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Supporting Information

Gold Mesoparticles with precisely Controlled Surface Topographies for Single-Particle Surface-Enhanced Raman Spectroscopy

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1. Methods

1.1 MD simulation

The method of MD simulation was similar to our previous report, which was performed in a Forcite package with the PCFF30 force field describing the interaction of the molecules. The force field of PCFF30 was based on the *ab initio* principle and empirical parameters.[1, 2] The optimizations of the molecule configurations were converged to the following criteria: the energy tolerance being less than 2.0×10^{-5} kcal/mol and the maximum displacement being less than 1.0×10^{-5} Å using a smart algorithm.

1.2 FDTD simulation

Six models based on the SERS samples were built and their geometric details are shown in the Supporting Information. The three-dimensional FDTD simulation was used to calculate the near field E-field amplitude patterns at excitation wavelengths of 532, 632, and 785 nm. The incident light was a plane wave propagating along the z-axis and polarized along the y-axis. It was assumed that each geometrical model was suspended in air (n_0=1.0). The frequency (ω) dispersive and complex dielectric function for Au, ε_{Au} (ω), was obtained from the handbook of

optical materials. The grid size was 5 nm and the size of the cross section of amplitude patterns was 1.4 μm×1.4 μm.

2. Calculation of the interaction energy between dopa molecules

The interaction energy (E_{inter}) between dopa molecules was calculated using following equation:

$$E_{inter}=E_{total} - n\times E_s \quad (1)$$

Where E_{total} and E_s are the potential energies of the whole system and single dopa molecule, n is the number of dopa molecules in the whole system. All the systems have been optimized using MD simulation methods before energy calculation. The process of the interaction energy calculation is show in the Table S1.

Table S1. Energies of dopa molecules calculated with MD simulation methods (unit: eV)

Number of dopa molecules in the system / n	Energy of the system / E_{total}	Energy of single dopa molecule / E_s	Interaction energy between dopa molecules / E_{inter}	Interaction energy for each hydrogen bond / $E_a= E_{inter}/2(n-1)$
2	0.3665	0.3866	-0.4066	-0.203
3	0.3245		-0.8353	-0.208

3. Estimation of SERS enhancement factor

The SERS enhancement factors of CV molecules on single Au mesoparticle were estimated according following expression:

$$EF=(I_{surface}/I_{solution})\times(N_{solution}/N_{surface}) \quad (2)$$

where $N_{solution}$ and $N_{surface}$ are the numbers of CV molecules probed in a reference 10^{-4} M CV aqueous solution and on the surface of single Au mesopartcile; and $I_{solution}$ and $I_{surface}$ are the signal intensities of CV molecule Raman spectra probed in CV aqueous solution and on the surface of single Au mesoparticle.

The effective excitation volume of the CV solution (concentration is 10^{-4} M) probed with the Raman microscope using a low-magnification objective (10×) was ~400 μm^3. Thus, the number of the probed CV molecules was:

$$N_{solution} = 6.02\times10^{23}\times10^{-4}\ m/L\ \times400\ \mu m^3 \sim 2.5\times10^7 \quad (3)$$

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

$$I_{solution} = 397/100 = 3.97\ (counts) \quad (4)$$

The SERS signal intensity of probed CV molecules on a single Au mesoparticle ($I_{surface}$) was estimated from the height of Raman spectra peak at 1172 cm^{-1}. The number of CV molecules probed on a single Au mesoparticle ($N_{surface}$) was estimated with following equation:

$$N_{surface} = D_{CV}\times S_p \quad (5)$$

where D_{CV} is the density of CV molecules on the Au mesoparticles substrate and S_p is the surface area probed on the single Au mesoparticle. The D_{CV} can be estimated as:

$$D_{CV} = N_{CV\text{-}total}/S_{total} = N_{CV\text{-}total}/(S_{si} + S_{mp\text{-}total}) = N_{CV\text{-}total}/(S_{si} + N_{mp}\times S_{mp}) \quad (6)$$

where, $N_{CV\text{-}all}$ is the total number of CV molecules adsorbed on the SERS substrate and S_{total} is the total surface area of the SERS substrate including the area of Si substrate (S_{si}) and the total surface area of all of the Au mesoparticles on the substrate ($S_{mp\text{-}total}$) which is the product of mesoparticle number (N_{mp}) and the surface area of a single Au mesoparticle (S_{mp}). Onto the SERS substrate with size of 0.7 cm× 0.7 cm, 50 μL of a 10^{-7} M aqueous CV solution were dropped. About 10% of the CV molecules were retained after rinsing the substrate as the method reported by Wang and Cai et al.[3, 4] Thus, the total number of CV molecules ($N_{CV\text{-}all}$) can be estimated as:

$$N_{CV\text{-}all}=50\times10^{-6}\ L\times10^{-7}\ mol/L\times6.02\times10^{23}\times10\%=3.0\times10^{11} \quad (7)$$

Assuming that the Au mesoparticles are arrayed on 40% surface area of the substrate, the number of the Au mesoparticles on the substrate (N_{mp}) can be estimated as:

$$N_{mp} = 40\%\times S_{si} / \pi r^2 \quad (8)$$

where r is the average radius of the Au mesoparticles. Depending on the following schematic images (Scheme S1), the surface area of a single Au mesoparticle was estimated as following equation, assuming 80% surface area of the base spherical mesoparticles is covered by tips:

$$S_{mp} = N_{tip}\times S_{tip}+20\%\times S_{sphere} \quad (9)$$

where N_{tip} and S_{tip} are the number and surface area of tips on mesoparticle; S_{sphere} is the surface area of the base spherical mesoparticles, on where the tips is covered, as shown in Scheme S1. The model (a) in Scheme S1 is used as example to estimate the surface area. The surface area of the base spherical mesoparticle (S_{sphere}) can be calculated as:

$$S_{sphere} = 4\pi r_b^2 \quad (10)$$

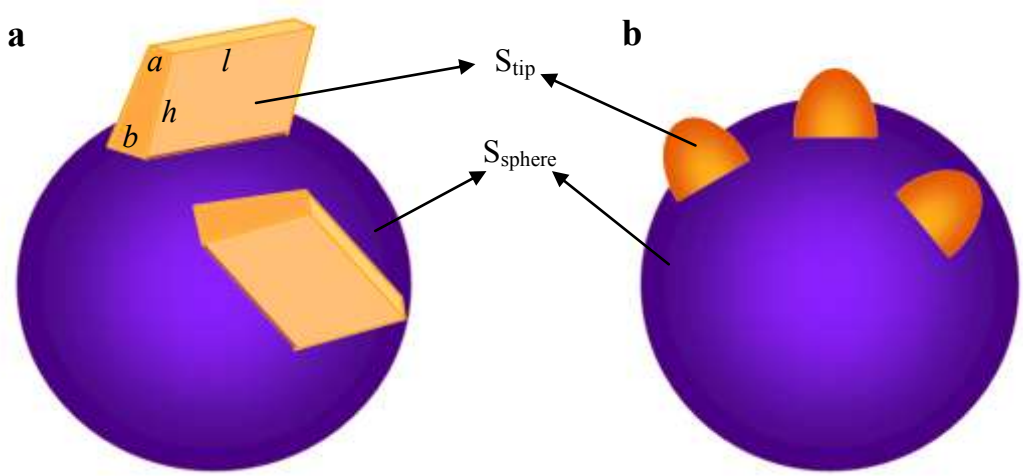
where r_b is the radius of the base spherical mesoparticle. Assuming 80% surface area of the base spherical mesoparticles is covered by tips, the number of tips can be estimated as:

$$N_{tip} = 80\% \times S_{sphere}/(b \times l) \quad (11)$$

where b and l are the width and length of the bottom surface of the tip. The surface area of a tip can be calculated as:

$$S_{tip} = (a+b) \times h + l \times a + h \times l \quad (12)$$

Where a and h are the width of the top surface of the tip and the height of the tip, as shown in Scheme S1a.

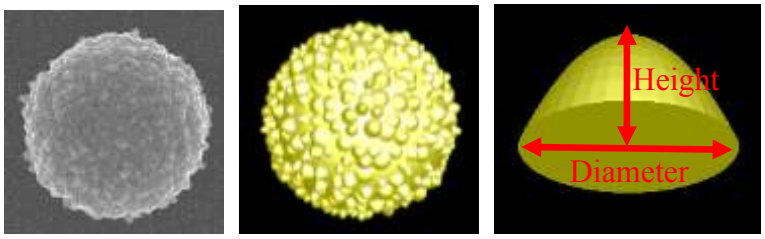


Scheme S1. Shape models being used to estimate the surface area of a single Au mesoparticle. (a) Mesoparticle model with surface being covered by blade-like tips. (b) Mesoparticle model with surface being covered by semispherical tips.

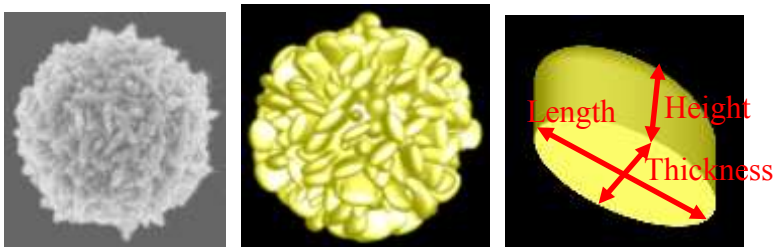
4. Geometry parameters for FDTD simulation

Model A: Sphere with smooth surface, which diameter is 1 μm.

Model B: Sphere with 960 nm in diameter covered with humps. The height of the humps is 20 nm and diameter is 50 nm, as shown in following image. The number of the humps is 374.



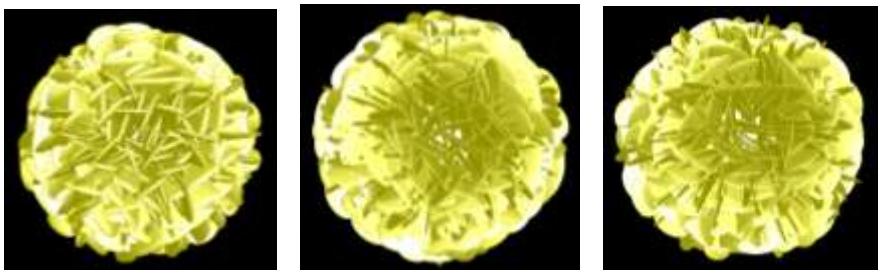
Model C: Sphere with 840 nm in diameter covered with humps and plates. The height and diameter of the humps are 60 nm and 80 nm, respectively. The height, length, and thickness of the plates are 80, 80 and 40 nm, respectively, as shown in following image. The numbers of humps and plates are 124 and 118, respectively.



Model D: Sphere with 500 nm in diameter covered with plates. The height, length, and thickness of the plates are 120, 120, and 15 nm, respectively. The number of the plates is 516.

Model E: Sphere with 500 nm in diameter covered with plates. The height, length, and thickness of the plates are 120, 120, and 10 nm, respectively. The number of the plates is 630.

Model F: The sizes of the sphere and plates are same with model E. The difference is that the number of plates is 778.



Model D Model E Model F

References

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2 H. Sun, *Macromolecules*, 1995, **28**, 701-712.
3 Y. Wang, M. Becker, L. Wang, J. Q. Liu, R. Scholz, J. Peng, U. Gosele, S. Christiansen, D. H. Kim and M. Steinhart, *Nano Lett*, 2009, **9**, 2384-2389.
4 W. B. Cai, B. Ren, X. Q. Li, C. X. She, F. M. Liu, X. W. Cai and Z. Q. Tian, *Surf. Sci.*, 1998, **406**, 9-22.

Figures and Captions

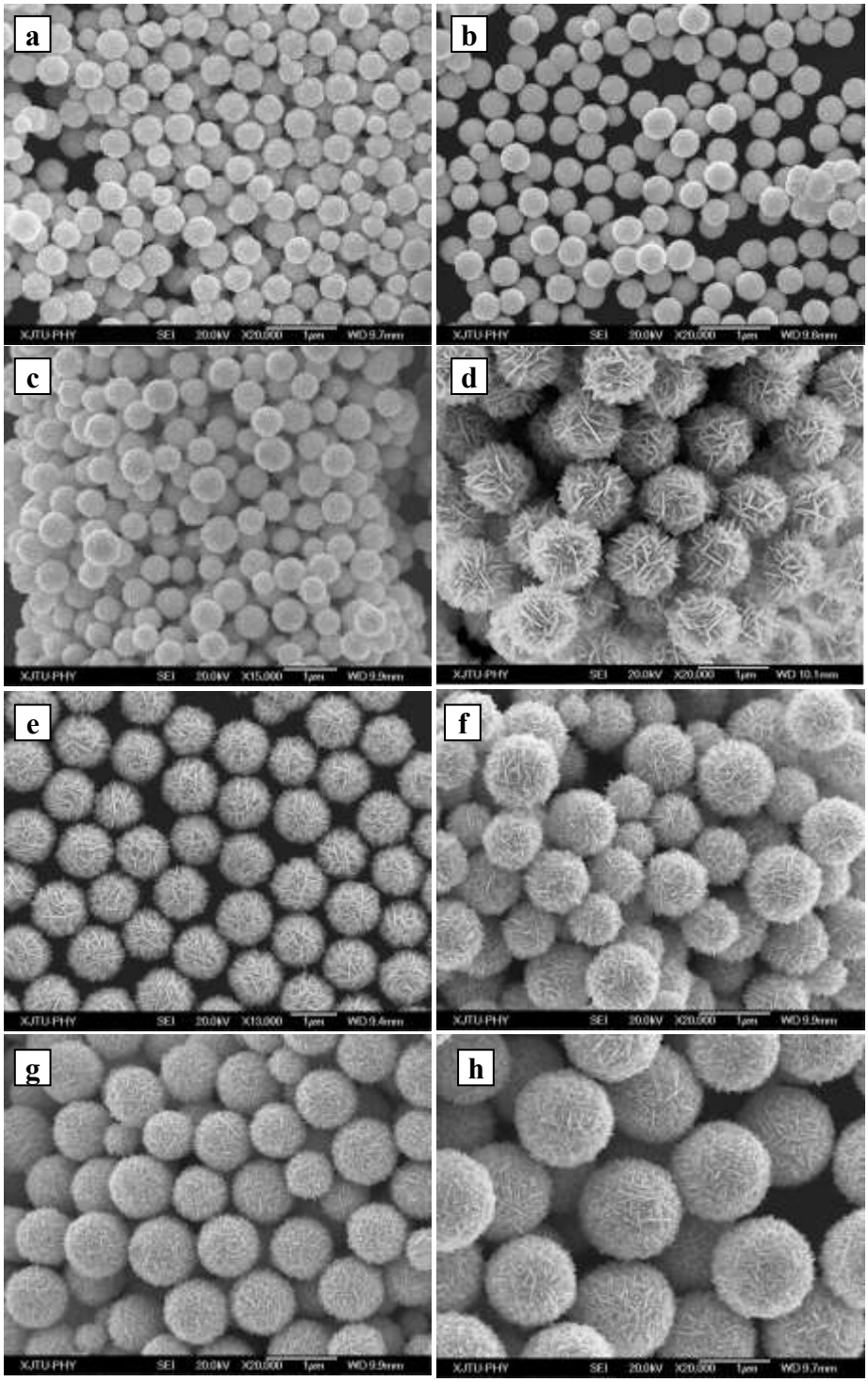

Fig. S1 SEM image of Au mesosuperstructures synthesized with the concentration of dopa/$HAuCl_4$ changing: (a) 0.5 mM/0.5 mM, (b) 1.0 mM/1.0 mM, (c) 1.5 mM/1.5 mM, (d) 2.0

mM/2.0 mM, (e) 2.5 mM/2.5 mM, (f) 3.0 mM/3.0 mM, (g) 4.0 mM/4.0 mM, and (h) 7.0 mM/7.0 mM.

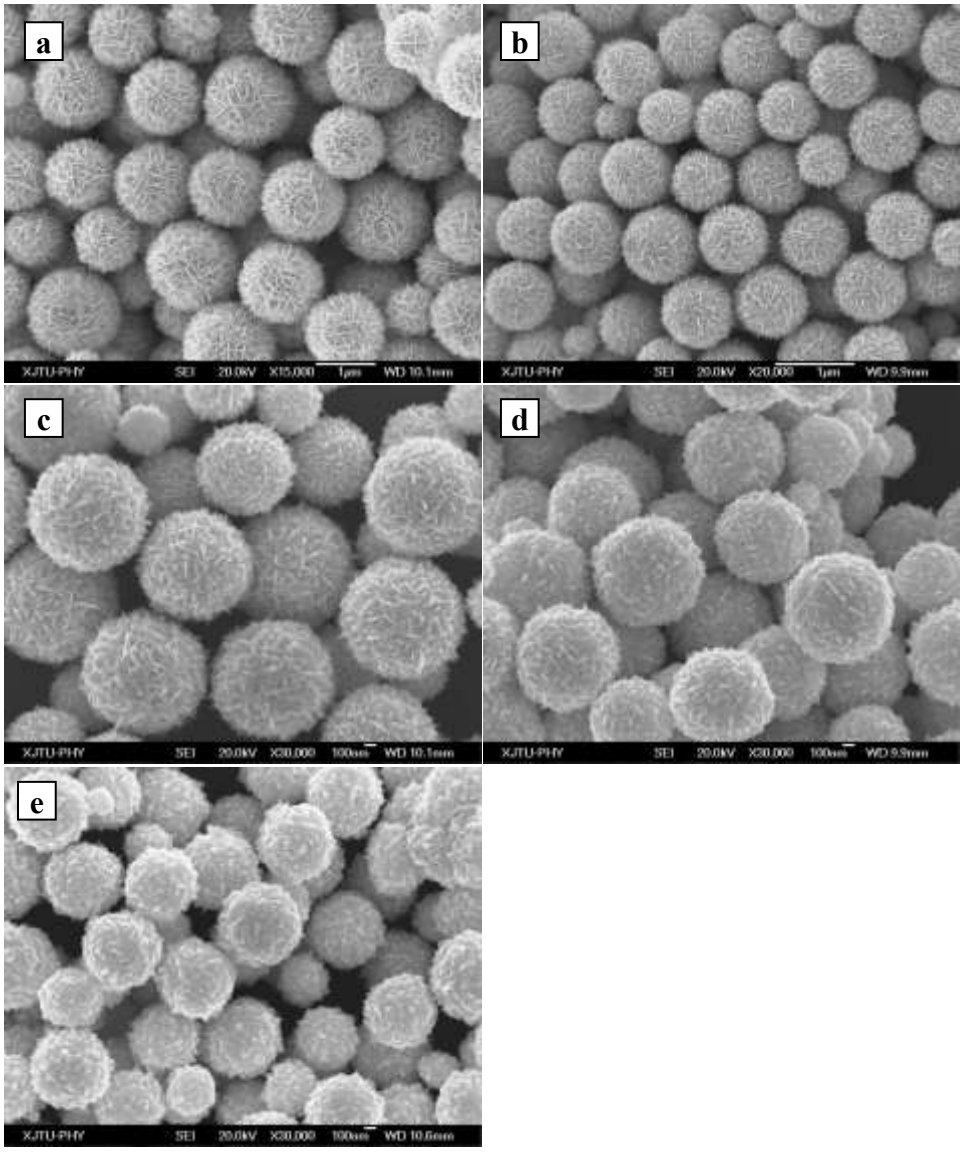

Fig. S2 SEM image of Au mesosuperstructures synthesized with different temperature: (a) 0 ℃, (b) 10℃, (c) 20 ℃, (d) 30 ℃, and (e) 40 ℃.

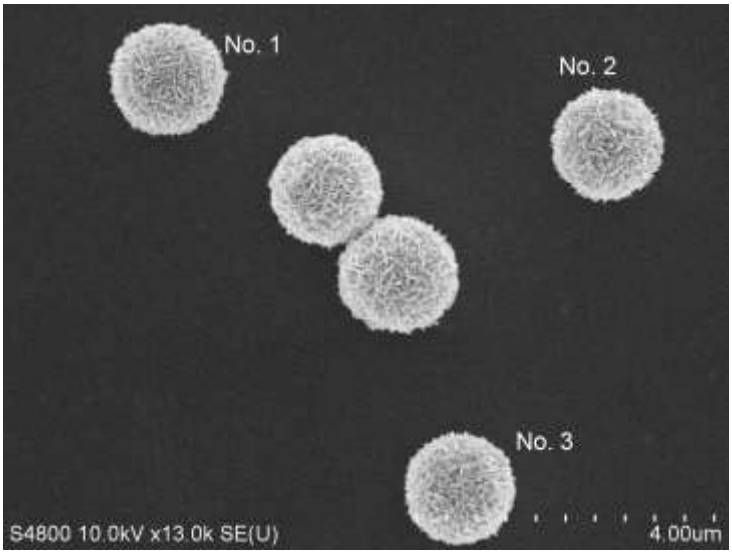

Fig. S3 SEM image of Au mesoparticle substrate for single-particle (sp-) SERS measurement. The individual Au mesoparticles such as that indicated in this image (No.1-3) was selected for the sp-SERS measurement.

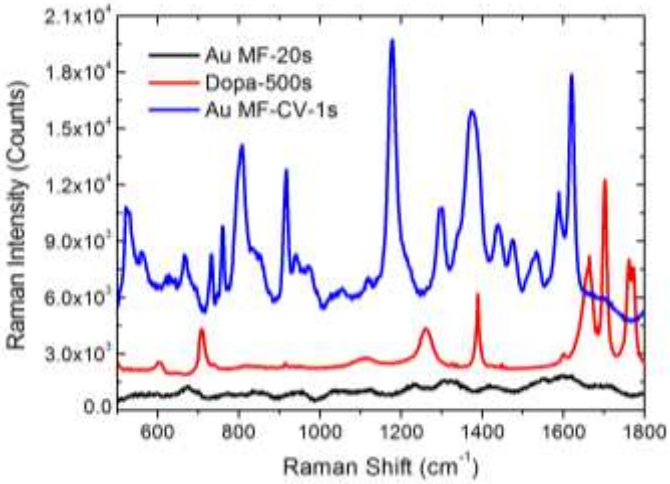

Fig. S4 SERS spectra of blank Au mesoparticles (sample S5, as prepared without adding any analyte; indicated as Au MF-20s), dopa powder (indicated as Dopa-500s), and Au mesoparticles adsorbed with 10^7 M CV analyte. The signal collection time was 20, 500 and 1 s, separately.

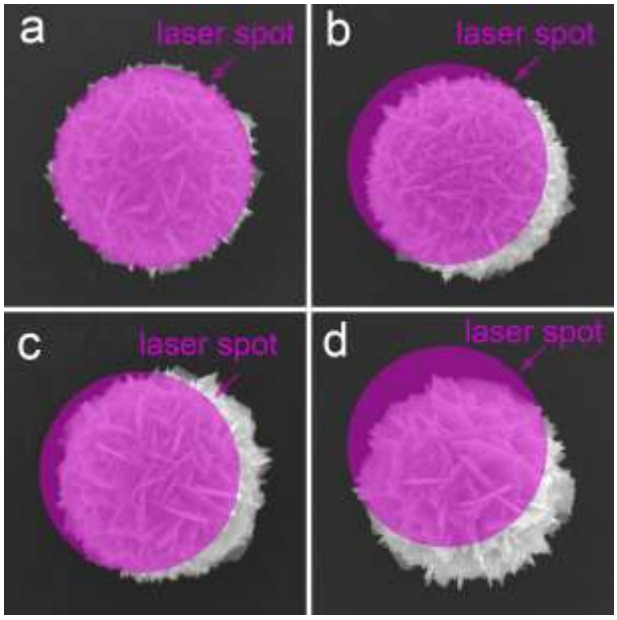

Fig. S5 Schematic illustration of the misalignment between the centers of laser spot and Au mesopartcile formed during the sp-SERS measurement.

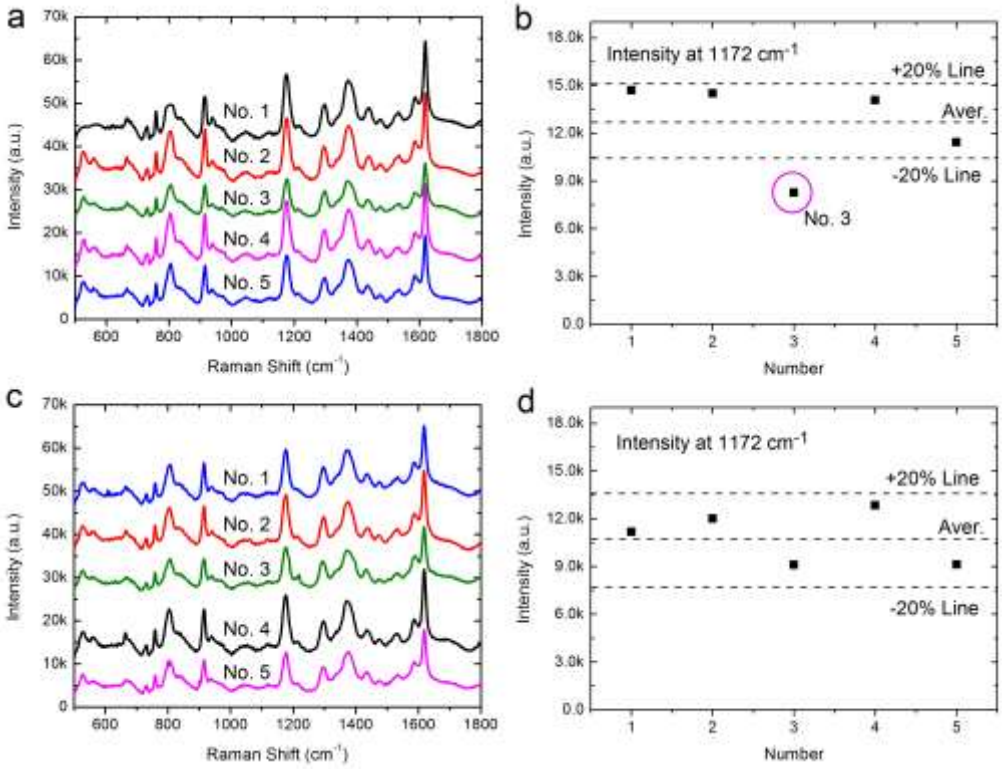

Fig. S6 Reproducibility of sp-SERS measured on one same Au mesoparticle for 5 times. (a,c) SERS spectra obtained from two individual Au mesoparticles for five times (No.1-5). (b,d) The correlated distributions of intensities at 1172 cm^{-1}.

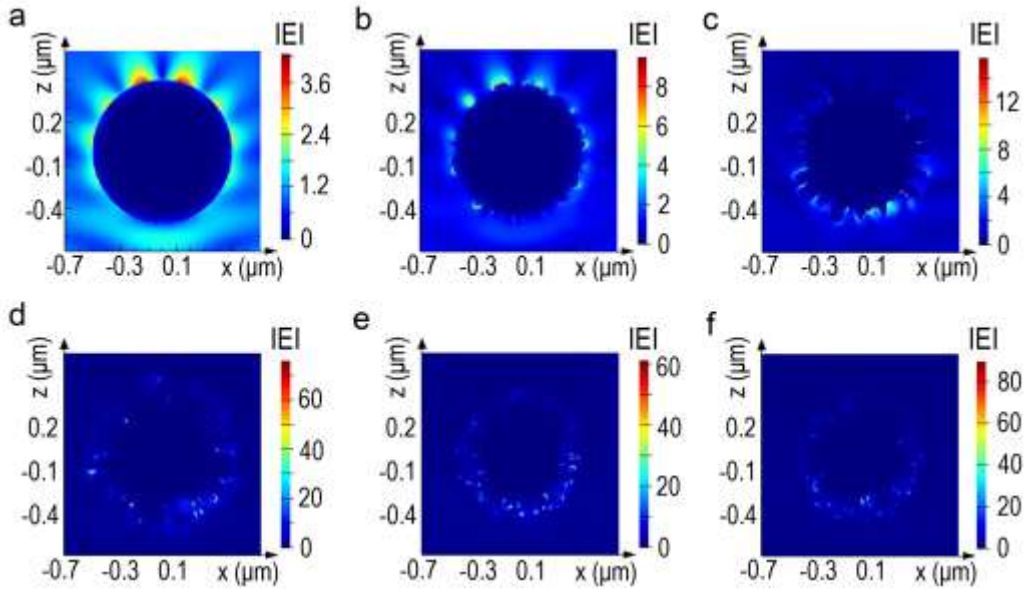

Fig. S7 E-field amplitude patterns obtained in x-z plane from FDTD theoretical simulation at the excitation electromagnetic wave of 633 nm for six mesoparticle models with different topographies: (a) model A, (b) model B, (c) model C, (d) model D, (e) model E, and (f) model F.

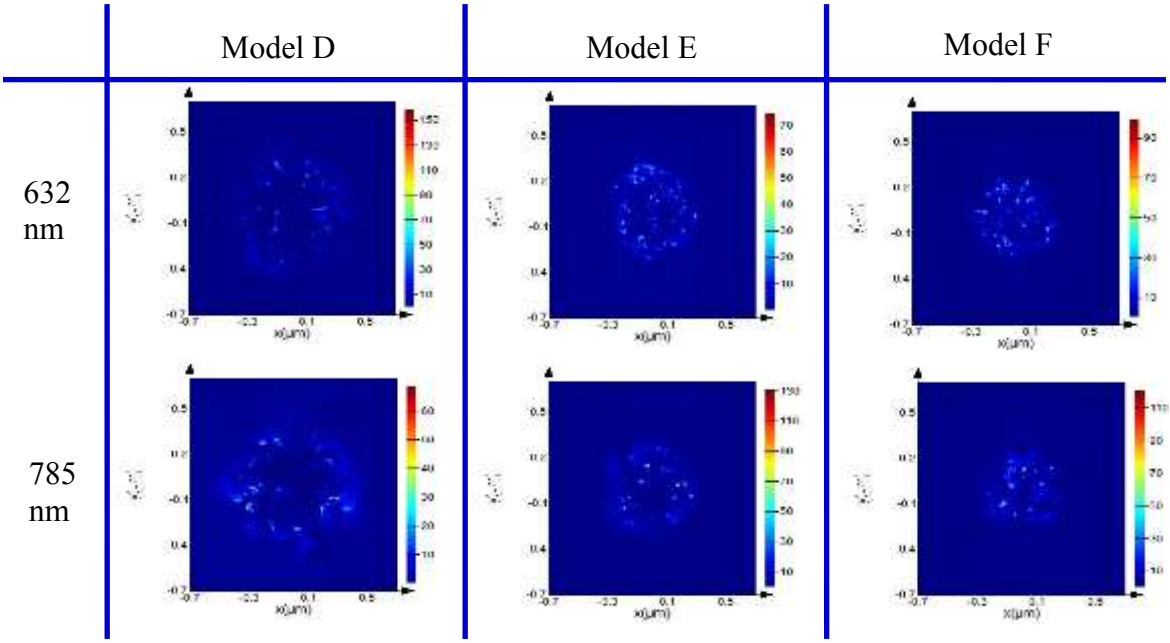

Fig. S8 Distributions of the local electric field intensity in the plane paralleled to x-y plane at z=0.35 μm.