiple Site for Highly Sensitive and Uniform Surface-Enhanced Raman Scattering Sensing

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S1 Calculation of SERS enhancement factor

The SERS enhancement factors of CV molecules on single Au@Au-Ag were estimated according to the following equation:[1]

$$EF = (I_{surface} / I_{solution}) \times (N_{solution} / N_{surface})$$

Where,

$N_{solution}$ represent the numbers of CV molecules probed in a reference 10^{-1} M CV aqueous solution;

$N_{surface}$ represent the numbers of CV molecules probed on the surface of single Au@Au-Ag;

$I_{solution}$ represent the signal intensities of CV molecule Raman spectra probed in CV aqueous solution;

$I_{surface}$ represent the signal intensities of CV molecule Raman spectra on the surface of single Au@Au-Ag;

The number of the probed CV molecules was:

$N_{solution} = 6.02 \times 10^{23} \times 10^{-1}\ \mathrm{M} \times 400\ \mu m^3 \sim 2.5\times10^{10}$

Where the effective excitation volume of the CV solution (concentration is 10^{-1} M) probed with the
Raman microscope using a low-magnification objective (10×) was ~400 μm^3.

Their Raman intensity obtained without the decreases by a D2 attenuation piece (×100) at the
peak of 1172 cm^{-1} was:

$I_{solution} = 667/100 = 6.67$ (counts)

The SERS signal intensity of probed CV molecules on a single Au@Au-Ag ($I_{surface}$) was estimated from the height of Raman spectra peak at 1172 cm^{-1}.

The number of CV molecules probed on a single Au@Au-Ag ($N_{surface}$) was estimated with following equation:

$N_{surface} = D_{CV} \times S_p$

Where,
D_{CV} represent the the density of CV molecules on the Au@Au-Ag substrate;
S_p represent the the surface area probed on the single Au@Au-Ag;

The D_{CV} can be caculated as following:

$D_{CV} = N_{CV\text{-}total}/S_{total} = N_{CV\text{-}total}/(S_{sio2} + S_{mp\text{-}total}) = N_{CV\text{-}total}/(S_{si} + N_{mp} \times S_{mp})$

Where,
$N_{CV\text{-}all}$ represent the total number of CV molecules adsorbed on the SERS substrate;
S_{total} represent the total surface area of the SERS substrate including the area of glass substrate and the total surface area of all of the Au@Au-Ag on the substrate;

$S_{mp\text{-}total} = N_{mp} \times S_{mp}$

Where,
N_{mp} represent the number of Au@Au-Ag;
S_{mp} represent the surface area of a single Au@Au-Ag;

SERS substrate with area of 0.7 cm × 0.7 cm, 25 μL of a 10^{-5} M aqueous CV solution were dropped.
Considering some aggregates (non-monolayer) exist in some areas, the number of the Au@Au-Ag on the substrate (N_{mp}) can be estimated as: $Np= 2 \times 50\% \times S_{sio2} / \pi r^2$

Where,
r represent the average radius of the Au@Au-Ag;
The surface area of a single Au@Au-Ag was estimated as following equation, assuming X% surface area of the base spherical particles is covered by spines:

$S_p = N_{tip} \times S_{tip} + X\% \times S_{sphere}$

N_{tip} represent the number of spines on Au@Au-Ag;
S_{tip} represent the surface area of spines on Au@Au-Ag;
S_{sphere} represent the surface area of the base sphere;

The surface area of the base sphere (S_{sphere}) can be calculated as: $S_{sphere} = 4\pi r_1^2$
Where,
r_1 represent the radius of the base sphere;

Assuming X% surface area of the base sphere is covered by spines, the number of spines can be estimated as: $N_{tip} = X\%\times S_{sphere}/(\pi r_a^2)$;
Where,
r_b represent the radius of the bottom surface of the spine;
The surface area of a spine can be calculated as following:

$\pi\times r_b\times(L+L_1) - \pi\times r_t\times(L+L_1) + \pi\times r_t^2$

Where,
L represent the length of the spine;
L_1 represent the length of the absence top part of the conus-like spine;
r_b represent the radius of the bottom surface of the spine;
r_t represent the radius of the top surface of the spine;

For Au@Au-Ag-1, the average radius of Au@Au-Ag-1 is 50nm, the radius of the base sphere is 40nm, the radius of the petal is 10nm.$I_{surface}$=10160 counts. X%=80%
(1) S_{sphere}=20096 nm^2

(2) The superficial area of single petal: $0.5\times 4\pi r_1^2$=628 nm^2

(3) N_{tip}=51.2
(4) S_p=36172.8 nm^2

(5)$N_p=9.7\times 10^9$

(6)$S_{ptotal}=3.5\times 10^{14}$nm

(7) $N_{CV\text{-}all}=1.5\times 10^{14}$

(8) D_{CV}=0.4

(9)$N_{surface}=1.45\times 10^4$

EF=2.619×10^9

For Au@Au-Ag-2, the average radius of Au@Au-Ag-2 is 75nm, the length of spine is 12nm, the radius of the base sphere is 63nm, the top radius of the spine is 3nm, the bottom radius of the spine is 5nm. $I_{surface}$=2418 counts. X%=50%
(1) S_{sphere}=49850.64 nm^2
(2) S_{tip} =246.1 nm^2
(3) N_{tip}=317.52

(4) $S_p=8.8\times 10^4$ nm^2

(5)$N_p=2.77\times 10^9$

(6)S_{ptotal}=2.44×10^{14}nm

(7) $N_{CV\text{-}all}$=1.5×10^{14}

(8) D_{CV}=0.559

(9)$N_{surface}$=4.92×10^{4}

EF=1.84×10^{8}

For Au@Au-Ag -3, the average radius of Au@Au-Ag-3 is 100nm, the length of spine is 32.5nm, the top radius of the spine is 3nm, the bottom radius of the spine is 5nm. $I_{surface}$=13098 counts. X%=80%
(1) S_{sphere}=57226.5 nm^2
(2) S_{tip} =649nm^2
(3) N_{tip}=583.2

(4) S_p=3.9×10^5 nm^2

(5)N_p=1.56×10^9

(6)S_{ptotal}=6.084×10^{14}nm

(7) $N_{CV\text{-}all}$=1.5×10^{14}

(8) D_{CV}=0.237

(9)$N_{surface}$=0.924×10^5

EF=5.313×10^8

S2 Electromagnetic field calculation of Au@Au-Ag

The 3D models of Au@Au-Ag is shown in the Fig.S12. The Au@Au-Ag-1 with 80 nm cores diameter and randomly covered by petals, the radius of the petal is 10nm. The Au@Au-Ag-2 with the radius of the base sphere is 63nm and randomly covered by thin spines, the length of spine is 12nm, the top radius of the spine is 3nm, the bottom radius of the spine is 5nm. The Au@Au-Ag-3 with the radius of the base sphere is 100nm and randomly covered by dense spines, the length of spine is 32.5nm, the top radius of the spine is 3nm, the bottom radius of the spine is 5nm.

The three-dimensional FDTD simulation was used to calculate the local electric field of the models at excitation wavelengths of 514 nm, 600 nm, 633 nm, 700 nm, 785 nm and 840 nm respectively. The incident light was a plane wave propagating along the x-axis and electric field direction was y-axis and magnetic field orientation was z-axis. It was assumed that each model was suspended in air (n0=1.0). The grid size was 1 nm and the scale bar of local electric field is based on the log value.

Table S1. A detailed Raman band assignment of CV and MG in Raman spectra relative to Ref 2.[2]

Raman band assignment	Raman shift of CV (cm^{-1})	Raman shift of MG (cm^{-1})
N-Phenyl stretching	~1362 and 1371	
C-H rocking	~1211	~1219
Ring C-H in-plane vibrations	~1177	~1169
Ring C-H out-plane vibrations	~732 and 810	~736 and 798
Ring skeletal vibrations of radical orientation	~528 and 915	~530 and 913
Out-of-plane vibrations of	~420	~421

Pheny-C-Phenyl

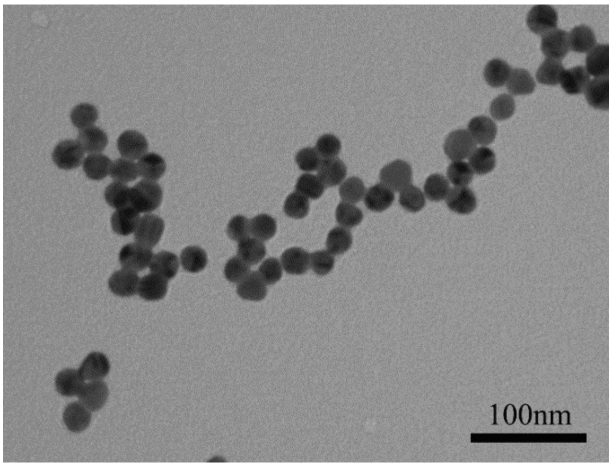


Figure S1. TEM image of Au nanoparticals used as seeds for the synthesis of Au@Au-Ag.

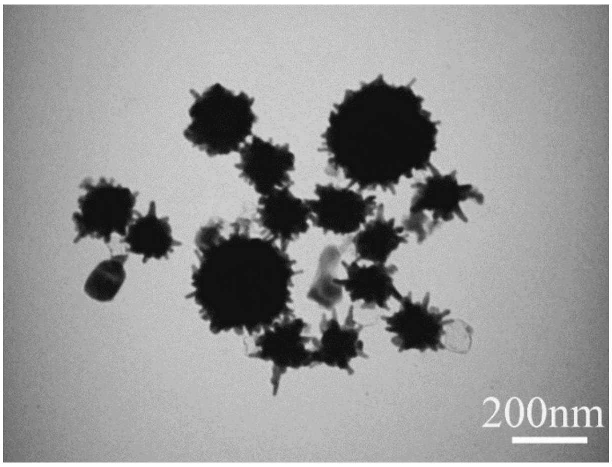


Figure S2. The added $AgNO_3$ solution was 240 uL, nonuniform morphology (Au@Au-Ag-4) was obtained.

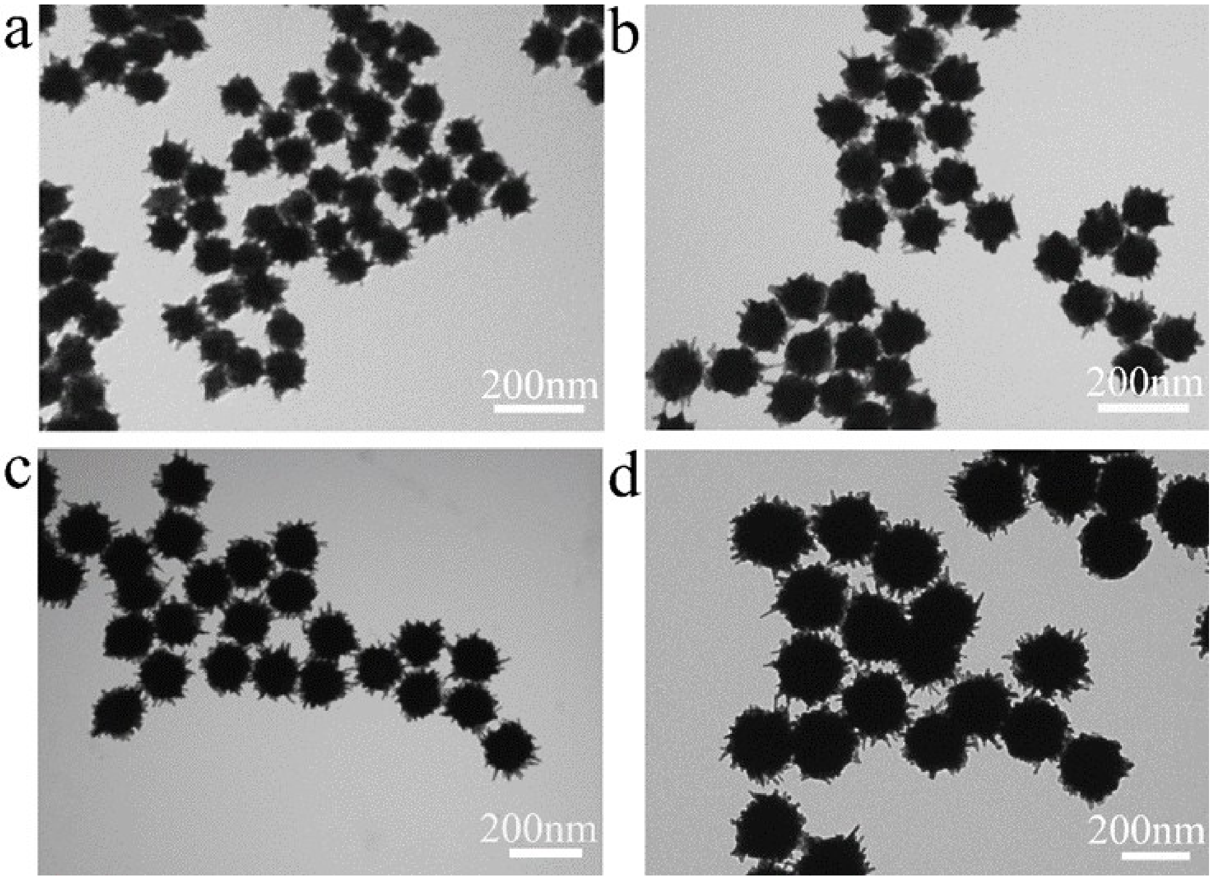


Figure S3. TEM of Au@Au-Ag-3 with different size synthesized via different seeds amount, the volume of $AgNO_3$ (10 mM) is consistent (96 uL), (a) 100 nm, (b) 120 nm, (c) 150 nm, (d) 300 nm, respectively.

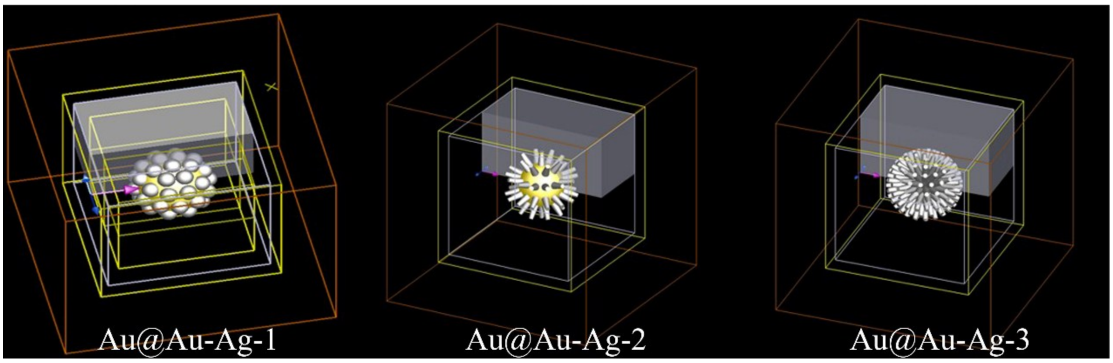


Figure S4. The finite difference time domain (FDTD) model of Au@Au-Ag. For Au@Au-Ag-1 model, the average radius is 50nm, the radius of the base sphere is 40nm, the radius of the petal is 10nm. For Au@Au-Ag-2 model, the average radius is 75nm, the length of spine is 12nm, the radius of the base sphere is 63nm, the top radius of the spine is 3nm, the bottom radius of the spine is 5nm. For Au@Au-Ag-3 model, the average radius is 100nm, the radius of the base sphere is 67.5nm the length of spine is 32.5nm, the top radius of the spine is 3nm, the bottom radius of the spine is 5nm.

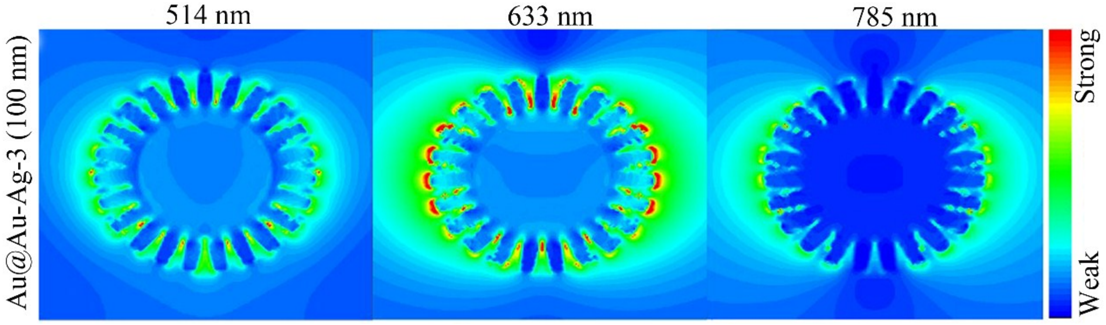


Figure S5. The FDTD calculation-based electromagnetic field enhancements and distributions of Au@Au-Ag-3 (100nm) at 514, 633 785 nm excitation wavelengths.

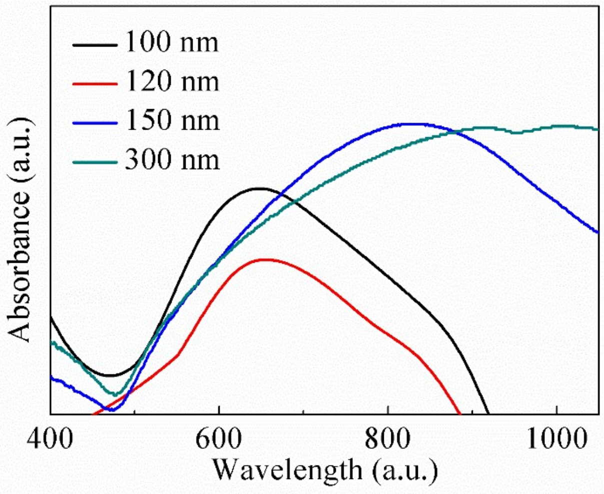


Figure S6. UV-vis spectra of Au@Au-Ag -3 with various particle sizes (100–300 nm) measured in

DI water shown in Fig. S3

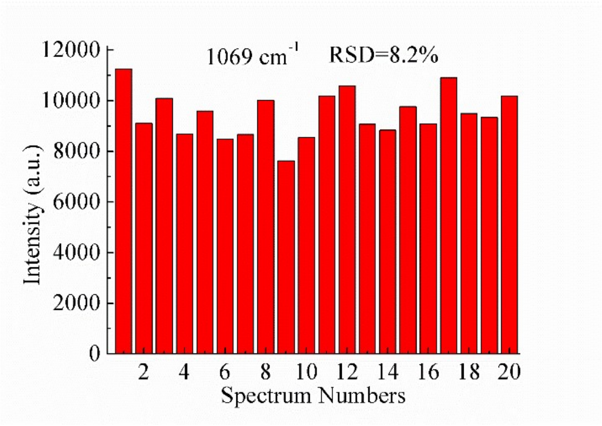


Figure S7. Histogram of SERS intensity at 1069 cm^{-1} of the 20 spectra in Fig. 6c

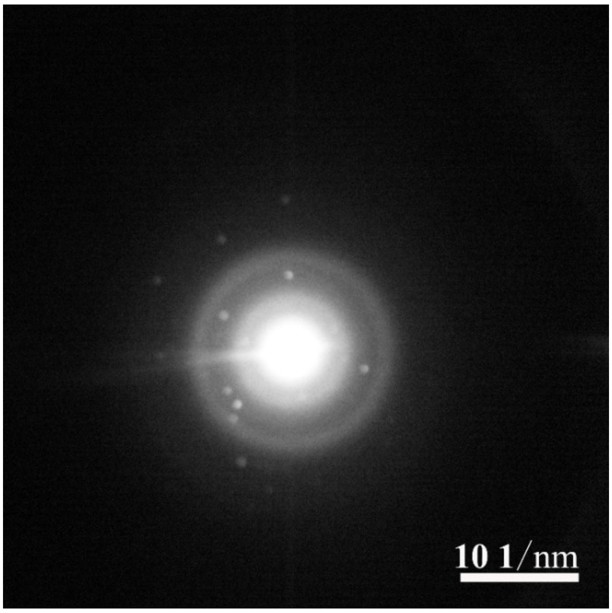


Figure S8. The single crystal diffraction spot of single Au nanoparticle used as seeds.

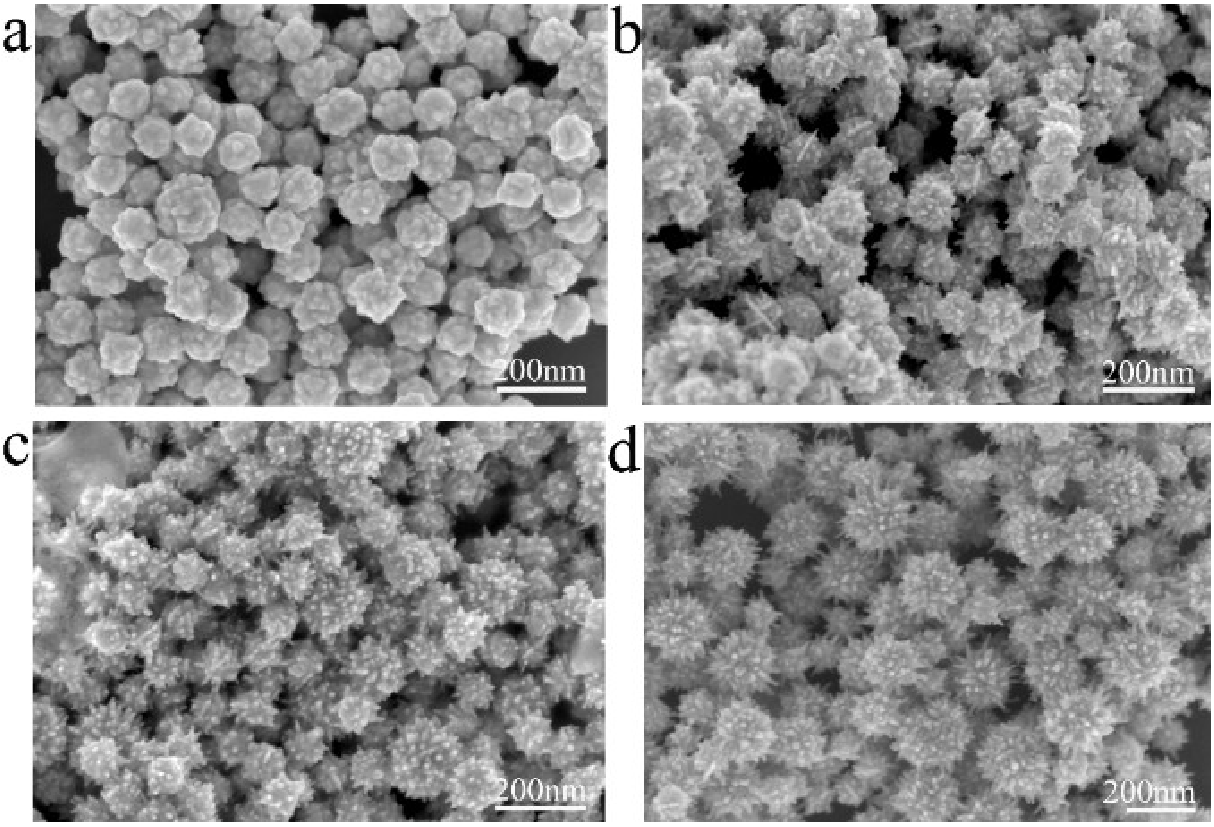
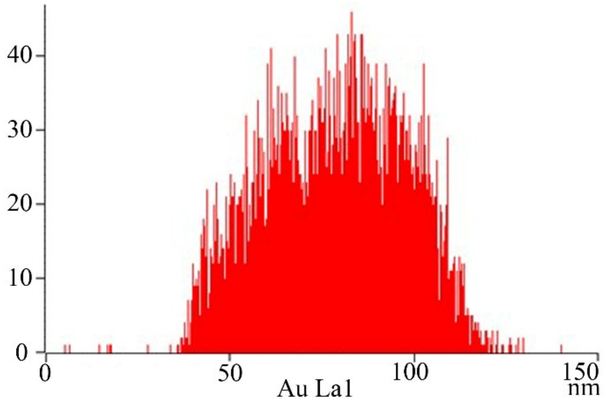
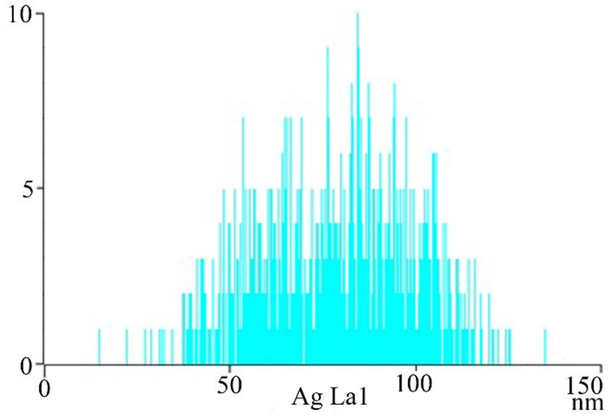


Figure S9. SEM of Au@Au-Ag synthesized via $AgNO_3$-controlled chemistry and seed-mediated growth route. (a) Au@Au-Ag-1, (b) Au@Au-Ag-2, (c) Au@Au-Ag-3, (d) Au@Au-Ag-4, respectively


40
30
20
10
0
0
50
100
150
Au La1
nm


10
5
0
0
50
100
150
Ag La1
nm

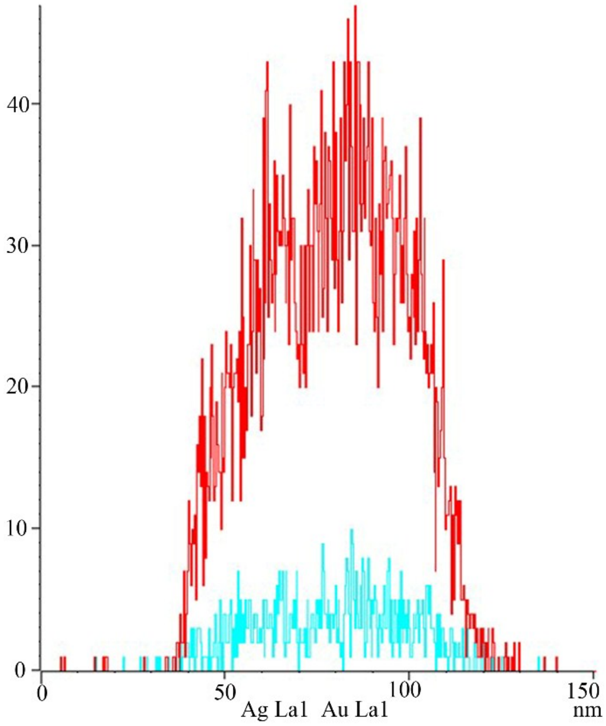


Figure S10. The element line scanning of Au@Au-Ag-3 (100nm). Under the chemical reduction, forming Au-Ag Alloy. The line scan results support this view because the profiles Ag and Au show the similar width.

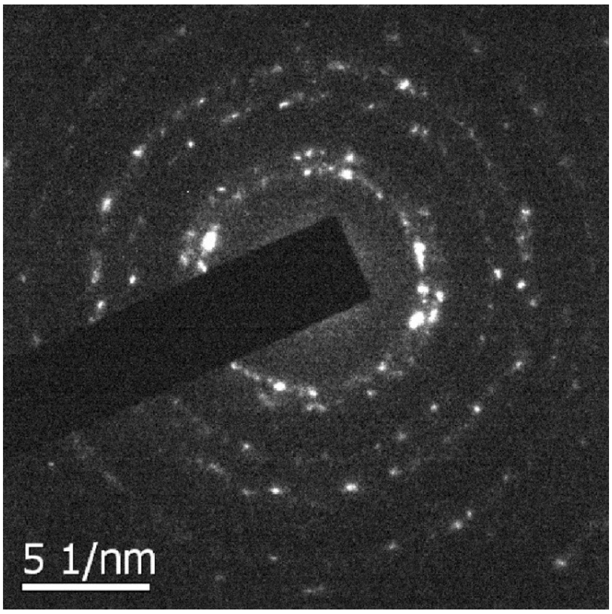


Figure S11. The SAED pattern of single particle Au@Au-Ag-3 with size of 100nm.

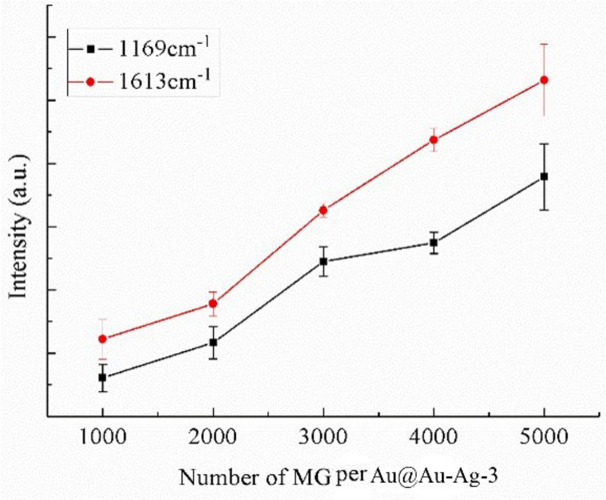


Figure S12. SERS intensity at 1169 and 1613 cm^{-1} as a function of the average number of MG molecules loaded in each particle.

References

1. Z. Liu, Z. Yang, B. Peng, C. Cao, C. Zhang, H. You, Q. Xiong, Z. Li and J. Fang, *Adv. Mater.*, 2014, **26**, 2431-2439.
2. J. Huang, D. Ma, F. Chen, M. Bai, K. Xu and Y. Zhao, *Anal. Chem.*, 2015, **87**, 10527-10534.