

Supporting Information

Enhancing Charge Transfer in W₁₈O₄₉/g-C₃N₄ Heterostructure *via* Band Structure Engineering for Effective SERS Detection and Flexible Substrate Applications

Lu Tan,^{a,b} Shuzhen Yue,^b Yongbing Lou,^{a,*} and Jun-Jie Zhu^{b,c,*}

^a *School of Chemistry and Chemical Engineering, Southeast University, Nanjing, Jiangsu 211189, China*

^b *State Key Laboratory of Analytical Chemistry for Life Science, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, Jiangsu 210023, China*

^c *Shenzhen Research Institute of Nanjing University, Shenzhen 518000, China*

**Corresponding author. E-mail: lou@seu.edu.cn (Y. Lou), jjzhu@nju.edu.cn (J.-J. Zhu)*

Table of Contents

Experimental section.....	S-3
Chemical and materials.....	S-3
Characterization of materials.....	S-3
Fabrication of the g-C ₃ N ₄ nanosheets.....	S-4
Fabrication of the W ₁₈ O ₄₉ /g-C ₃ N ₄ (WCN) heterostructure.....	S-4
SERS measurement of the WCN-based substrates.....	S-4
Fabrication of the flexible SERS chips.....	S-5
Detection in real samples.....	S-5
Calculations of enhancement factor (EF).	S-5
Calculation of the energy levels.....	S-6
Computational details.....	S-7
Figure S1.....	S-8
Figure S2.....	S-8
Figure S3.....	S-8
Figure S4.....	S-9
Figure S5.....	S-9
Figure S6.....	S-9
Figure S7.....	S-10
Figure S8.....	S-10
Figure S9.....	S-11
Figure S10.....	S-11
Figure S11.....	S-11
Figure S12.....	S-12
Figure S13.....	S-12
Figure S14.....	S-13
Table S1.....	S-14
Table S2.....	S-15
Table S3.....	S-16
References.....	S-17

Experimental section

Chemical and materials.

Tungsten hexachloride (WCl_6), dicyandiamide, crystal violet (CV) and ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. Malachite green (MG) was acquired from Aladdin Reagent Co., Ltd. Rhodamine 6G (R6G), methylene blue (MB) and methyl orange (MO) were bought from Sigma-Aldrich. The nylon filter membrane (50 mm in diameter) with a pore size of 0.22 μm was purchased from Shanghai Titan Technology Co., Ltd. All the other chemicals were of analytical grade and used without further treatment. The ultrapure water (resistance over 18 $\text{M}\Omega\text{ cm}$ at 25 $^\circ\text{C}$) used in this work was obtained using a Milli-Q water purification system.

Characterization of materials.

X-ray power diffraction (XRD) on Bruker D8 Advance X-ray diffractometer was recorded to study the crystal structure with $\text{Cu K}\alpha$ radiation and a scanning rate of 5 $^\circ\text{ min}^{-1}$ from 10 $^\circ$ to 80 $^\circ$. The morphologies, microstructures and Energy-dispersive spectroscopy (EDS) were obtained with a Hitachi S4800 field-emission scanning electron microscopy (FESEM, 20 kV). The detailed parameters of the materials were collected by Transmission electron microscopy (TEM) images on a JEM-1011 transmission electron microscope (TEM, 100 kV). Fourier transform infrared (FTIR) spectra were obtained using a Nicolet 6700 spectrophotometer (Nicolet Co., USA) with a KBr pellet. X-ray photoelectron spectroscopy (XPS) was operated to analyze the compositions and chemical states of the samples on a PHI5000 Versa Probe spectrometer with an $\text{Al K}\alpha$ as an X-ray source. The optical absorption spectra and band gap were obtained on a UV-Vis-NIR spectrophotometer (Shimadzu, UV-3600) with 200 nm to 800 nm in the Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) mode. In-situ electron paramagnetic resonance (EPR) signals were collected to investigate the oxygen vacancies at room temperature, where 10 mg of powder was weighed and put into the sample tube for testing. The electrochemical measurements were examined on the CHI660E electrochemical workstation with a three-electrode quartz cell. In this section, 0.1 M of Na_2SO_4 aqueous solution was employed as the electrolyte, indium tin oxide (ITO) conducting glass coating with the WCN samples, platinum wire and

Ag/AgCl (saturated KCl) electrode was applied as the working electrode, counter electrode and reference electrode, respectively. A Xenon lamp (150W) was used as the light source in the photocurrent response measurement.

For the calculation of relative standard deviation (RSD) spot-to-spot on WCN, the WCN was tested for sensing 10^{-6} MG and 20 spectra were randomly collected from each sample and the average values were used for the RSD calculation.

Fabrication of the g-C₃N₄ nanosheets.

Graphitic carbon nitride (g-C₃N₄) nanosheets were fabricated by a two-step calcination method. In detail, dicyandiamide (6 g) was placed in a muffle furnace and heated to 550 °C with a rate of 2.5 °C·min⁻¹ for 240 min. The as-prepared powders were grind and heated at 500 °C for 120 min with a temperature increment rate of 2 °C·min⁻¹ to obtain the g-C₃N₄ nanosheets.

Fabrication of the W₁₈O₄₉/g-C₃N₄ (WCN) heterostructure.

The WCN heterostructure was prepared *via* a facile solvothermal method. In a typical procedure, the WCl₆ (50 mg) precursor solution was first dispersed in ethanol (30 mL) by sonication for 5 min. After that, the g-C₃N₄ nanosheets of a given amount (50 mg) were added into the above solution and kept stirring for 45 min under room temperature to obtain a uniform suspension. Then the mixture was sealed into a Teflon-lined stainless steel autoclave and heated at 160 °C for 10 h. After completion of the reaction, the mixture was cooled down to room temperature. The final precipitates were collected via centrifugation, treated with water and ethanol three times, and dried under vacuum at 60 °C for 12 h before future use. In addition, the W₁₈O₄₉ nanomaterials were prepared for comparison under similar conditions in the absence of g-C₃N₄ nanosheets.

SERS measurement of the WCN-based substrates.

CV, MB, MG, MO and R6G were used to evaluate the SERS behaviors of WCN materials. The WCN (10 mg) was dispersed in deionized water (10 mL). Then 20 μL of this substrate's suspension was dropped on a glass substrate (0.25 cm²) and dried in a vacuum oven at 60 °C to form a uniform substrate. Then 10 μL of Raman molecule solution was added to the fabricated substrate and dried at 60 °C for 30 min before the

Raman measurements. A Reflex Confocal microRaman spectroscopy system (inVia, Renishaw, UK) was operated to collect the Raman spectra with a 50× objective. Laser 633 nm was applied as the excitation source and the laser power was 1.7 mW. All the Raman spectra were recorded with an acquisition time of 10 s and averaging the signals collected at five random spots.

Fabrication of the flexible SERS chips.

The flexible SERS substrate was prepared by a filtration process to decorate the WCN heterostructure on the nylon filter membrane. Typically, the suspension of WCN in ethanol (40 mL, 1mg mL⁻¹) was passed through the nylon filter membrane by vacuum filtration, leaving the WCN loaded on the filter membrane. The as-prepared flexible substrate was dried under vacuum at 60 °C overnight and the resulting substrate was cut into pieces (0.5 × 0.5 cm²) for each Raman test.

Detection in real samples.

To evaluate the application of WCN substrates in detecting real contaminated samples, the fish bought from the local market was used as the model and carefully washed with deionized water. Then, 20 μL solutions of MG molecules with different concentrations were dropped onto the surface and evaporated naturally at room temperature. Ethanol solutions were applied to extract the MG molecules from the primed surface of the fish, and the flexible WCN-based SERS chips were employed to wipe the model's surfaces carefully and slowly. After drying for 30 min at room temperature, the chips were measured by a Raman spectrometer and the procedure was repeated at least three times on ten random points.

Calculations of enhancement factor (EF).

The enhancement factor (EF) The enhancement factor (EF) was calculated to estimate the potentiation of the proposed substrate according to the following equations:

$$EF = \frac{I_{SERS}}{I_{bulk}} \times \frac{N_{bulk}}{N_{SERS}} \quad (1)$$

where I_{SERS} and I_{bulk} represent the peak intensities of SERS and the normal Raman at 1617 cm⁻¹. Simultaneously, N_{SERS} and N_{bulk} are the valid molecule number on the WCN substrate and the practical number of probe molecules in the Raman detection view.

The number of probe molecules (N_{bulk}) in standard Raman detection can be calculated in the following equation:

$$N_{bulk} = \frac{\rho h S_{Raman} N_A}{M} \quad (2)$$

$$S_{Raman} = \pi \left(\frac{d_{laser}}{2} \right)^2 \quad (3)$$

$$d_{laser} = \frac{1.22\lambda}{N.A.} \quad (4)$$

$$h = \frac{3.28\eta d_{laser}}{N.A.} \quad (5)$$

where S_{Raman} is the laser radiation area, M is the molecular weight (463.5 g mol⁻¹) and N_A is the Avogadro constant. In equation (4), d_{laser} is the diameter of the laser, and it could be inferred from the equation (4). In the equation (4), λ is the wavelength of the laser (633 nm) and $N.A.$ represents the numerical aperture of 20× objective ($N.A. = 0.4$). As for the laser radiation depth, η is the refractive index of water (1.33). ρ is the density of bulk MG (1.0448 g cm⁻³) and h is the laser radiation depth, which could be calculated in equation (5) to be 21 μm.

Given that the molecules were distributed in a monolayer on the substrate, and the valid probe number on WCN substrate in the SERS detection can be calculated using the following equation:

$$N_{SERS} = CV N_A \frac{S_{SERS}}{S_{substrate}} \quad (6)$$

Where, C is the molar concentration of the analyte solution, V is the volume of the droplet, N_A is the Avogadro constant, S_{SERS} is the area of laser radiation in SERS detection, similar to S_{Raman} in the same conditions. $S_{substrate}$ is the area of the substrate (0.25 cm²).

Calculation of the energy levels.

The position of the conduction band (CB) and valence band (VB) for semiconductors could be calculated according to the following equation:

$$E_{CB} = E_{VB} - E_g \quad (7)$$

Where E_{CB} labels the energy level of CB, E_{VB} is the energy level of VB and E_g is the band gap.

The optical band gap energies of the samples are determined using the Kubelka–

Munk function ¹:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (8)$$

where α , h , ν , A and E_g are the absorption coefficient, Planck's constant, light frequency, proportionality constant and band gap, respectively.

The corresponding energy levels for the vacuum could be calculated by subtracting the energy level from the -4.5 eV.

Computational details

All the calculations are performed in the framework of the density functional theory with the projector augmented plane-wave method, as implemented in the Vienna ab initio simulation package ². The generalized gradient approximation proposed by Perdew, Burke, and Ernzerhof is selected for the exchange-correlation potential ³. The long-range van der Waals interaction is described by the DFT-D2 approach ⁴. The cut-off energy for the plane wave is set to 500 eV. The energy criterion is set to 10^{-4} eV in the iterative solution of the Kohn-Sham equation. A vacuum layer of 15 Å is added perpendicular to the sheet to avoid artificial interaction between periodic images. The Brillouin zone integration is performed using a $1 \times 1 \times 1$ k-mesh. All the structures are relaxed until the residual forces on the atoms have declined to less than 10^{-3} eV. When we calculate the system containing malachite green cation, we subtract an electron because malachite green cation carries a positive charge.

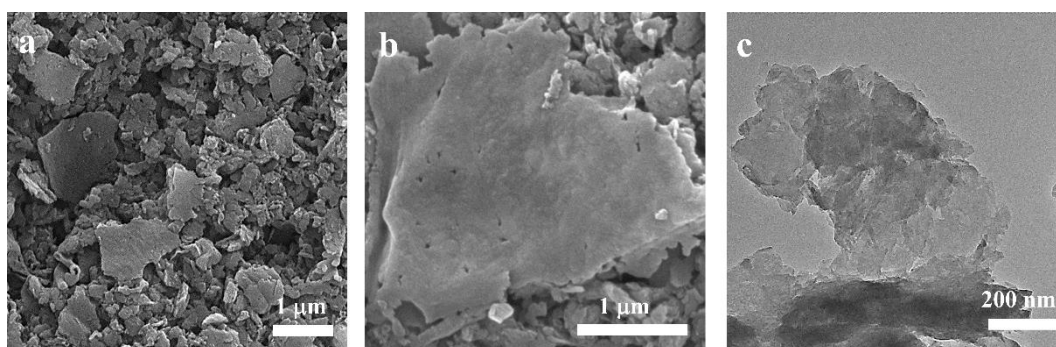


Figure S1. (a,b)SEM and (c) TEM images of g-C₃N₄.

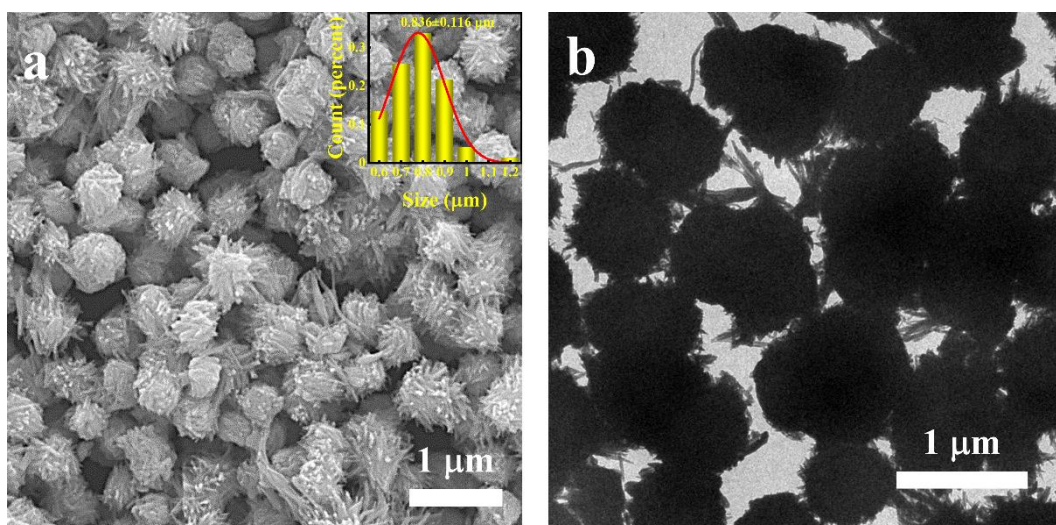


Figure S2. (a) SEM and (b) TEM images of W₁₈O₄₉. Insets: the size distribution of W₁₈O₄₉.

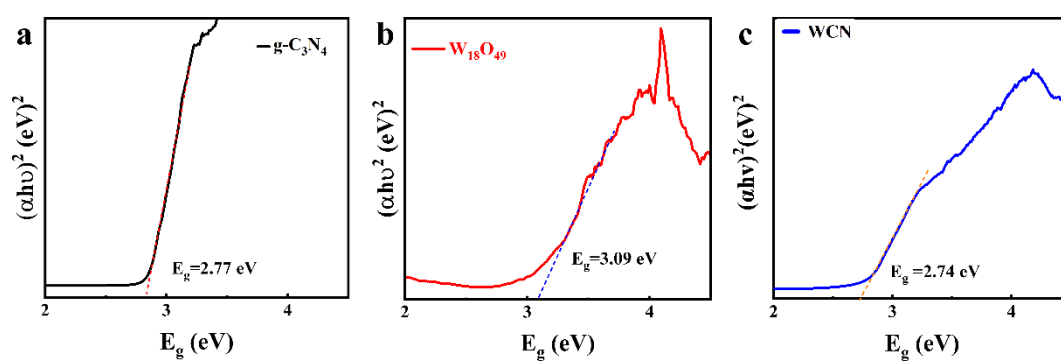


Figure S3. The Tauc plots of (a) g-C₃N₄ nanosheets, (b) W₁₈O₄₉ and (c) WCN samples by the Kubelka–Munk method vs. the photo energy.

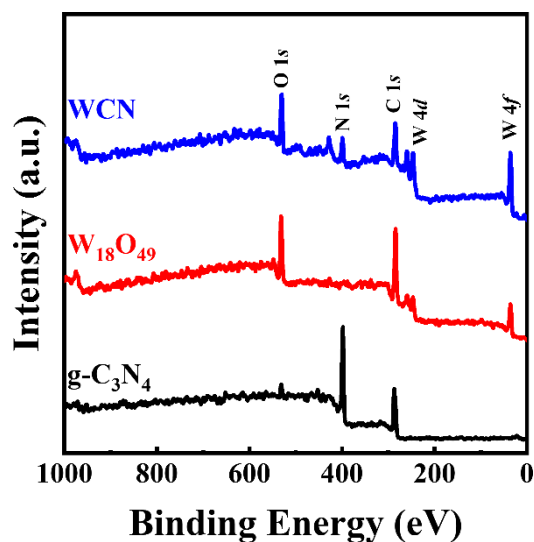


Figure S4. The XPS survey spectra of g-C₃N₄, W₁₈O₄₉ and WCN-2.

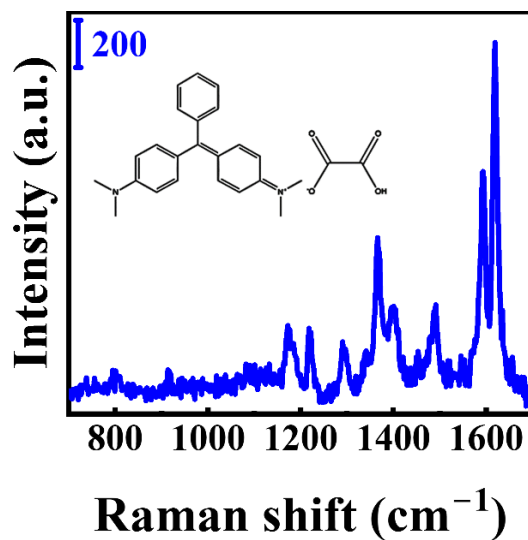


Figure S5. The typical Raman spectrum and the molecular formula of MG.

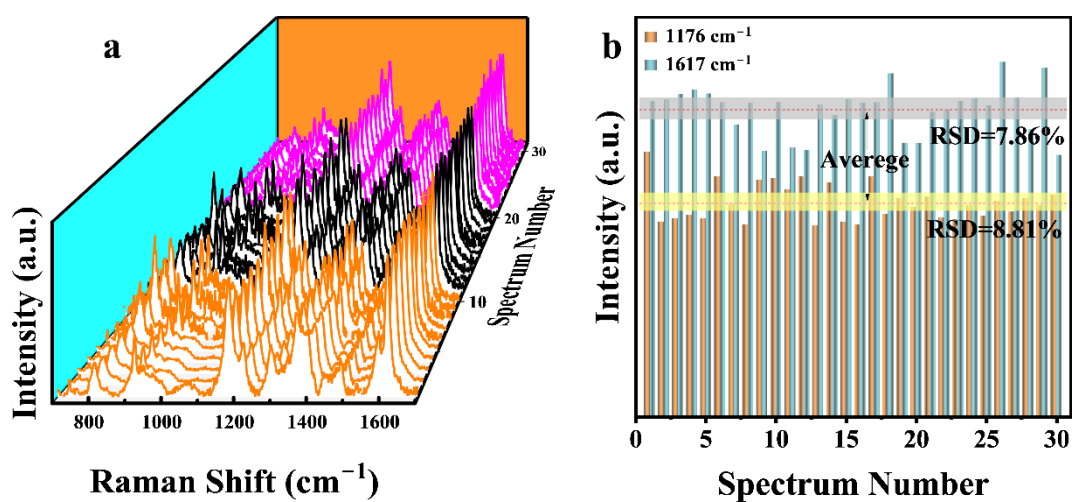


Figure S6. (a) SERS spectra of 10⁻⁶ M MG collected from 10 random spots on three

batches (No. 1-10: 1st batch, No. 11-20: 2nd batch, No. 21-30: 3rd batch) of WCN substrates, and (b) the corresponding peak intensity at 1176 cm^{-1} and 1617 cm^{-1} .

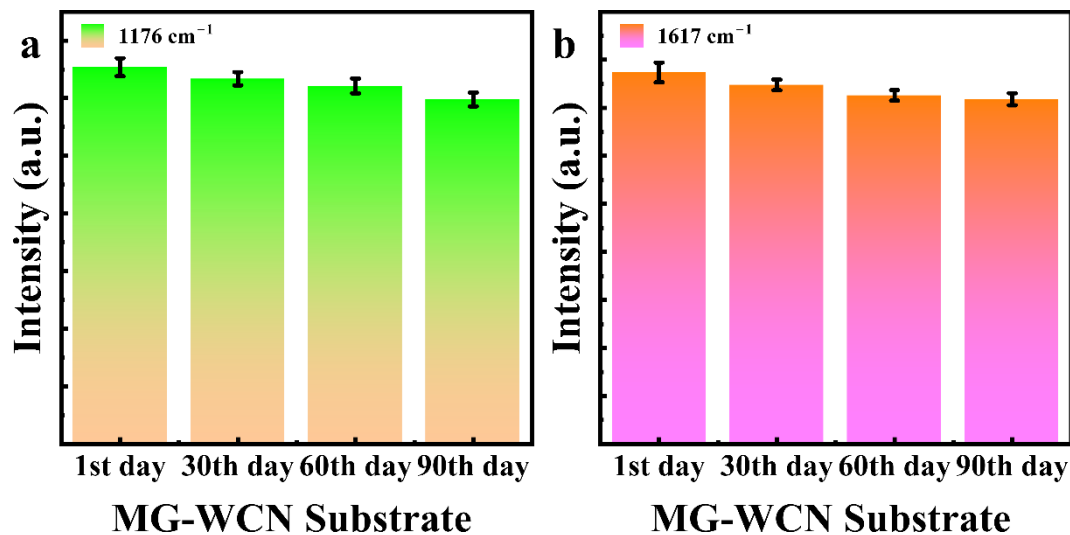


Figure S7. Peak Intensity stability at (a) 1176 cm^{-1} and (b) 1617 cm^{-1} of MG collected on WCN-2 during 90 days storage.

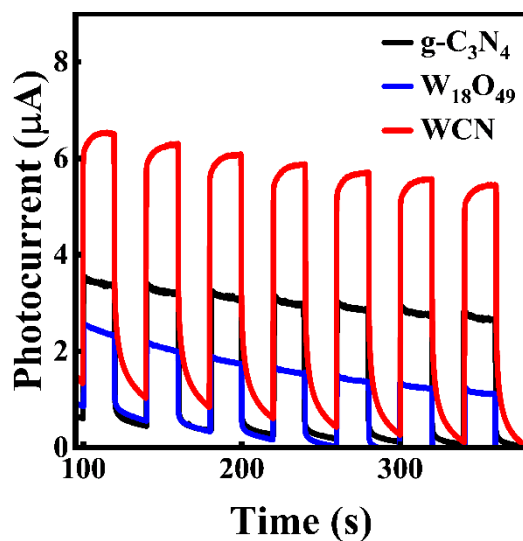


Figure S8. Transient photocurrent responses of $g\text{-C}_3\text{N}_4$ nanosheets (black line) $\text{W}_{18}\text{O}_{49}$ (blue line) and WCN (red line) samples in $0.2\text{ M Na}_2\text{SO}_4$ aqueous solutions ($\text{pH}=6.8$) under the irradiation of visible light with light on and off every 20 seconds.

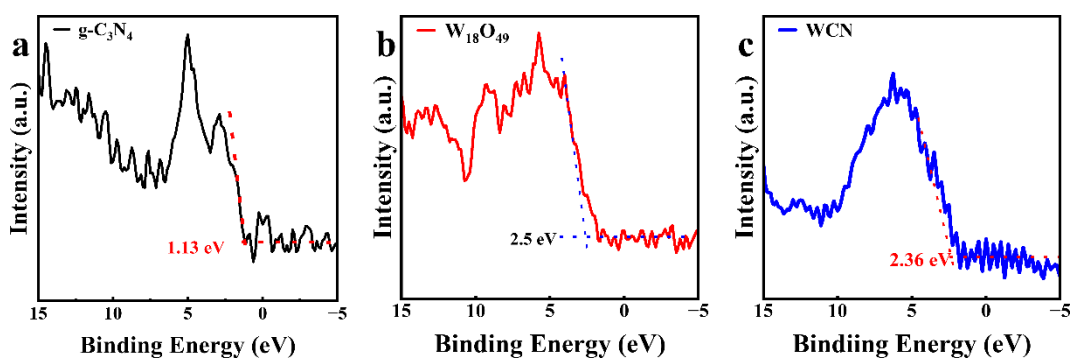


Figure S9. VB-XPS spectra of (a) $g\text{-C}_3\text{N}_4$ nanosheets, (b) $\text{W}_{18}\text{O}_{49}$ and (c) WCN-2 samples.

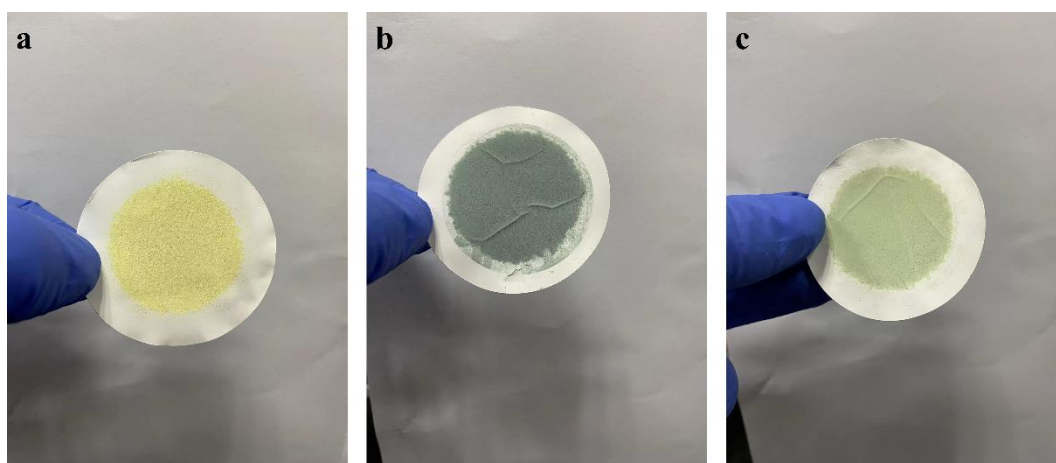


Figure S10. The images of flexible SERS substrates constructed by (a) $g\text{-C}_3\text{N}_4$, (b) $\text{W}_{18}\text{O}_{49}$ and (c) WCN supported by nylon filter membrane.

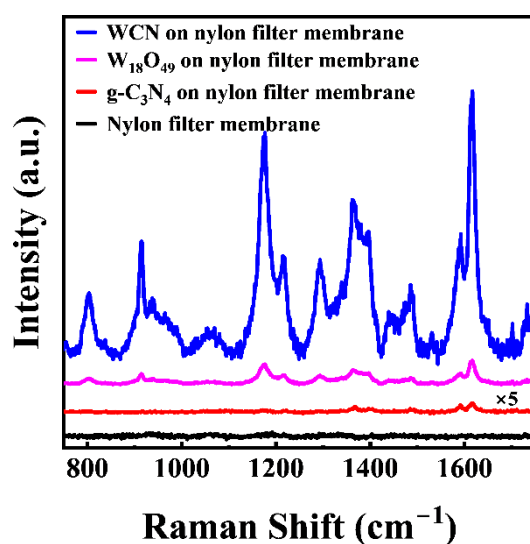


Figure S11. The Raman spectra of MG collected on the nylon filter membrane supported $g\text{-C}_3\text{N}_4$ (red line), $\text{W}_{18}\text{O}_{49}$ (magenta line), WCN-2 (blue line) and bare nylon filter membrane (black line).

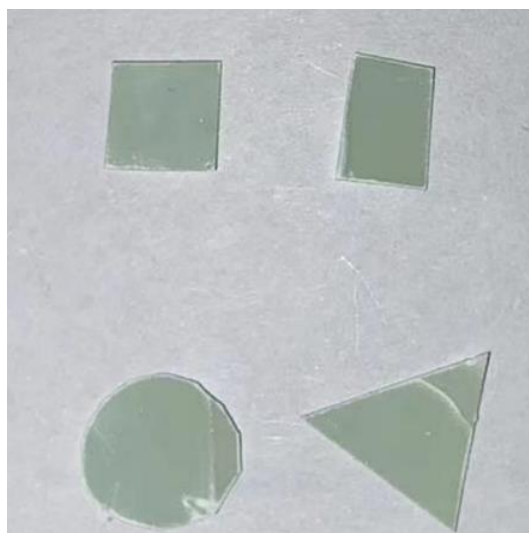


Figure S12. The images of small pieces of flexible substrates with required shapes, such as squares, circles, rectangles, and triangles.

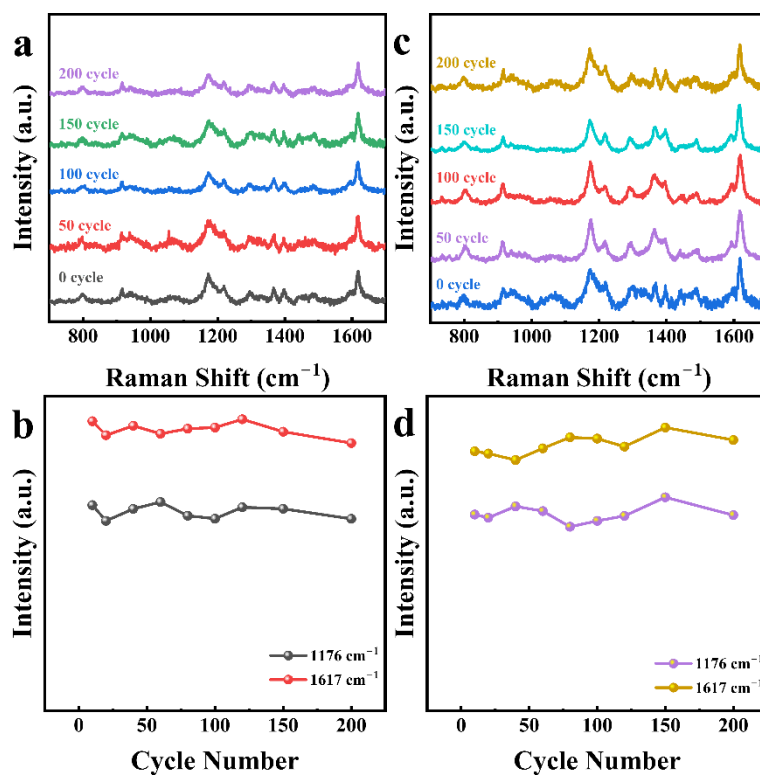


Figure S13. The mechanical stability flexible WCN substrates. The collected SERS spectra after (a) torsions and (b) bends tests for 200 times. The SERS intensity at 1176 cm^{-1} and 1617 cm^{-1} after (c) torsions and (d) bends tests for 200 times.

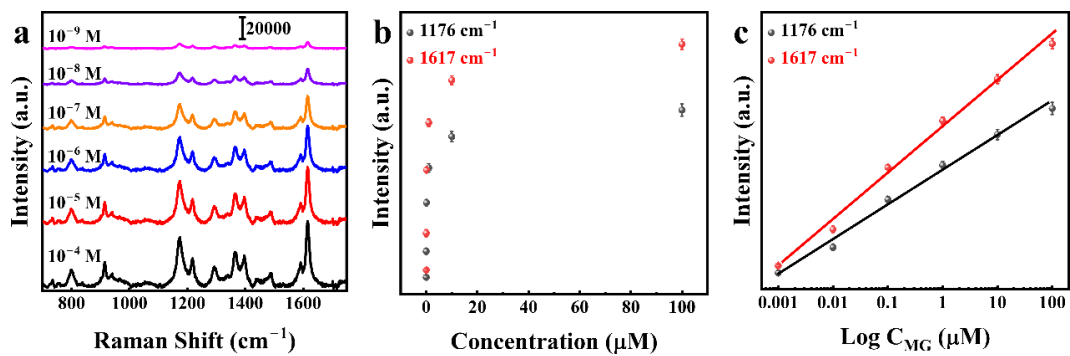


Figure S14. Raman signals obtained from the detection of MG molecules adsorbed by the flexible substrate from the glass slides.

Table S1. Raman shift of characteristic peaks and tentative vibrational assignments of MG ⁵.

Normal Raman (cm ⁻¹)	SERS (cm ⁻¹)	Assignments
1172	1176	$\nu(\text{C-H})$
1219	1218	$\nu(\text{C-H})$
1396	1397	$\nu(\text{C-N})$
1485	1488	$\nu(\text{C-C}) + \beta(\text{C-H})$
1592	1592	$\nu(\text{C-C})$
1618	1617	$\nu(\text{C-C})$

ν = stretching, β = bending

Table S2. Comparisons of the limit of detection and enhancement factor among different SERS substrates.

No.	SERS substrate	Raman probe	EF	LOD	Ref.
1	Ag NPs @ PDMS	MG	6.1×10^6	1.0×10^{-6} M	6
2	Ag/PDMS	MG	2.1×10^5	1.0×10^{-7} M	7
3	VO ₂	R6G	3.8×10^5	1.0×10^{-9} M	8
4	Ag/TiO ₂	TMTD	1.4×10^5	1.2×10^{-10} M	9
5	W ₁₈ O ₄₉ /g-C ₃ N ₄	MG	2.6×10^7	1.9×10^{-10} M	This work

Table S3. Comparisons of the limit of detection of MG among different detection methods.

No.	Method	LOD	Ref.
1	Colorimetry	1.6×10^{-8} M	10
2	Fluorescence	4.6×10^{-10} M	11
3	Electrochemistry	5.0×10^{-8} M	12
4	SERS	1.9×10^{-10} M	This work

References

1. Z. You, B. Wang, Z. Zhao, Q. Zhang, W. Song, C. Zhang, X. Long and Y. Xia, *Adv. Mater.*, 2023, **35**, 2209129.
2. G. Kresse and D. Joubert, *Physical Review B*, 1999, **59**, 1758-1775.
3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
4. S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of Chemical Physics*, 2010, **132**, 154104.
5. M. U. Amin, L. Li, R. Zhang and J. Fang, *Talanta*, 2023, **251**, 123800.
6. H. Zhang, N. Zhao, H. Li, M. Wang, X. Hao, M. Sun, X. Li, Z. Yang, H. Yu, C. Tian and C. Wang, *ACS Appl. Mater. Interfaces*, 2022, **14**, 51253-51264.
7. P. Kumar, R. Khosla, M. Soni, D. Deva and S. K. Sharma, *Sensors and Actuators B: Chemical*, 2017, **246**, 477-486.
8. H. Guan, Z. Tian, Q. Kong and G. Xi, *Chem. Commun.*, 2021, **57**, 4815-4818.
9. J. Yang, G. Song, L. Zhou, X. Wang, L. You and J. Li, *Appl. Surf. Sci.*, 2020, DOI: 10.1016/j.apsusc.2020.147744, 147744.
10. J. Jia, S. Yan, X. Lai, Y. Xu, T. Liu and Y. Xiang, *Food Anal Method*, 2018, **11**, 1668-1676.
11. J. Qiu, L. Na, Y. Li, W. Bai, J. Zhang and L. Jin, *Food Chem.*, 2022, **390**, 133156.
12. B. Yang, D. Bin, T. Tian, Y. Liu and B. Liu, *ChemElectroChem*, 2020, **7**, 659-664.