Electronic Supplementary Information for:

Gold Nanoparticle Superlattice Monolayer with Tunable Interparticle Gap for Surface-Enhanced Raman Spectroscopy

Huayang Wang, Ling Yao, Xi Mao, Ke Wang,* Lihua Zhu, and Jintao Zhu*

Key Laboratory of Materials Chemistry for Energy Conversion and Storage (HUST) of Ministry of Education, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology (HUST), Wuhan 430074, China

*E-mail: Kewang@hust.edu.cn (K. W.); jtzhu@mail.hust.edu.cn (J. Z.)

Additional figures:

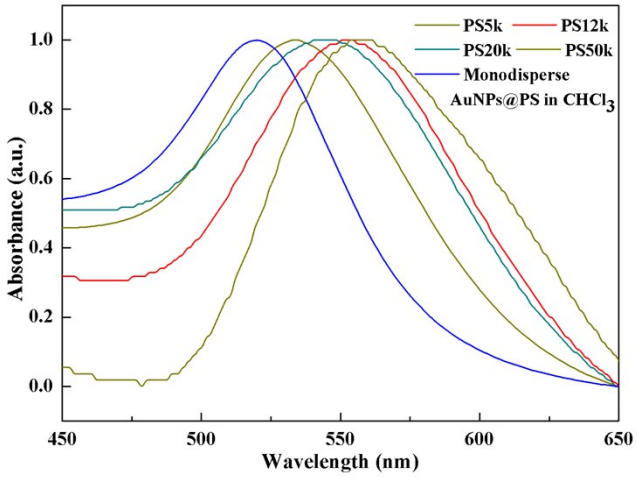

Fig. S1 UV-vis spectra of Au NPs@PS SM formed from 24 nm Au NPs with different M_w of tethered PS and corresponding monodispersed Au NPs@PS in chloroform. Clearly, UV-vis spectra shows single bands, while broadening red-shift of plasmon occurred due to the near-field coupling interaction among Au NPs.

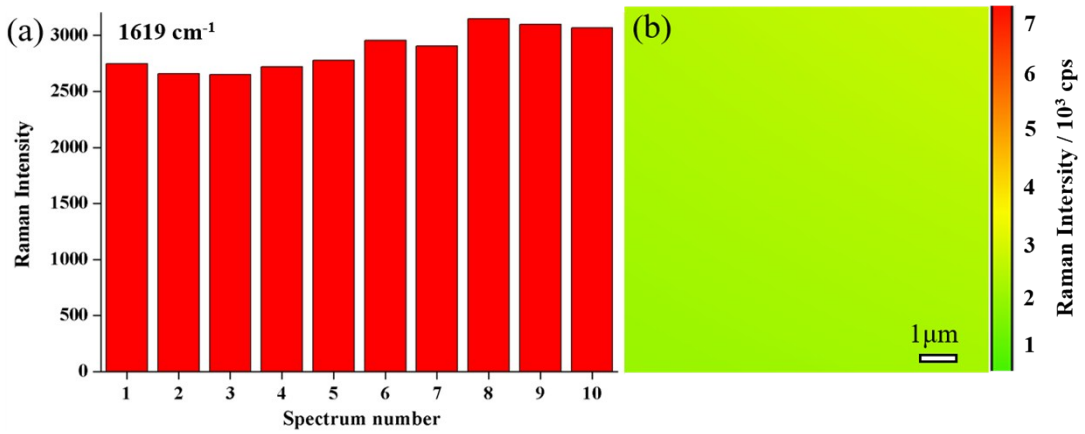

Fig. S2 (a) The relative standard deviation of Raman signal intensity at 1619 cm^{-1} in the SERS spectra shown in Fig. 3 (PS_{12k}). (b) SERS mapping result of CV at 1619 cm^{-1} on Au NPs SM, interparticle gap was 7.68 nm.

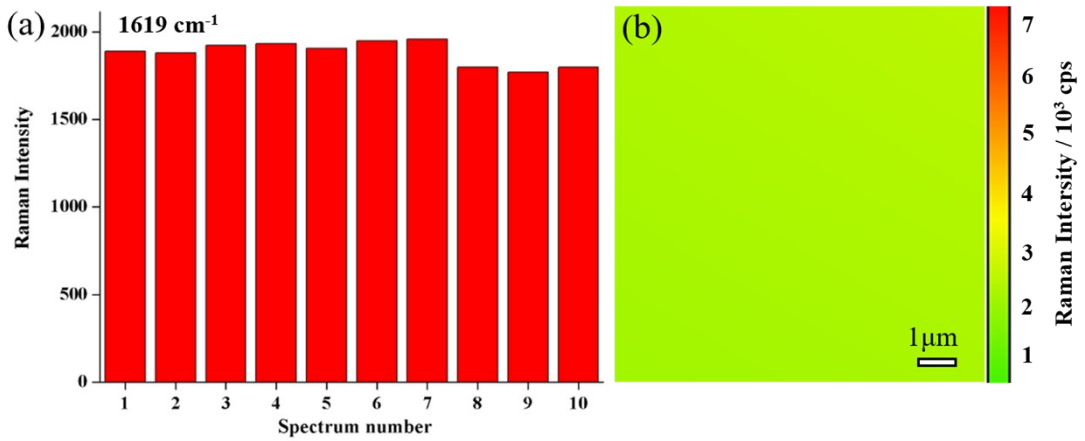

Fig. S3 (a) The relative standard deviation of Raman signal intensity at 1619 cm^{-1} in the SERS spectra shown in Fig. 3 (PS_{20k}). (b) SERS mapping result of CV at 1619 cm^{-1} on Au NPs SM, interparticle gap was 11.32 nm.

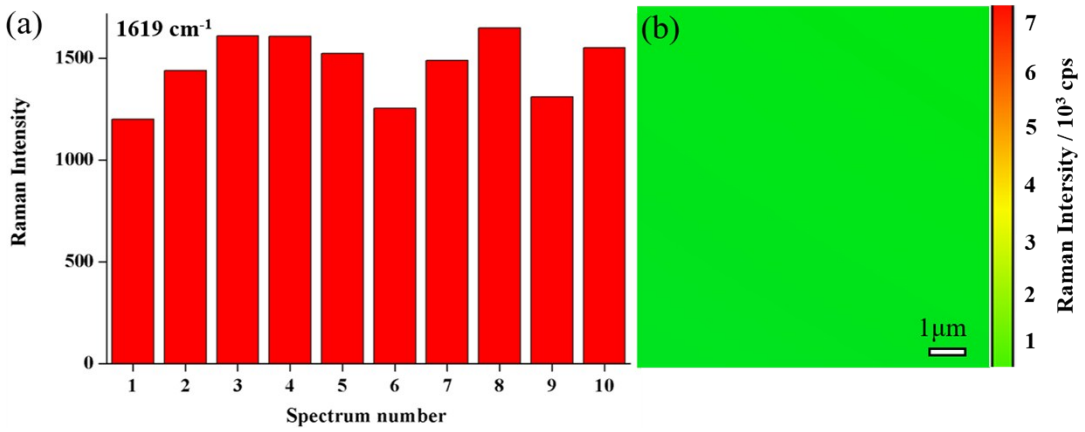

Fig. S4 (a) The relative standard deviation of Raman signal intensity at 1619 cm^{-1} in the SERS spectra shown in Fig. 3 (PS_{50k}). (b) SERS mapping result of CV at 1619 cm^{-1} on Au NPs SM, interparticle gap was 28.83 nm.

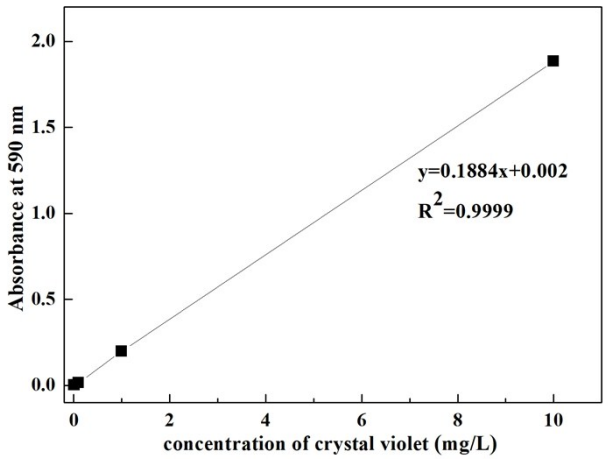

Fig. S5 Standard curve of crystal violet performed by recording the absorbance at 590 nm against different concentrations with UV-Vis spectrophotometer.

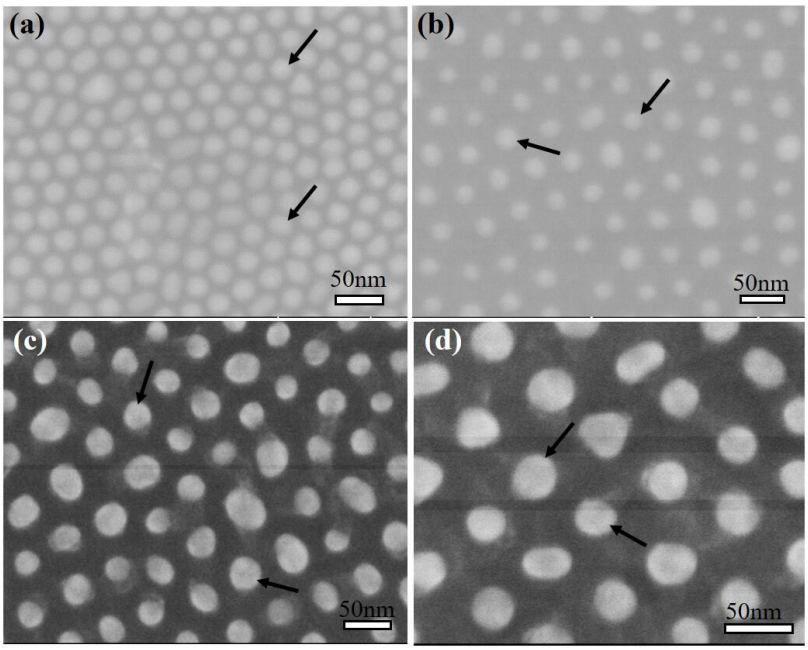

Fig. S6 SEM images of Au NPs (indicated by arrows) after plasmon treatment. (a) Au NPs@PS_{5k}; (b) Au NPs@PS_{12k}; (c) Au NPs@PS_{20k}; (d) Au NPs@PS_{50k}, respectively. The SEM images show that plasmon treatment will not destroy the shape of Au NPs.

Table S1 Quantifying the amount of crystal violet adsorbed on the surface of Au NPs.

Different M_n (g/mol) modified Au NPs	Initial absorbance of crystal violet A_0	Initial concentration of crystal violet C_0 (mg/L)	Final absorbance of crystal violet A	Final concentration of crystal violet C (mg/L)	Change of concentration of crystal violet ΔC (mg/L)	Amount of CV adsorbed on AuNPs, w =ΔC×V (ng)
AuNPs@PS_{5k}	0.199	1.00	0.187	0.982	0.018	18
AuNPs@PS_{12k}	0.199	1.00	0.178	0.934	0.066	66
AuNPs@PS_{20k}	0.199	1.00	0.164	0.860	0.140	140
AuNPs@PS_{50k}	0.199	1.00	0.127	0.663	0.337	337

Note: Variation of concentration of crystal violet was obtained through standard curve of crystal violet against different concentrations, y=0.1884x+0.002 (Fig. S5). The initial volume of crystal violet solution V_0=1.00 mL, while in the incubation process the change of volume of crystal violet solution is negligible, that is V=1.00 mL.

Calculation for enhancement factors (EFs) of SERS for crystal violet:

Laser spot diameter: $D_L = \frac{1.22\lambda}{NA}$

Focal depth: $L_0 = \frac{2\pi}{\lambda} D_0$

Focal volume: $V_0 = (\frac{\pi}{2})^{1.5} D_L^2 L_0$

$N_{\mathrm{BULK}} = \frac{V_0 \rho}{M} N_A$

$N_{\mathrm{SERS}} = \frac{\pi(\frac{D_L}{2})^2}{S} cVN_A$

$N_{\mathrm{BULK}}/N_{\mathrm{SERS}} = \frac{23.44\rho\lambda S}{w(NA)^2}$

NA = Numerical Aperture = 0.5

N_A = Avogadro constant = 6.02×10^{23} mol^{-1}

λ = Wavelength of the laser (nm) = 633

ρ = Density of the solution of crystal violet (g cm^{-3}) = 1.19

S=Area of the substrate (cm^2)=0.36

W=Weight of the crystal violet in the solution adsorbed on the substrate (ng)