Supporting information for:

The Impact of Surface Chemistry on the Interfacial Evaporation-Driven Self-Assembly of Thermoplasmonic Gold Nanoparticles

Feiyu Zheng[1,2,†], Yingyue Zhang[1,2,†], Liuchang Dong[1,2,†], Dengwu Zhao[1,2], Rui Feng[1,2], Peng Tao[1,2], Wen Shang[1,2], Benwei Fu[1,2], Chengyi Song[1,2,] and Tao Deng[1,2,]**

[1] The State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, P.R.China

[2] Center of Hydrogen Science, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, P.R.China

[†]Feiyu Zheng, Yingyue Zhang and Liuchang Dong contributed equally to this work.

Corresponding author: Chengsi Song, Email: chengyi2013@sjtu.edu.cn; Tel: +86 66107748

Tao Deng, Email: dengtao@sjtu.edu.cn; Tel: +86 54745582

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1. SERS measurement

The as-prepared aqueous AuNPs solution was poured into the cuvette, and exposed to laser illumination. The 2D assemblies on the surface of solution were carefully transferred onto silicon wafers and dried in air for further SERS measurements. R6G was used as a probe molecule for measuring the SERS performance of assembled film. R6G aqueous solutions with different concentrations (10^{-4} M, 10^{-5} M, 10^{-6} M and 10^{-7} M) were prepared and stored for SERS test. 100 uL of a specific R6G aqueous solution was dropped onto the assembled AuNPs film, and dried thoroughly. A confocal Raman microscope with 532 nm and 785 nm laser as excitation source was used to measure the SERS performance of these samples, respectively. SERS spectra were measured using a 50X objective with an N.A. of 0.75, and the laser power of 532 nm and 785 nm was 0.15 mW and 0.1 mW, respectively.

2. Analysis of ligand density

We used X-ray photoelectron spectroscopy (XPS, AXIS Ultra DLD, Japan) to quantify the ligand density on AuNPs in the samples of UOA and POA according to previous work[1,2]. As-prepared sample solutions were dropped, and dried on silicon wafers for XPS tests, respectively. The size of synthesized AuNPs was around 10 nm (Figure S2), which was consistent with the detection depth of XPS. As for sample UOA and POA, atomic concentrations of N and Au elements were listed in Table S2. According to the proportions in Table S2 and diameters of UOA and POA in Figure

S2, the ligand density of POA was calculated to be 16.53 (ligand/nm^2). As for UOA, the calculated ligand density was 77.49 (ligand/nm^2).

3. Calculation of SERS enhancement factor

The SERS enhancement factor (EF) can be calculated by the following formula:

$$EF = \frac{I_{SERS}/I_{SW}}{C_{SERS}/C_{SW}}$$

where I_{SERS} and I_{SW} correspond to the Raman intensities of R6G on the assembled 110-nm AuNP film and Si wafer, respectively, and C_{SERS} and C_{SW} denote the molar concentration of R6G aqueous solution on the assembled 110-nm AuNP film (10^{-7} M) and Si wafer (10^{-4} M), respectively. The calculated EF values of SERS are 1.4×10^5 (785 nm) and 3.6×10^5 (532 nm).

4. Supplementary Figures and table

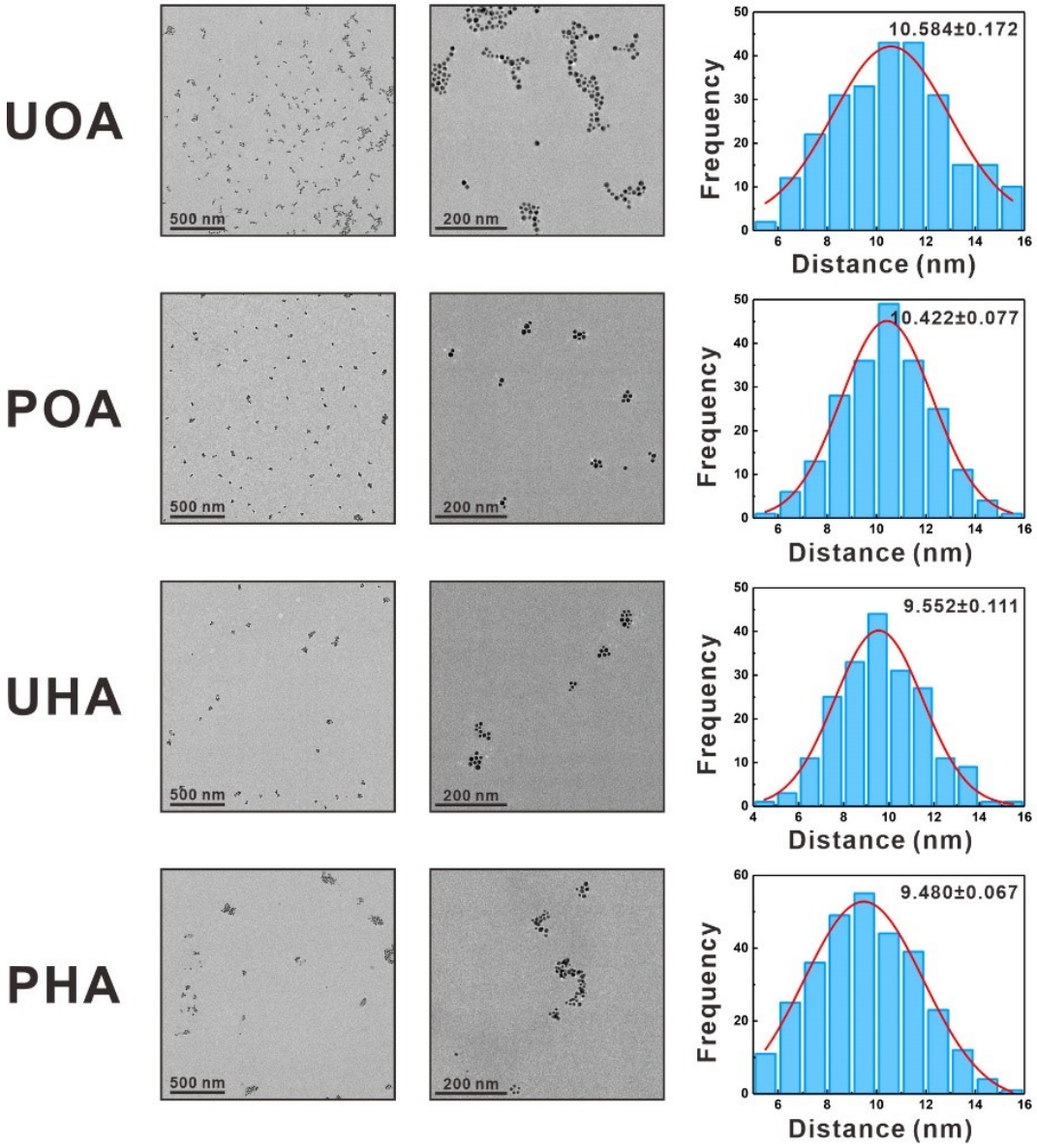


Figure S1. TEM characterization and size distribution of UOA, POA and hexadecane thiol capped nanoparticles.

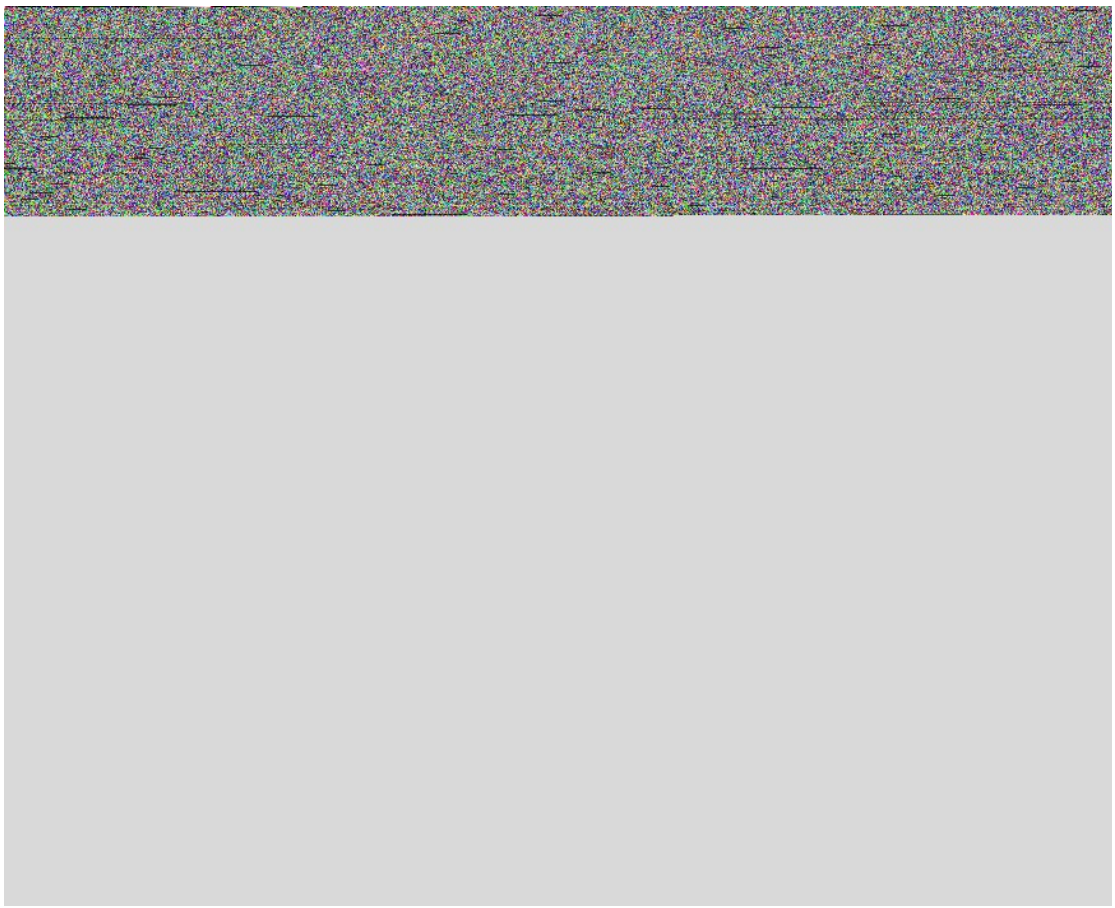
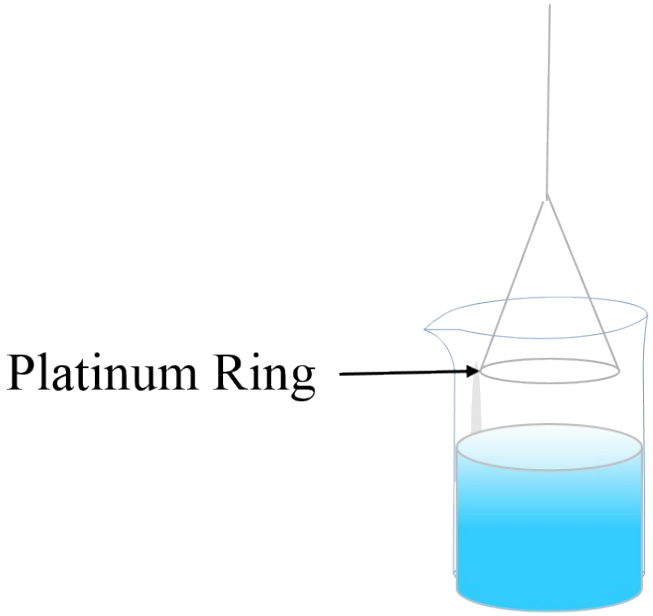


Figure S2. TEM images of the surface structure of assembled films from three different colloidal AuNPs chloroform solutions after being exposed to light illumination.



	Surface tension(mN/m)
Chloroform	28.886
Chloroform+AuNP	28.947
Chloroform+AuNP, Thiol	28.824
Chloroform+AuNP, Purified	28.893

Figure S3. Surface tension measurements of chloroform, and colloidal AuNPs in chloroform (JYW200 surface tension test machine).

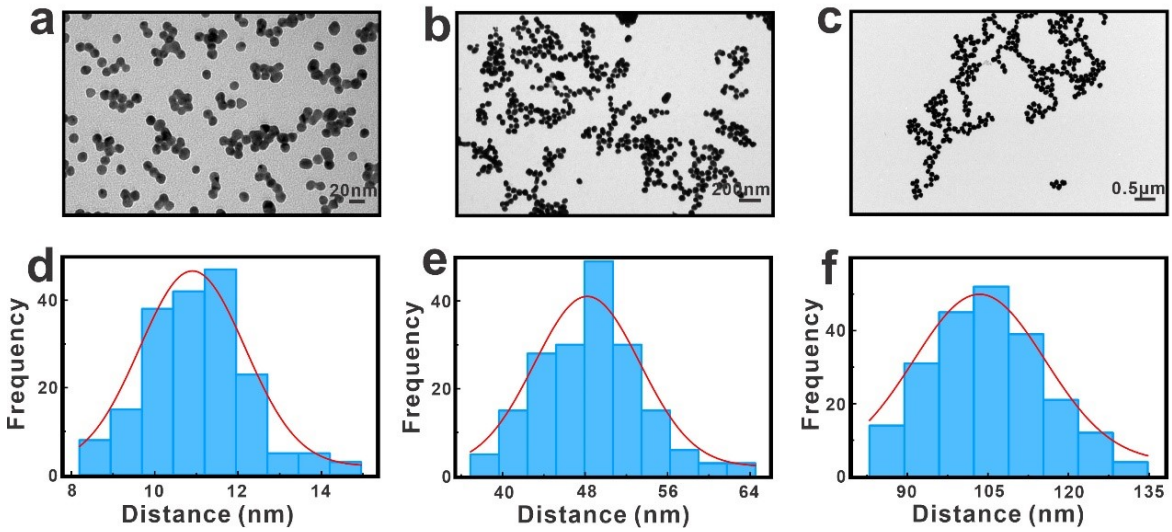


Figure S4. Transmission electron microscopy (TEM) images of aqueous AuNPs solutions with different AuNPs sizes (10-nm AuNPs (a), 50-nm AuNPs (b) and 110-nm AuNPs (c)). d), e) and f) are the corresponding actual size distributions of 10-nm, 50-nm and 100-nm AuNPs, that is d) 11.41±2.84 nm, e) 49.98±11.69 nm and f) 108.39±22.17 nm.

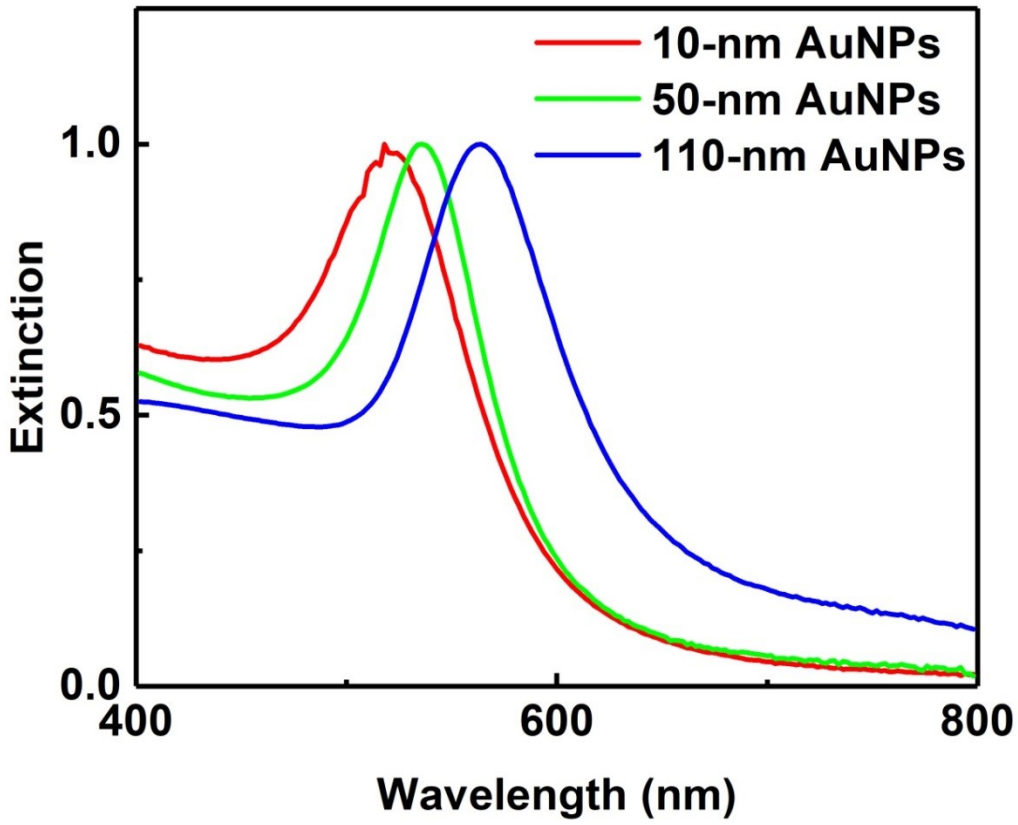


Figure S5. Normalized UV-Vis spectra of aqueous AuNPs solutions with different AuNP sizes.

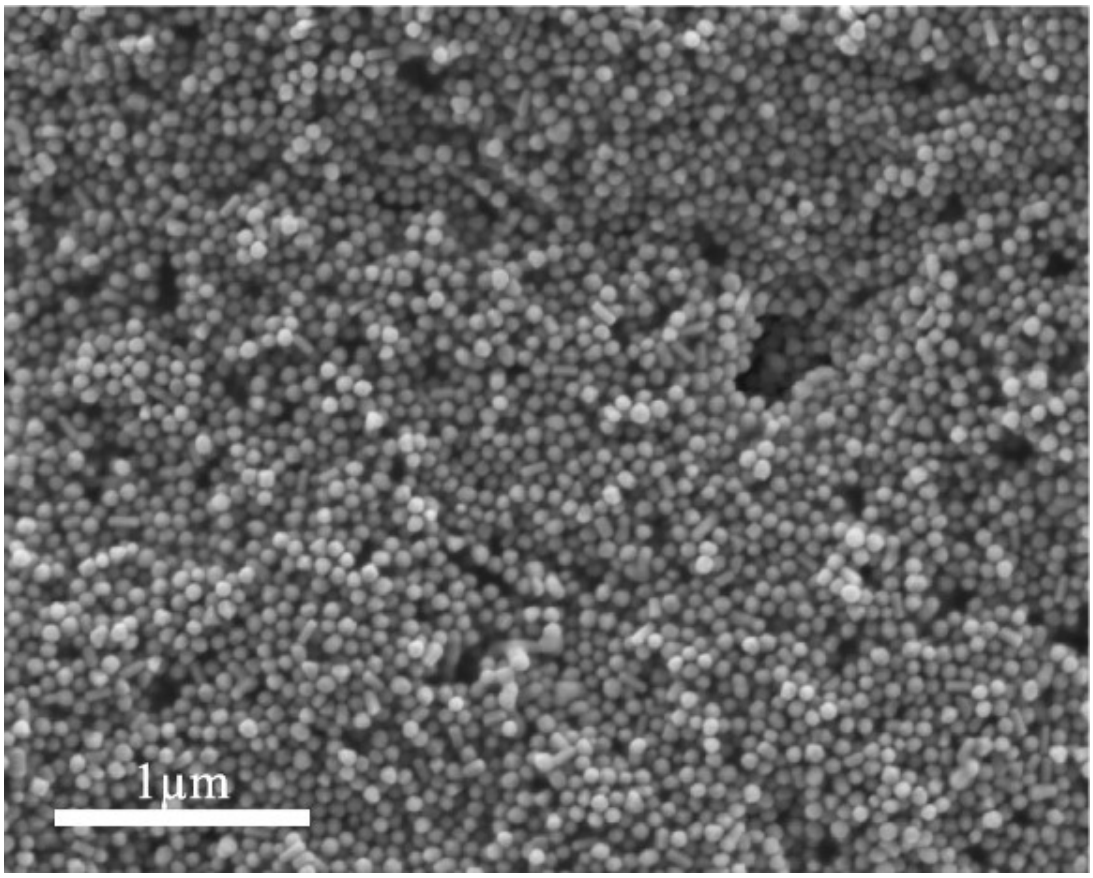


Figure S6. Scanning electron microscopy (SEM) image of self-assembled 110-nm AuNPs at the interface of water/air.

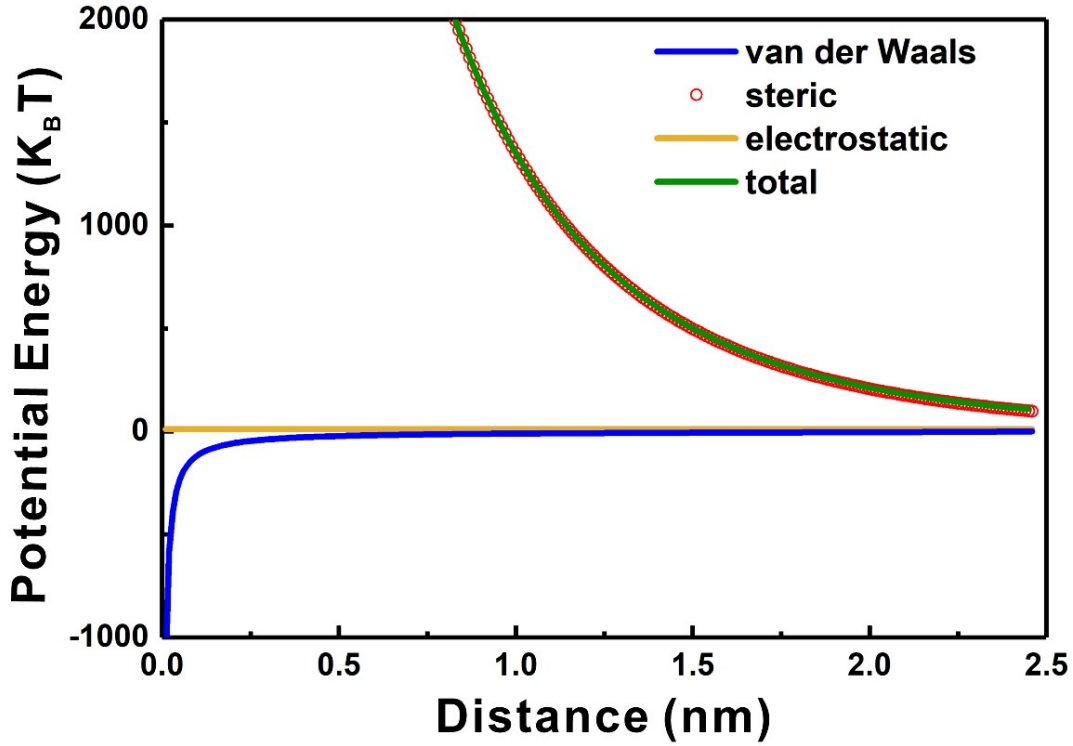


Figure S7. Plots of theoretically calculated Van der Waals, steric, electrostatic repulsion and total potential energies of 10-nm AuNPs solution.

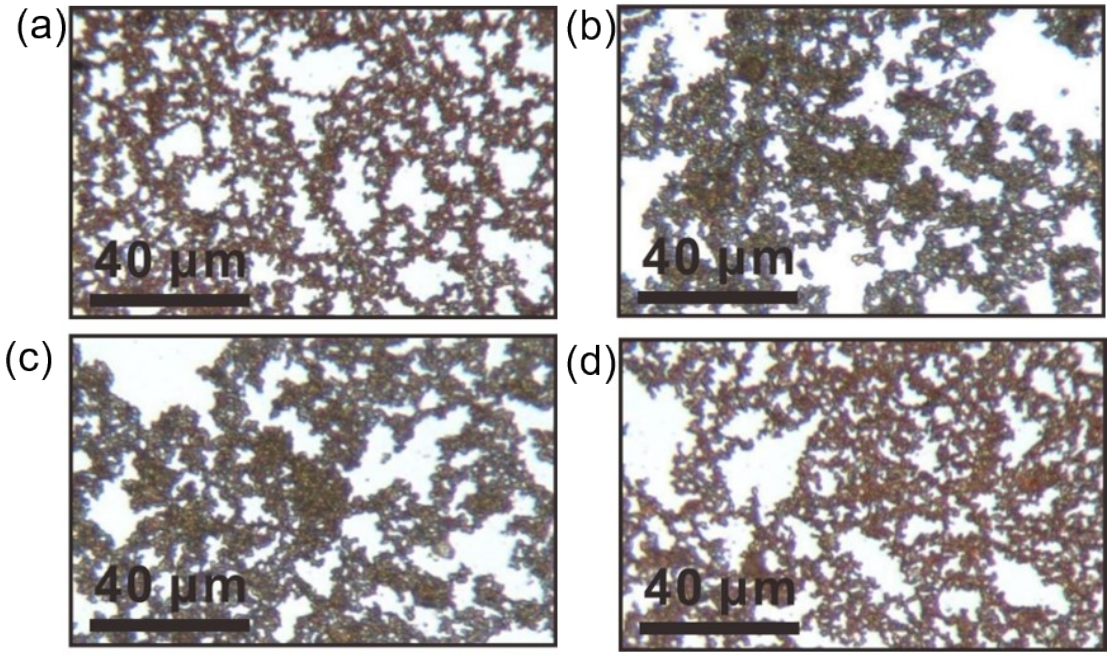


Figure S8. The optical images with a 50X objective at different concentration (10^{-4} M(a), 10^{-5} M (b), 10^{-6} M (c) and 10^{-7} M(d)) of R6G.

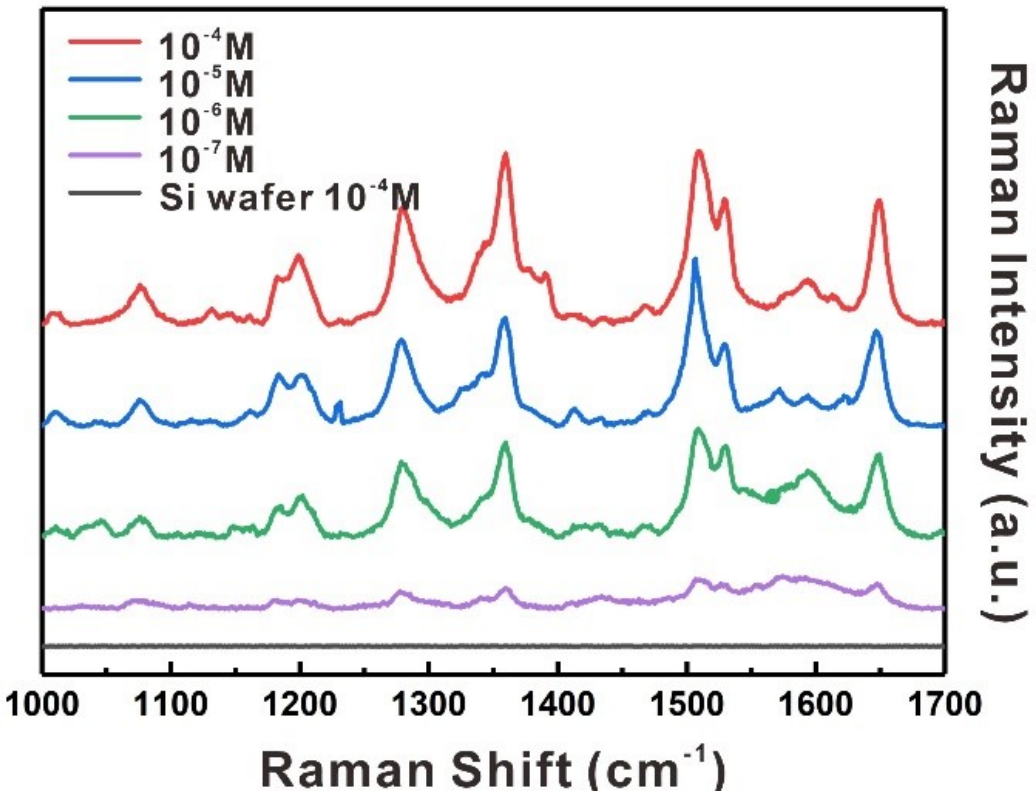


Figure S9. SERS spectra of R6G solutions with different concentrations on the assembled 110-nm AuNPs film and Si wafer detected at 785 nm.

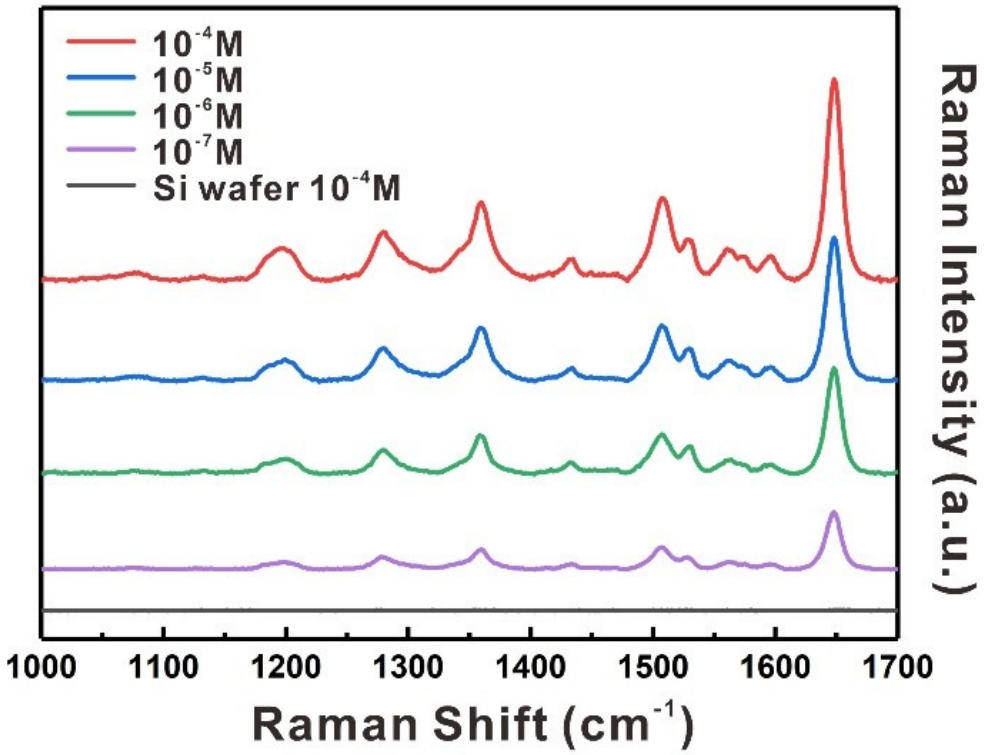


Figure S10. SERS spectra of R6G solutions with different concentrations on the assembled 110-nm AuNPs film and Si wafer detected at 532 nm.

Table S1. The Hamaker constant calculation results of each material used in the calculation.

Material	Hamaker constant (10^{-20}J)
Oleylamine	6.13
Hexadecanethiol	6.2
Chloroform	5.8
Sodium citrate	4.75
Water	3.71
Gold	31.2

Table S2. XPS results of proportions for N and Au elements in UOA and POA.

Sample name	N %AT conc	Au %AT conc	N/Au	Ligand density (ligand/nm^2)
UOA	42.94	57.06	0.75	77.49
POA	13.79	86.21	0.16	16.53

5. Reference

1 M. P. Seah, *Surf. Interface Anal.*, 2012, **44**, 1353–1359.

2 Z. J. Farrell and C. Tabor, *Langmuir*, 2018, **34**, 234–240.