Supporting information for

Tunable Plasmonics of Hollow Raspberry-like Nanogold for Robust Raman Scattering Detection of Antibiotic on Portable Raman Spectrometer

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Sample preparation

Au seed

The synthesis of normal Au (N-Au) particles is described by a seed-growth method. Firstly, the synthesis of Au seed is the same as Ag seed. 1 mL of $HAuCl_4 \cdot 4H_2O$ (1%) aqueous solution was dissolved with 150 mL of water and then boiled under vigorous stirring. Then, 5 mL of Trisodiumcitrate (NaCt) (1%) aqueous solution was used as a reductant and quickly added. The reaction was allowed to proceed for 30 min. This solution was used as Au seeds to prepare N-Au.

N-Au particle

5 mL CTAB (1%) and 1 mL $HAuCl_4 \cdot H_2O$ (5 mM) were added into a flask under vigorous stirring. Then, 70 μL AA (0.1 M) was added as reductant. The solution was used as growth solution. 4 mL of above Au seed solution was added into it under mild magnetic stirring for 10 min. Then the mixture was setting quietly for 1h to allow the N-Au growing completely. The dispersions were centrifuged (5 min at 4000 rpm), and the precipitates were washed three times with ultrapure water. Finally, the samples were both concentrated in at a 10:1 scale. The Au NRs obtained were labelled N-Au.

Enhancement factor calculation

The optical enhancement properties of the R-like Au-2 were tested using crystal violet (CV) as a model analyte. The following equation was used to estimate the enhancement factors (EF):

$$EF = \frac{I_{SERS}}{N_{surf}} \div \frac{I_{Raman}}{N_{bulk}}$$

where I_{SERS} and I_{Raman} are the integrated intensities of a vibrational mode in SERS and Raman spectra, respectively, N_{surf} and N_{bulk} are the numbers of molecules probed in the SERS and Raman measurements.

Herein, I_{SERS} represents the SERS intensities at 913 cm^{-1} collected from CV with the concentration of 10^{-10} M as shown in Fig. 4A, which is about 1460 cnts. I_{Raman} represents the Raman intensities at 913 cm^{-1} collected from CV with the concentration of 10^{-9} M on Si wafers, which is about 250 cnts under the similar experimental setup as shown in Fig. S6

N_{surf} is the average number of adsorbed molecules in the scattering volume for the SERS measurements. 1 μL of R-Like colloidal produced a deposition area of 1 mm in diameter. Considering an area ratio of approximately 6 $\times 10^5$ ($\pi \times 0.52\ mm^2/\pi \times 0.652\ \mu m^2$) between the deposition area and the laser spot and assuming uniform distributions of all particles and molecules, there was an average of 10^8 molecules ($10^8 = 10^{-10}$ M $\times 6 \times 10^{23}$ molecules/mol/6 $\times 10^5$) within the scope of the laser spot (1.29 μm in diameter). N_{bulk} is the average number of molecules in the scattering volume for the Raman measurements, and can be calculated to be about 10^{13} within the scope of the laser spot.

A conservative EF for the CV molecules on the R-like Au colloidal can be calculated to be about 10^6.

Figures and tables:

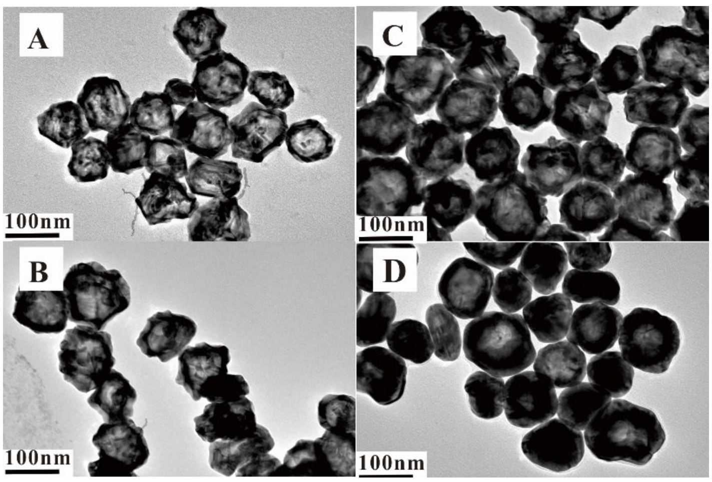

Fig. S1 TEM images of R-like Au particles growing for 60 min with the concentrations $HAuCl_4 \cdot 4H_2O$ from 2.5 to 10 mM which were labelled: (A) R-like Au-1, (B) R-like Au-2, (C) R-like Au-3, (D) R-like Au-4

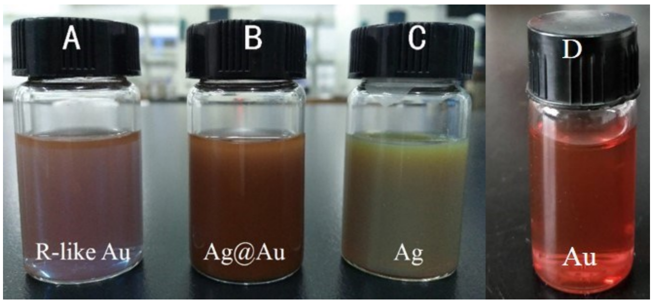

Fig. S2. Optical photograph of particles: (A) R-like Au-2, (B) Ag@Au, (C) Ag seed, (D) Au seed

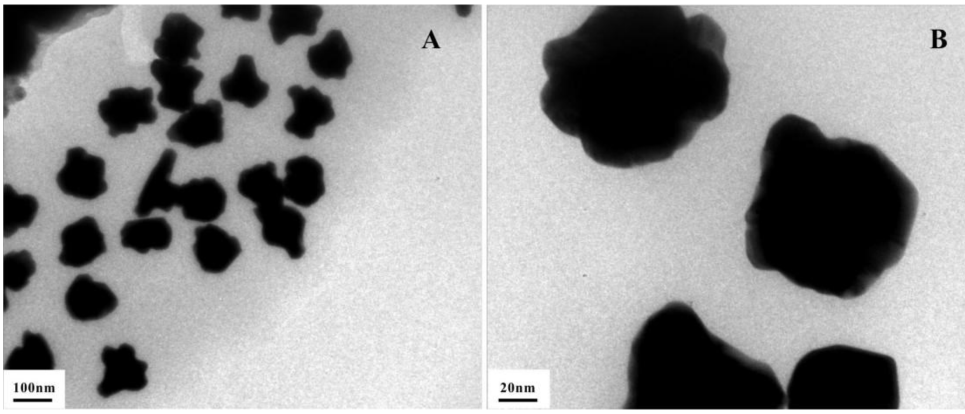

Fig. S3. N-Au particles: TEM images (A) and enlarged details (B)

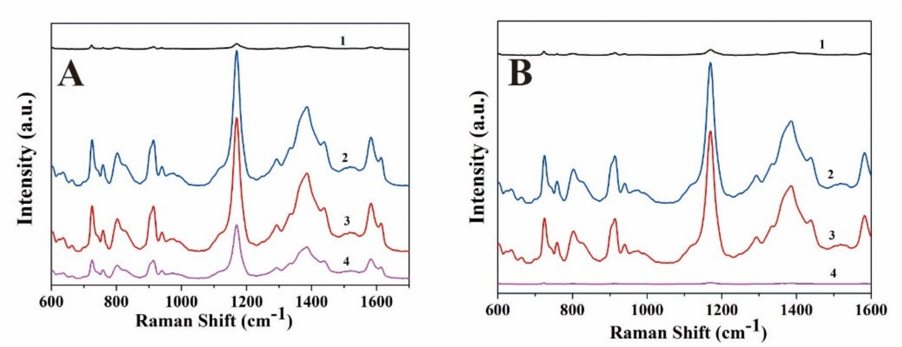

Fig. S4. SERS spectra of 10^{-9} M CV molecules collected on R-like-Au (1-4) of newly prepared (A) and stored for three months (B), respectively

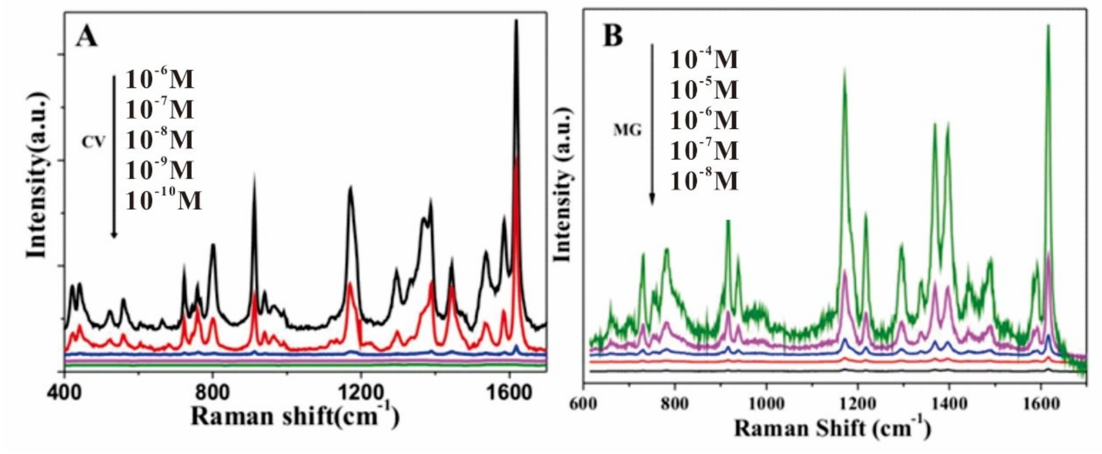

Fig. S5. SERS spectra of CV with concentrations ranging from 10^{-6} M to 10^{-10} M (A) and MG with concentrations ranging from 10^{-4} M to 10^{-8} M (B) on the N- Au

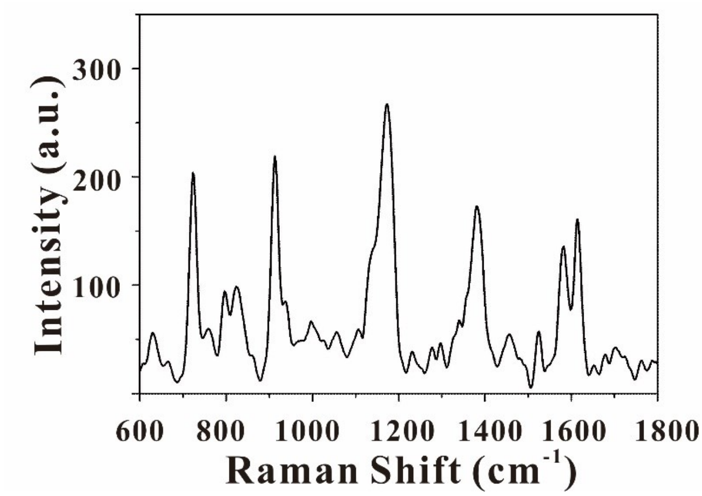

Fig. S6 The Raman spectrum of CV with concentration of 10^{-5} M on Si wafers

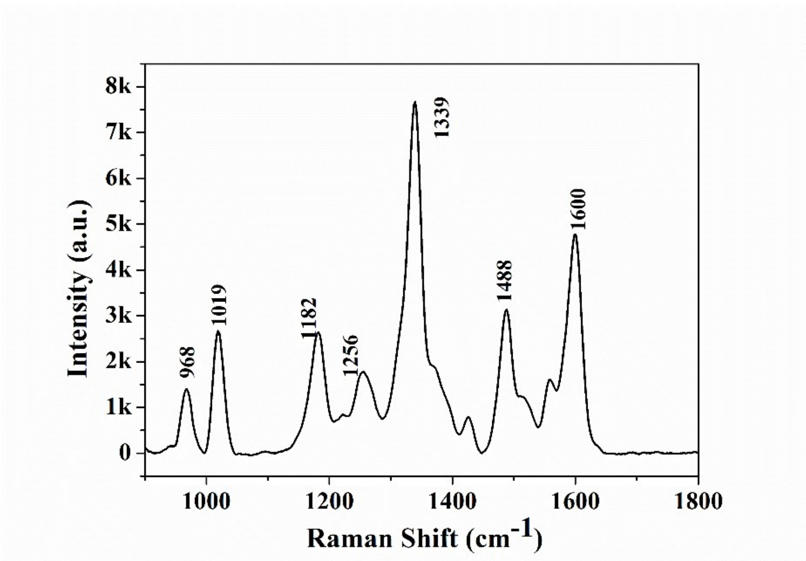

Fig. S7. SERS spectrum of NFT standard solution on the R-like Au-2

Table S1 Comparison of the SERS spectra of standard and simulated solution of NFT in frequency and assignment

NFT			
No.	$SERS/cm^{-1}$ (standard solution)	$SERS/cm^{-1}$ (simulated solution)	assignment
1	1600	1600	ν(C=N) • in-plane • symmetric • stretch
2	1488	1484	ν(ring) • in-plane • symmetric • stretch
3	1339	1339	ω(H-C-H)vs(ring)
4	1256	1256	ι(H-C-H)ω(C-H)ν(C-O)
5	1182	1176	ω(C-H)β(H-C-H)ν(NO_2)
6	1019	1021	ν(C-O)ν(C-C)
7	968	968	ω(H-C-C-H)

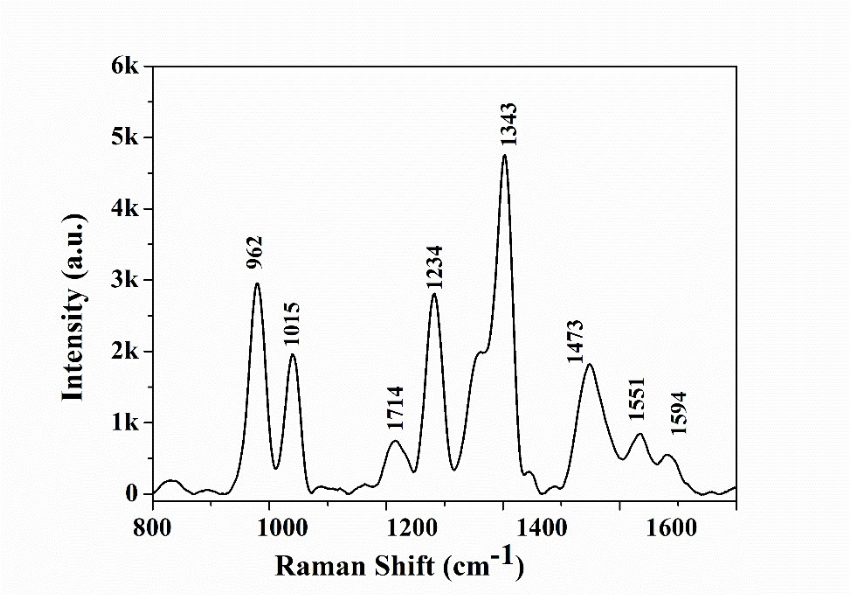

Fig. S8. SERS spectrum of NFZ standard solution on the R-like Au-2

Table S2 Comparison of the SERS spectra of standard and simulated solution of NFZ in frequency and assignment

NFZ			
No.	$SERS/cm^{-1}$ (standard solution)	$SERS/cm^{-1}$ (simulated solution)	assignment

1	1594	no	ν(C=N) in-plane symmetric stretch
2	1551	1559	νas(NO_2)νs(ring)
3	1473	1471	ν(ring) in-plane symmetric stretch
4	1343	1343	ω(H-C-H)νs(ring)
5	1234	1236	νs(C-N-N)ν(C-O)ω(C-H)
6	1174	1152	ω(C-H)β(H-C-H)ν(NO_2)
7	1015	1017	ν(C-O)ν(C-C)
8	962	964	ω(H-C-C-H)