

Supplementary

Nanoporous Ag-Decorated Ag₇O₈NO₃ Micro-Pyramids for Sensitive Surface-Enhanced Raman Scattering Detection

Linfan Guo ¹, Haibin Tang ², Xiujuan Wang ³, Yupeng Yuan ¹ and Chuhong Zhu ¹

¹ School of Chemistry and Chemical Engineering, School of Materials Science and Engineering, Anhui University, Hefei, 230601, China

² Key Laboratory of Materials Physics, Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei, 230031, China

³ School of Microelectronics, Hefei University of Technology, Hefei, 230009, China

* Correspondence: Email: chzhu@ahu.edu.cn or chzhu@issp.ac.cn

S1. Estimation of enhancement factor

For estimation of the enhancement factor of the nanoporous Ag-decorated Ag₇O₈NO₃ micro-pyramids, 10 μ L (volume of the reference analyte solution, denoted as V_{Ref}) of 10^{−2} M (concentration of the reference analyte solution, denoted as C_{Ref}) R6G ethanol solution was dispersed on a polyvinyl chloride film, and formed a spreading area of π mm² (surface area of the polyvinyl chloride film covered by analyte molecules, denoted as S_{Ref}). The enhancement factor is calculated by comparing the ratios of R6G molecules on a nanoporous Ag-decorated Ag₇O₈NO₃ micro-pyramid (Curve I in Figure. S10) to the corresponding un-enhanced signals from a pure R6G on the polyvinyl chloride film (reference sample, Curve II in Figure. S10):

$$EF = \frac{I_{\text{SERS}}N_{\text{Ref}}}{I_{\text{Ref}}N_{\text{SERS}}} = \frac{I_{\text{SERS}}C_{\text{Ref}}V_{\text{Ref}}S_{\text{SERS}}}{I_{\text{Ref}}C_{\text{SERS}}V_{\text{SERS}}S_{\text{Ref}}} \quad (\text{S1})$$

where I_{SERS} and I_{NRS} are the Raman intensities of the spectra, N_{SERS} and N_{Ref} are the number of R6G molecules illuminated by the laser absorbed on the nanoporous Ag-decorated Ag₇O₈NO₃ micro-pyramid and in the reference sample, respectively. For the pure R6G on the polyvinyl chloride film with an area of π mm² (S_{Ref}), considering the laser spot is a circle with a diameter of 5 μ m, the number of the R6G molecules illuminated by the laser (N_{Ref}) is $10^{-2} \times 10^{-5} \times 6.02 \times 10^{23} \times \pi(5\mu\text{m}/2)^2/\pi \text{ mm}^2 = 3.76 \times 10^{11}$. For the estimation of N_{SERS} and I_{SERS} , 10 μ L (volume of the analyte solution used for SERS, denoted as V_{SERS}) of a 10^{−11} M (concentration of the analyte solution employed for SERS, denoted as C_{SERS}) R6G ethanol solution was dispersed to 4 mm² (surface area of the SERS substrate covered by analyte molecules, denoted as S_{SERS}) of the nanoporous Ag pyramids. Supposing that all R6G molecules are absorbed on the nanoporous Ag pyramids, N_{SERS} was estimated to be $10^{-11} \times 10^{-5} \times 6.02 \times 10^{23} \times \pi(5\mu\text{m}/2)^2/4 \text{ mm}^2 = 295$. For the band at 1648 cm^{−1}, $I_{\text{SERS}}/I_{\text{Ref}}$ was 0.44. Therefore, the enhancement factor for the band at 1648 cm^{−1} is calculated to be 5.6×10^8 .

S2. Experimental

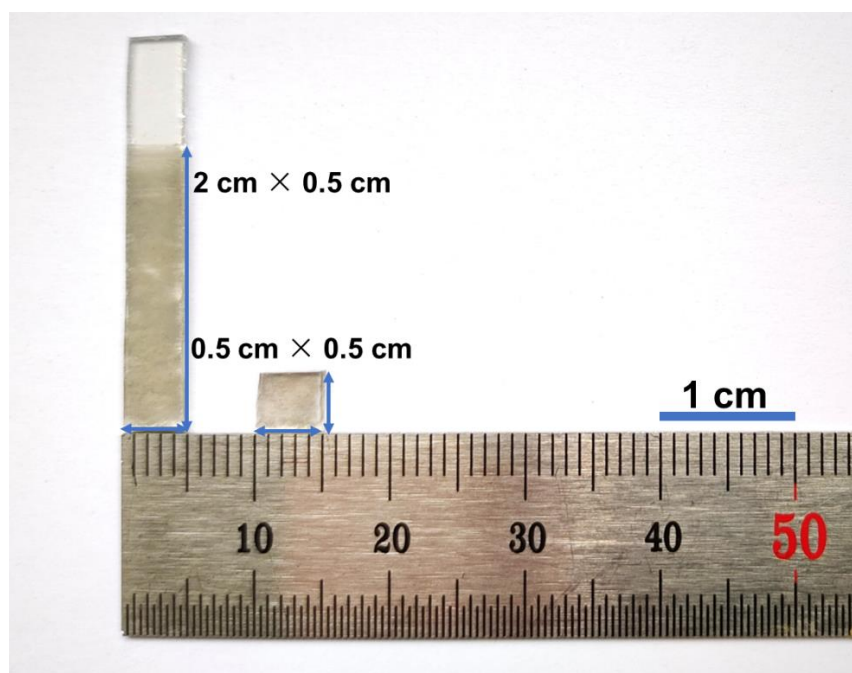


Figure S1. The fabricated nanoporous Ag-decorated $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids on ITO glass ($2\text{ cm} \times 0.5\text{ cm}$) (left) and the actual substrate cut down for SERS detection ($0.5\text{ cm} \times 0.5\text{ cm}$) (right).

S3. Characteristics of $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids

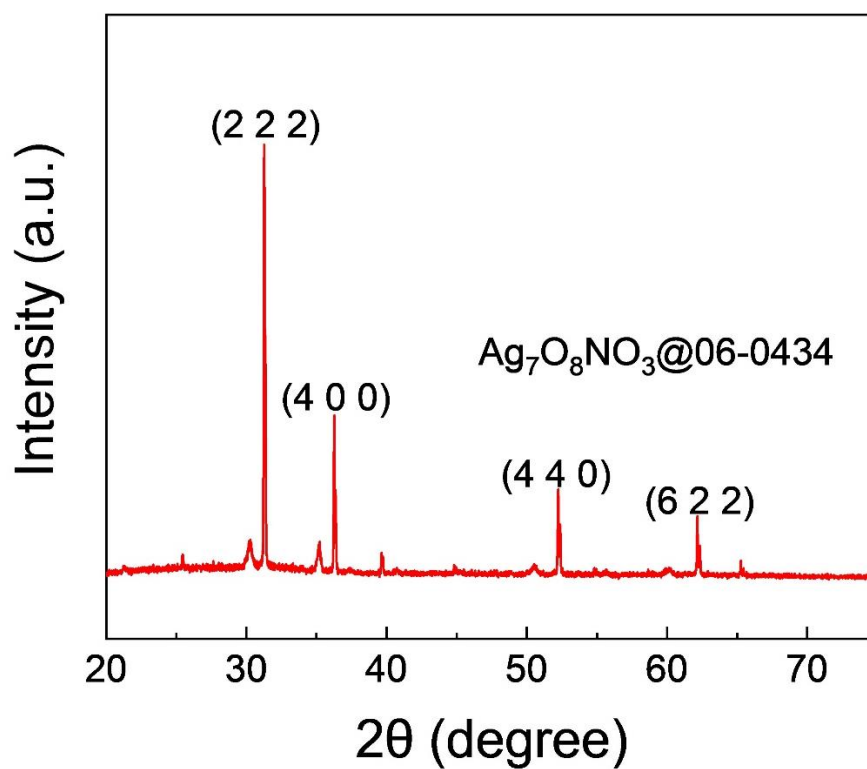


Figure S2. X-ray diffraction pattern of the electrodeposited materials achieved under electrodeposition voltage of 3 V and electrodeposition duration of 300 s.

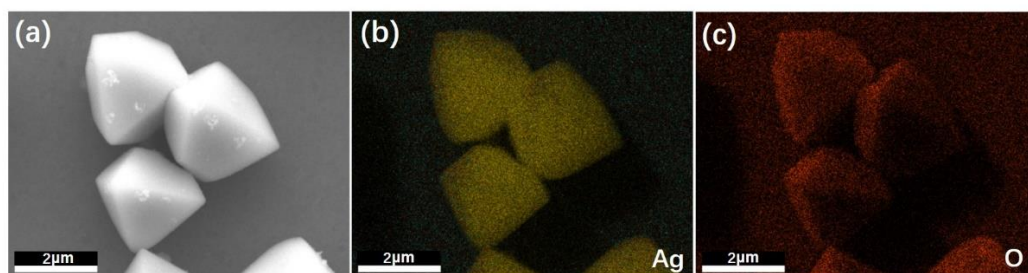


Figure S3. Energy-dispersive X-ray (EDX) mapping images of electrodeposited materials: (a) bright-field image; (b) Ag element mapping; (c) O element mapping.

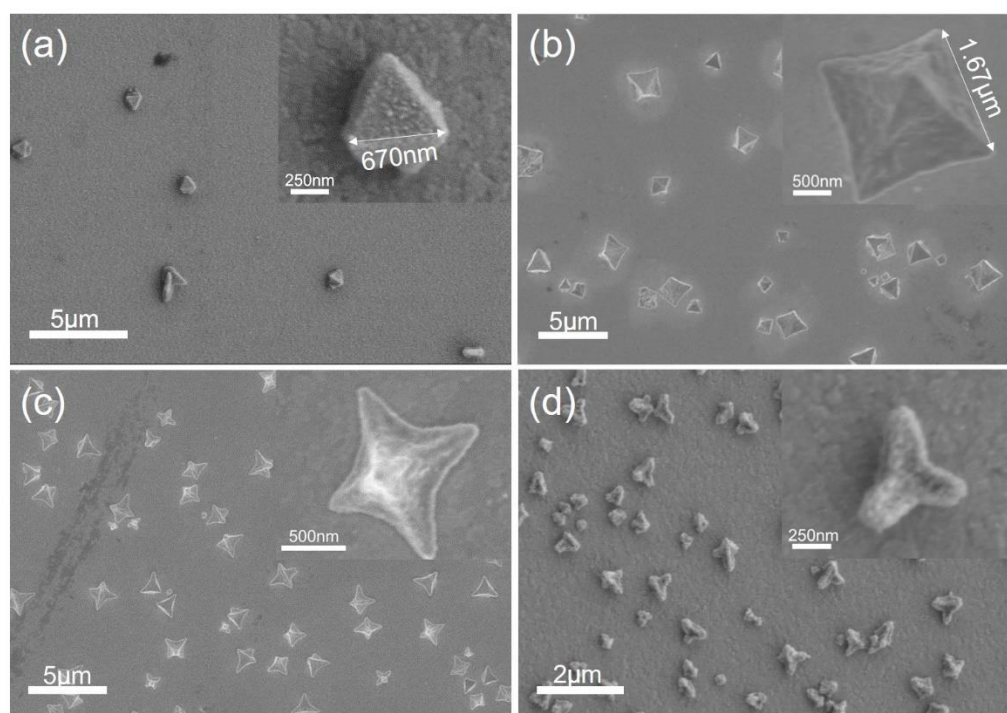


Figure S4. SEM images of the $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids' morphology evolution under the same electrodeposition time (10 s), while the electrodeposition voltage was increased from 1.5 V to 10 V: (a) 1.5 V; (b) 3 V; (c) 5 V; (d) 10 V. The insets are magnified images.

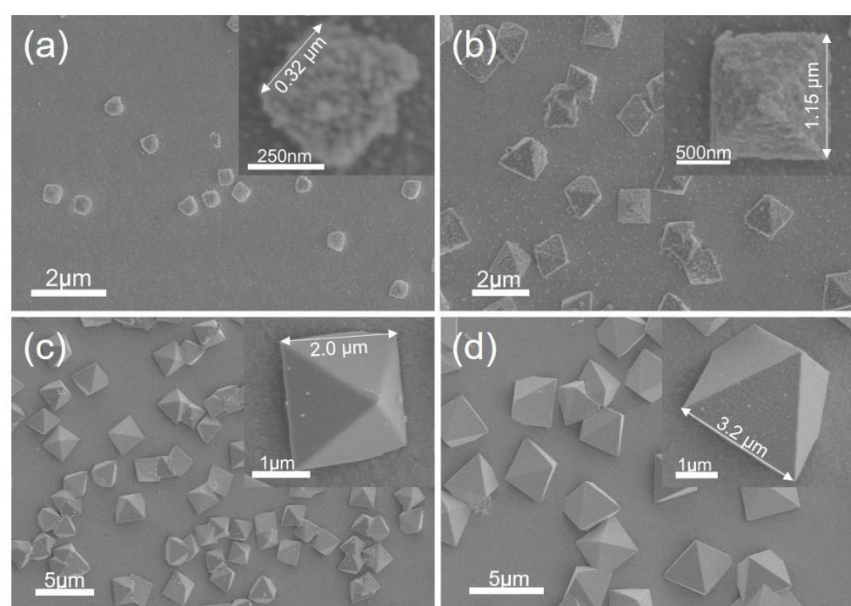


Figure S5. SEM images of the $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids' morphology evolution under the same electrodeposition voltage (3 V), while the electrodeposition time was increased from 1 s to 300 s: (a) 1 s; (b) 60 s; (c) 180 s; (d) 300 s. The insets are magnified images.

S4. Fabrication of nanoporous Ag-decorated $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids

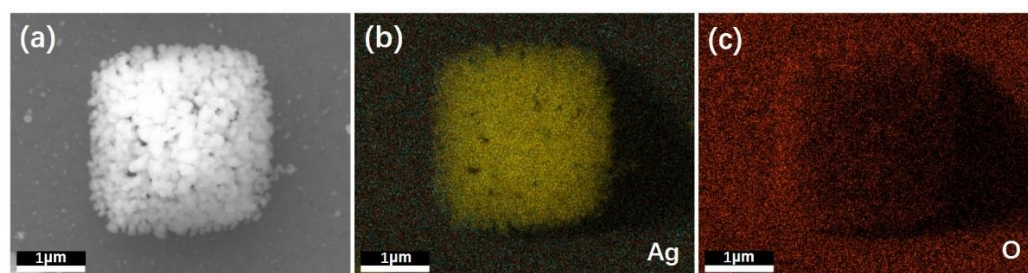


Figure S6. Energy-dispersive X-ray (EDX) mapping images of nanoporous Ag-decorated $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids: (a) bright-field image; (b) Ag element mapping; (c) O element mapping.

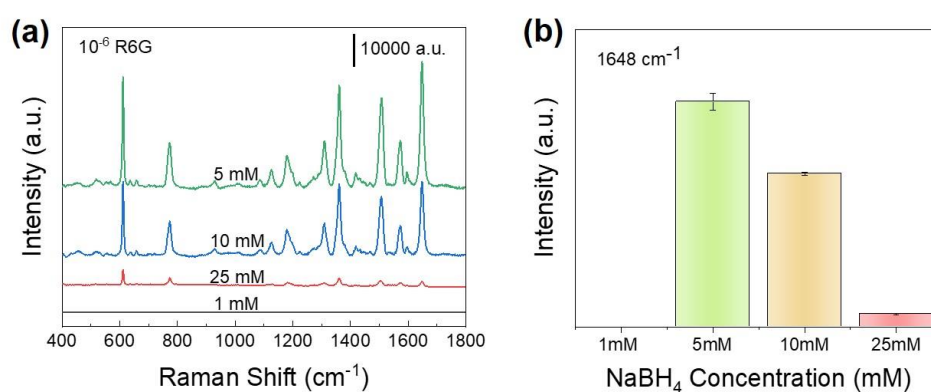


Figure S7. (a) SERS signals of R6G (10^{-6} M) collected from nanoporous Ag-decorated $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids reduced by using NaBH_4 solution with different concentrations. (b) The peak intensity of 1648 cm^{-1} detected on the nanoporous Ag-decorated $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids corresponding to (a).

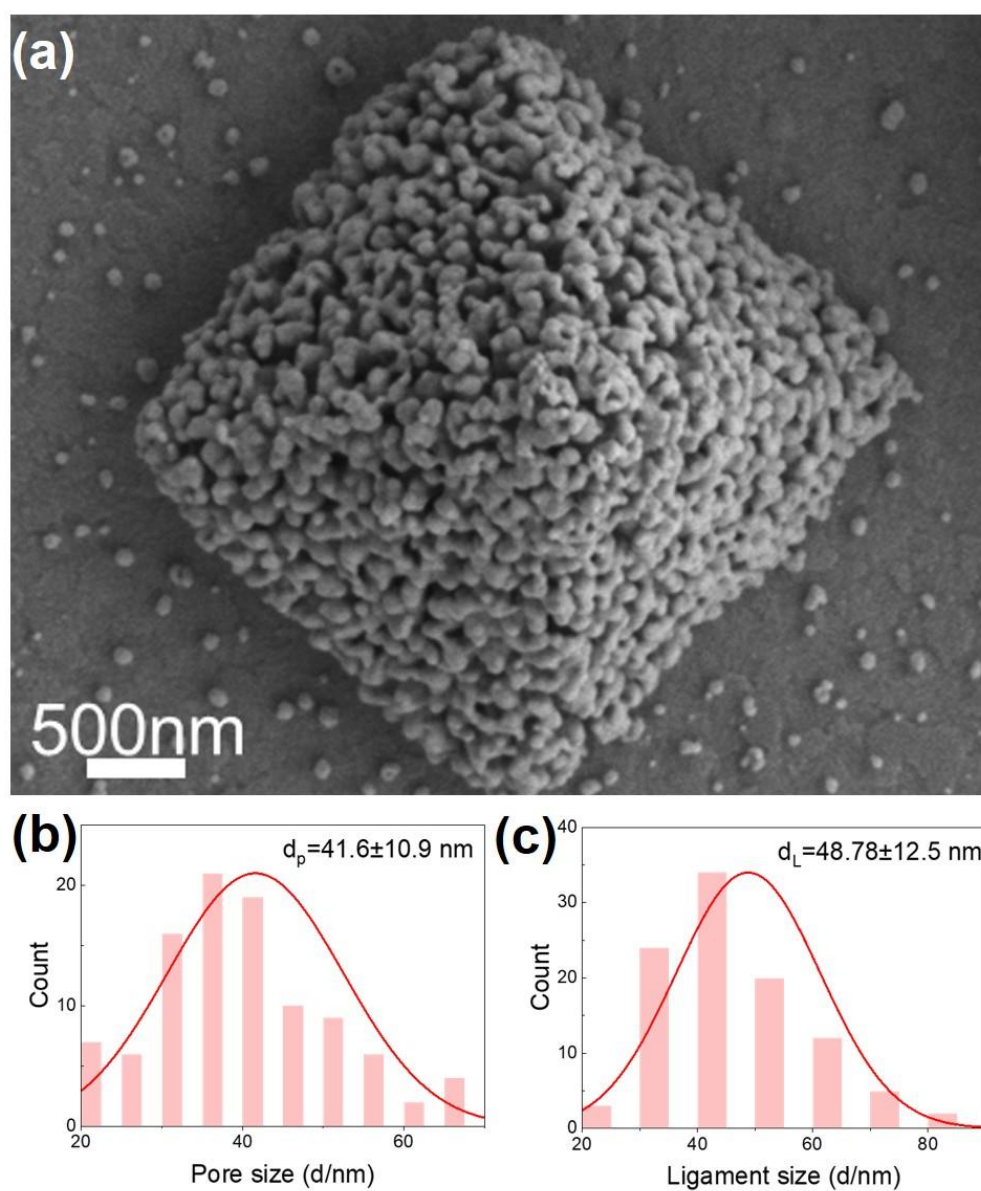


Figure S8. (a) Morphology of nanoporous Ag-decorated $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids, which was fabricated by reducing $\text{Ag}_7\text{O}_8\text{NO}_3$ in a 0.005 M NaBH_4 solution. (b) and (c) shows the pore/ligament size distribution within the nanoporous Ag-decorated $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids obtained by measuring 100 nanopores.

S5. SERS performance

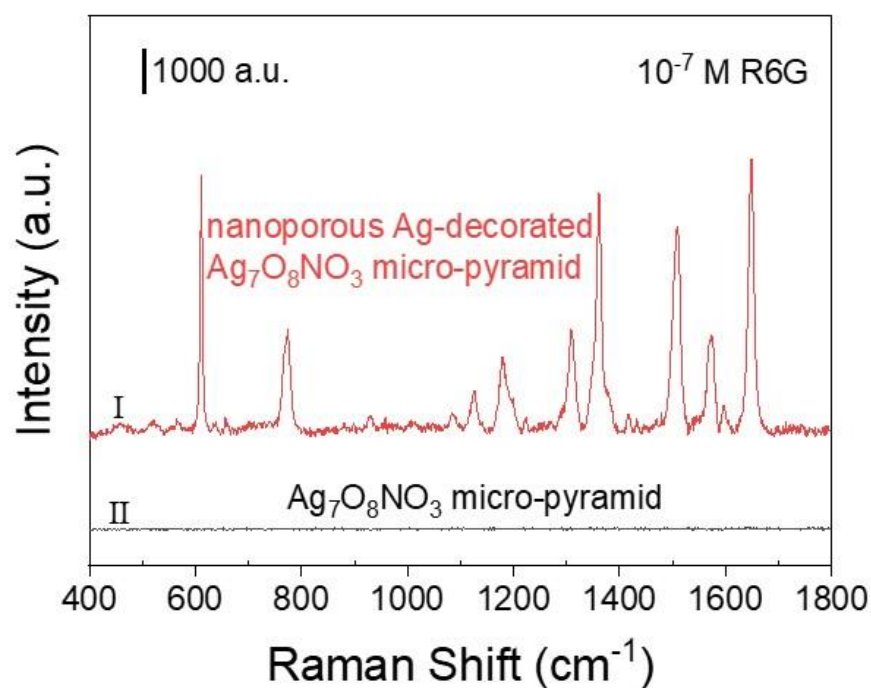


Figure S9. (Curve I) SERS spectrum of 10^{-7} M R6G absorbed on the nanoporous Ag-decorated $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids, and (curve II) SERS spectrum of 10^{-7} M R6G absorbed on the $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids. The spectra were acquired with acquisition time of 10 s.

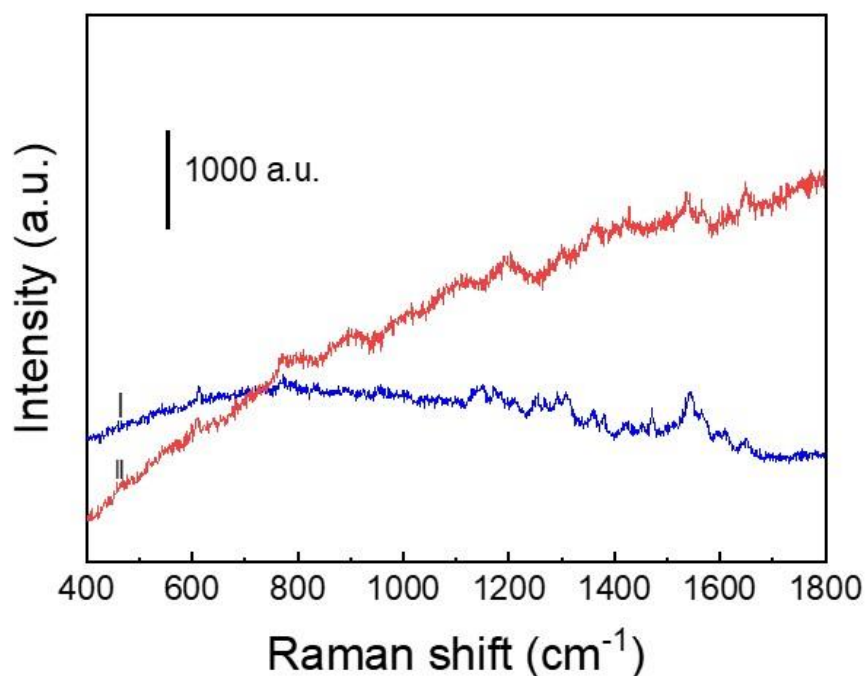


Figure S10. (Curve I) SERS spectrum of 10^{-11} M R6G absorbed on the nanoporous Ag-decorated $\text{Ag}_7\text{O}_8\text{NO}_3$ micro-pyramids, and (curve II) the normal Raman spectrum of R6G polyvinyl chloride film. The spectra were acquired with acquisition time of 10 s.

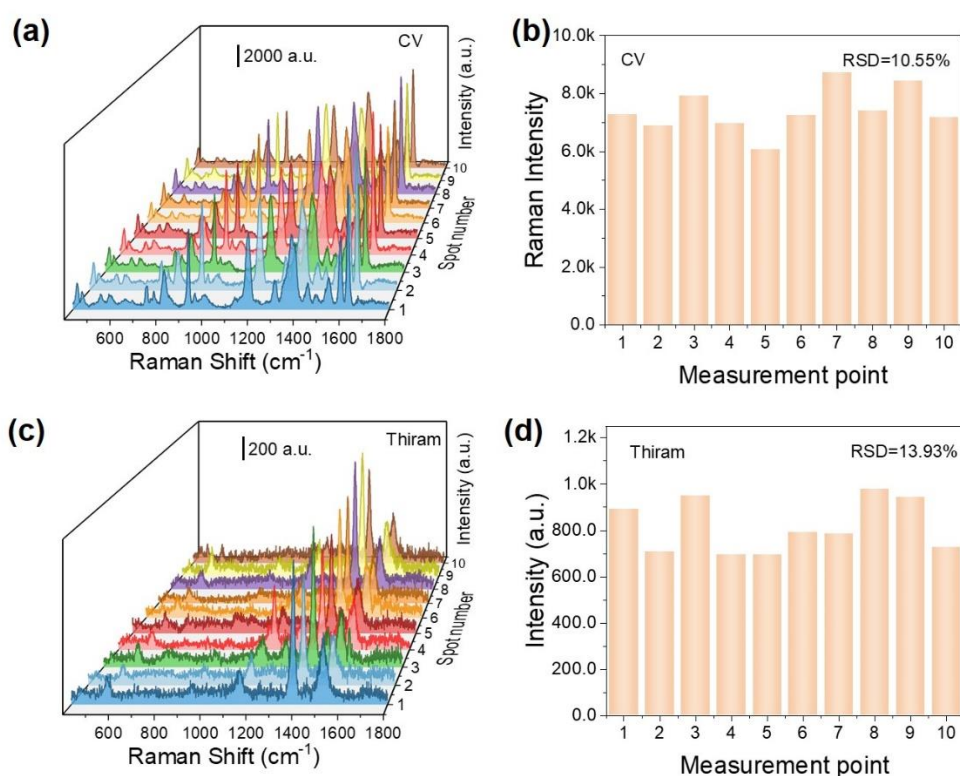


Figure S11. (a) and (b) Raman spectra collected from 10 randomly selected sites on nanoporous Ag-decorated Ag₇O₈NO₃ micro-pyramids in the detection of 10⁻⁵ M CV and the RSD values of 1618 cm⁻¹ (CV) peaks, respectively. (c) and (d) Raman spectra collected from 10 randomly selected sites on nanoporous Ag-decorated Ag₇O₈NO₃ micro-pyramids in the detection of 10⁻⁵ M thiram and the RSD values of 1384 cm⁻¹ (thiram) peaks, respectively.

S6. Comparison of LODs between various SERS substrates

Table S1.

SERS substrate	LOD (R6G)	Ref.
nanoporous Ag-decorated Ag ₇ O ₈ NO ₃ micro-pyramids	10 ⁻¹⁵ M	This work
PA-Ag@C film	10 ⁻¹⁰ M	[1]
nano-Ag/Au@Au film	1 × 10 ⁻¹³ M	[2]
GO/Au@Ag NBs membranes	1.12 × 10 ⁻¹⁰ M	[3]
ZnO/Ag Core-Satellite Nanostructures	1 × 10 ⁻¹³ M	[4]
Ag NRs/O-g-C ₃ N ₄ substrate	8.2 × 10 ⁻¹⁰ M	[5]
Ag@Fe ₂ O ₃ hybrid materials	9.3 × 10 ⁻¹⁰ M	[6]
ball-like Ag nanorod aggregates	5 × 10 ⁻⁹ M	[7]
flower-like Ag@CuO Substrate	2.6 × 10 ⁻⁸ M	[8]

References

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