

Electronic Supplementary Material (ESI) for Nanoscale

**Silver Nanoislands over Silica Spheres Platform: Enriching Trace-Amount
Analytes for Ultrasensitive and Reproducible SERS Detections**

Zhongshun Wang[‡], *Lei Feng*[‡], *Dongyang Xiao*, *Ning Li*, *Yao Li*, *Danfeng Cao*, *Zuosen
Shi*, *Zhanchen Cui*, and *Nan Lu*^{*}

State Key Laboratory of Supramolecular Structure and Materials, Jilin University,
Changchun 130012, P. R. China

Table of content

1. Photograph and contact angle (CA) characterization of the paint layer
2. Scanning electron microscope (SEM) characterization
3. Finite difference time domain (FDTD) simulation
4. SERS measurement using a bench-top Raman spectrograph
5. Calculation of the SERS enhancement factor
6. Investigation of the saturated region
7. Evaluation of the reproducibility using 10^{-11} M of R6G

1. Photograph and contact angle (CA) characterization of the paint layer

The photograph of the paint layer is shown in Fig. S1(a). The glass slide is 7.4 cm in length and 2.5 cm in width. The slide is covered by a layer of white membrane, which is the paint layer. Since the spray coating technique is not area limited, the paint layer can spread over larger substrates. The covered part shows a homogeneous opacity, which demonstrates the macroscopic uniformity of the paint layer.

The hydrophobicity of the paint layer was characterized by measuring the CA between the water droplet and the paint layer. Fig. S1(b) shows the CA variation at different moments during the evaporation of 10 μL water. It is clearly that the CA is close to 150° in the first 40 min, which reveals the super-hydrophobicity of the paint. From 40 min to 50 min, the CA decreases gradually, resulting from the impalement of the Cassie drop.

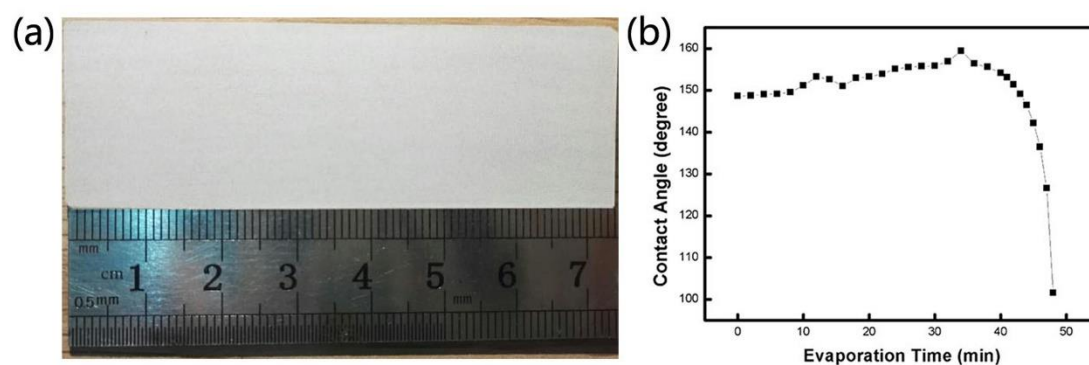


Fig. S1 (a) Photograph of the paint layer coated on a glass slide. (b) CA variation at different moments during the evaporation of 10 μL water on the paint layer.

2. Scanning electron microscope (SEM) characterization

Fig. S2 shows the SEM photographs in different levels of magnification of the paint layer and the SNOSS platform. Fig. S2(a) and (b) reveal the paint layer. Fig. S2(c) and (d) indicate that the introduction of silver coating could form the silver nanoislands providing an extra roughness in a smaller scale.

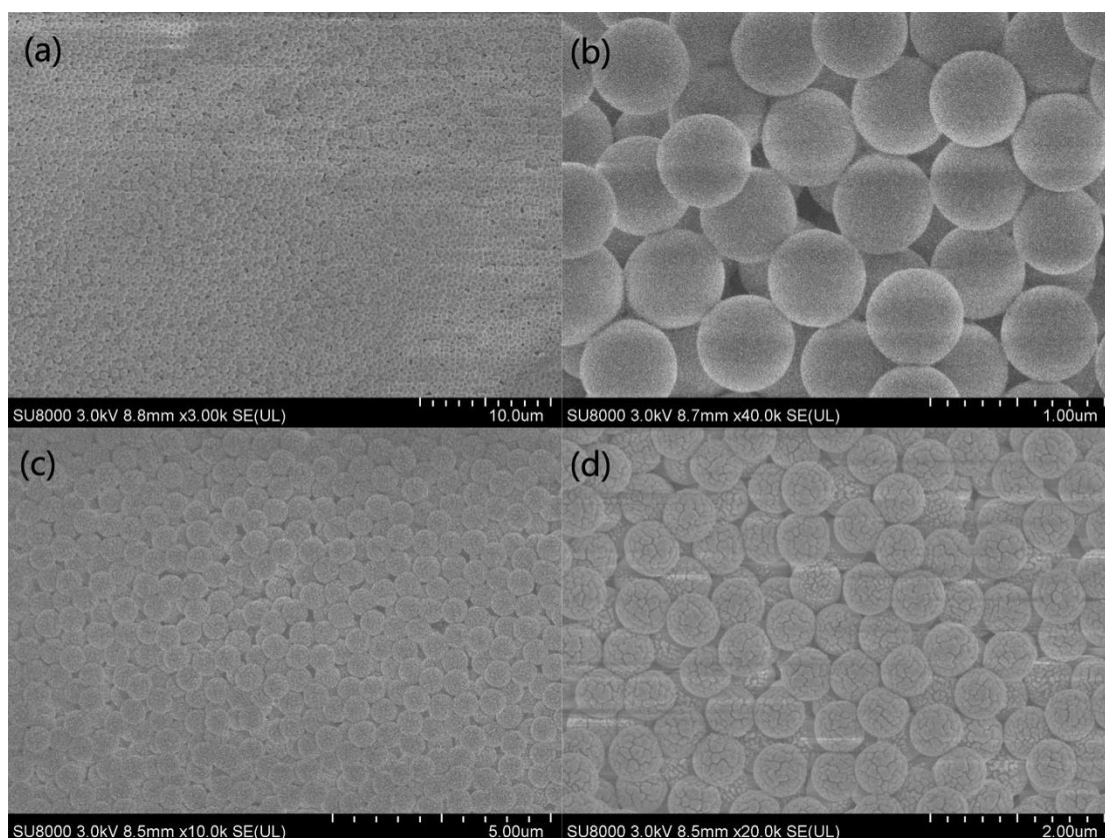


Fig. S2 (a) 3000 times and (b) 40000 times magnified SEM photographs of the super-hydrophobic paint layer. (c) 10000 times and (d) 20000 times magnified SEM photographs of the SNOSS platform.

3. Finite difference time domain (FDTD) simulation

We did FDTD simulation to investigate the plasmonic property of the SNOSS platform. The model in the simulation is not rigorously conformal with the surface structure of the SNOSS, because of its complexity and randomness, as shown in Fig. S3(a). We cut out a small part of the center silica sphere in Fig. S3(a). The extracted part is shown in Fig. S3(b). It was imported into the Lumerical FDTD Solution software as a planar texture of silver as shown in Fig. S3(c). The recognition of the imported SEM was based on the contrast ratio, where the bright area was modeled as silver, and the dark area was modeled as air. The texture was 40 nm in height and placed on a planar glass substrate. Refractive indexes of silver and glass are acquired from the Palik's handbook.¹ The boundary conditions of the simulation region are stabilized PML in all the three dimensions. A total-field-scatter-field source was placed above the texture, and the wavelength ranged from 332 nm to 732 nm. Uniform mesh was used whose scale was $0.9 \times 0.9 \times 0.9 \text{ nm}^3$. A profile monitor was placed at the top of the glass to record the distribution of the electric field (E-fields) at 532-nm wavelength using the standard Fourier transform. Other parameters were set as default. Notably, the simulated E-fields only serve as a representative for the plasmonic property of certain nanoislands. Instead of quantitatively calculating the enhancement factor of the platform, we aim to showing the feature of the E-field distribution and the capability of the nanoislands to produce SERS hot spots.

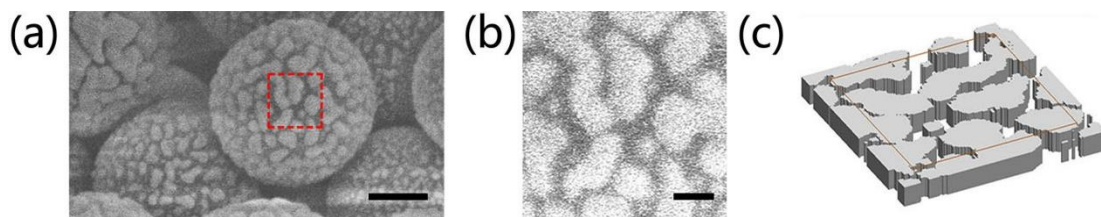


Fig. S3 (a) SEM photograph of the SNOSS structure. Scale bar is 200 nm. (b) The circled part in (a) after being imported into the FDTD software. Scale bar is 40 nm. (c) Schematic illustration of the simulation model. The part in gray color stands for the silver texture which was built referring to (b).

4. SERS measurement using a bench-top Raman spectrograph

We used highly precise bench-top Raman spectrograph (LabRAM HR Evolution laser-confocal Raman spectrograph, Horiba) to detect R6G molecules with a concentration lower than 10^{-15} M. The limit of detection (LOD) can be further lowered to 10^{-16} M. The spectrum is shown in Fig. S4. It was taken under a 20 times magnified objective. The laser power was 2.5% illuminating and the signal was integrated for 20 s.

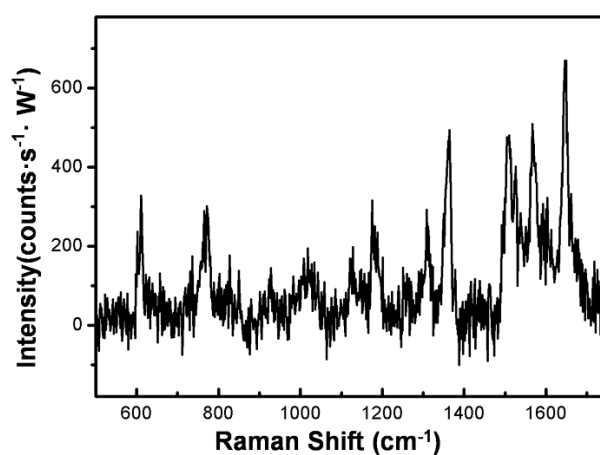


Fig. S4 Raman spectrum of R6G ($10 \mu\text{L}$, 10^{-16} M) enriched on the SNOSS.

5. Calculation of the SERS enhancement factor

We estimated the analytical enhancement factor (AEF), which is defined as the average enhancement for every R6G molecule on the SNOSS platform vs. on a silicon wafer. The calculation is expressed as the equation below:

$$AEF = \frac{I_{\text{platform}}/N_{\text{platform}}}{I_{\text{reference}}/N_{\text{reference}}} \quad (1)$$

where I_{platform} is the Raman intensity of the molecules on the platform, $I_{\text{reference}}$ is the Raman intensity of the molecules on the silicon wafer, N_{platform} is the number of the molecules on the platform which are excited by the laser. $N_{\text{reference}}$ is the number of the molecules on the silicon wafer which are excited by the laser. The surface of SNOSS platform is composed of hierarchical structures, which includes discrete silver nanoislands with various shapes and sizes located on the silica spheres. It is difficult to predict the number of molecules in a small local area because the distribution of Ag islands in local area is not uniform. However, the laser source of the portable fiber spectrometer is $\sim 75 \mu\text{m}$ diameter, which is 150 times of that of silica sphere ($\sim 500 \text{ nm}$), in terms of statistics, the number of molecules is nearly equal in each laser spot when the concentration of R6G molecules is high (10^{-11} M). So we calculate the AEF based on the assumption that the number of molecules in each laser spot is the same.² N can be calculated by:

$$N = A_{\text{laser}} \times \rho \quad (2)$$

where A_{laser} is the cross-section area of the laser beam, and ρ is the density of the molecules. ρ can be described as:

$$\rho = C \times V / A \quad (3)$$

where C stands for the concentration of the analyte solution, V stands for the volume of the droplet, and A stands for the deposition area of the analyte molecules. Since the A_{laser} is constant on both the platform and the silicon wafer, equation (1) can be expressed as:

$$\text{AEF} = \frac{I_{\text{platform}} / (C_{\text{sample}} \times V_{\text{sample}} / A_{\text{sample}})}{I_{\text{reference}} / (C_{\text{reference}} \times V_{\text{reference}} / A_{\text{reference}})} \quad (4)$$

The reference spectrum was acquired by testing the Raman signal of 20 μL ($V_{\text{reference}}$) 10^{-3} M ($C_{\text{reference}}$) R6G deposited on a silicon wafer, as shown in Fig. S5(a). $I_{\text{reference}}$ at 1362 cm^{-1} is $2.03 \times 10^6 \text{ count} \cdot \text{W}^{-1} \cdot \text{s}^{-1}$. Fig. S5(b) shows the photograph of the analyte spot, which is circled within the yellow line. The area of the circle is 7.93 mm^2 , which is regarded as $A_{\text{reference}}$. Accordingly, for 10 μL (V_{sample}) 10^{-11} M (C_{sample}) R6G deposited on the platform, I_{platform} is $7.72 \times 10^6 \text{ count} \cdot \text{W}^{-1} \cdot \text{s}^{-1}$ and A_{sample} is $3.92 \times 10^4 \mu\text{m}^2$. As a result, the AEF approximate to 3.76×10^7 .

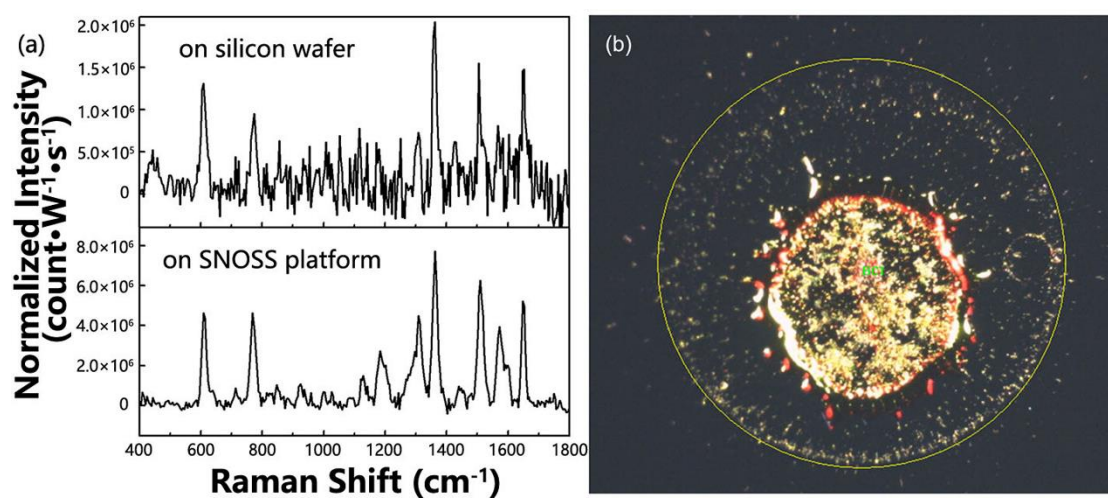


Fig. S5 (a) Raman spectra of R6G (20 μL , 10^{-3} M) deposited on the silicon wafer (top) and R6G (10 μL , 10^{-11} M) deposited on the SNOSS platform (bottom). (b) The micrograph of R6G (20 μL , 10^{-3} M) deposited on the silicon wafer. The yellow circle stands for the deposition area, which is 7.93 mm^2 .

6. Investigation of the saturated region

We measured the Raman spectra of R6G with the concentration from 10^{-9} M to 10^{-6} M to investigate the start of saturated region. The Raman spectra are shown in Fig S6. Clearly, 10^{-7} M of R6G shows the highest intensity at 1362 cm^{-1} Raman shift. The results indicate the start of saturation concentration is in the range of 10^{-6} M to 10^{-8} M. According to the experimental measurements, the concentration of 10^{-7} M could be the start of saturated region.

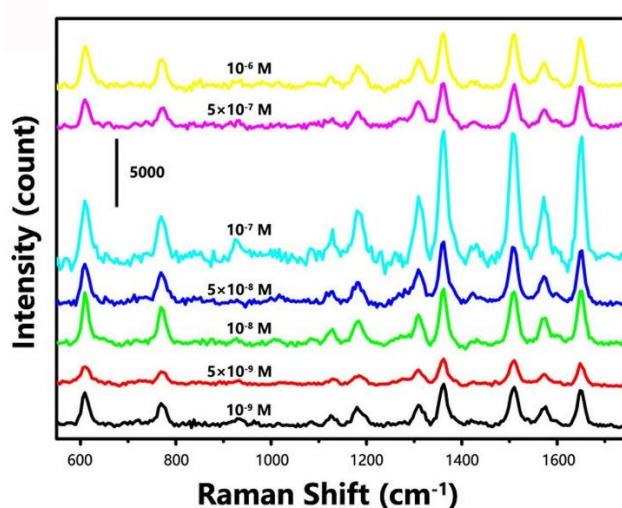


Fig S6 Raman spectra of R6G with the concentration in the range of 10^{-9} M to 10^{-6} M.

The Raman spectra were acquired under the laser power of 4.5×10^{-5} W and integrated for 0.5 s.

7. Evaluation of the reproducibility using 10^{-11} M of R6G

The reproducibility is evaluated by collecting the Raman spectra of R6G ($10\ \mu\text{L}$, 10^{-11} M) on 15 spots, which are spaced by $\sim 0.5\ \text{cm}$ on one piece of SNOSS platform. 25 spectra were collected on each spot, and one spot was randomly chosen from the 15 spots to evaluate the reproducibility of one spot, as presented in Fig. S7(a). The peak intensities at $1362\ \text{cm}^{-1}$ Raman shift of the 25 spectra are presented in Fig. S7(b), the relative standard deviation is 10.88%. The relative standard deviation of the intensities collected on the 15 spots is in the range of 7.86% to 13.59%. Fig. S7(c) presents the average peak intensities at $1362\ \text{cm}^{-1}$ Raman shift of the 15 spots, the relative standard deviation is 10.09%, which represents the spot-to-spot reproducibility of this platform.

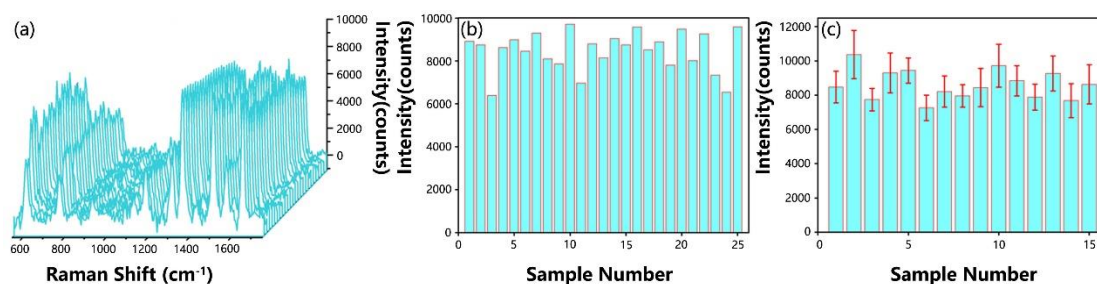


Fig. S7 (a) Raman spectra of R6G ($10\ \mu\text{L}$, 10^{-11} M) droplets enriched on SNOSS platforms, which were acquired under the laser power of 1.6×10^{-3} W and integrated for 0.7 s. (b) Collection of the peak intensities at $1362\ \text{cm}^{-1}$ Raman shift measured on one spot. (c) Collection of the average peak intensities at $1362\ \text{cm}^{-1}$ Raman shift of the 15 spots. The lines represent one standard deviation. Number of measurements $n=25$.

References

- 1 E. D. Palik, *Handbook of Optical Constants of Solids*, Academic Press, Orlando, FL 1985, **1**, 429-443.
- 2 J. A. Huang, Y. L. Zhang, Y. Zhao, X. L. Zhang, M. L. Sun and W. Zhang, *Nanoscale*, 2016, **8**, 11487-11493.