

Supporting Information

Efficient Multiplexed Label-free Detection by Flexible MXene/Graphene Oxide Fibers with Enhanced Charge Transfer and Hot Spots Effect

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Contents

- 1. Calculation of Raman Enhanced Factor (EF)**
- 2. Establishment of standard color barcodes**
- 3. Supporting Figures**
- 4. Supporting Tables**

1. Calculation of Raman Enhanced Factor (EF)

The EF was calculated according to the well-known formula:

$$EF = \frac{(I_{SERS}/N_{SERS})}{(I_{REF}/N_{REF})} \quad S1-1$$

Here N_{SERS} and N_{REF} are the number of probe molecules respectively excited by the SERS substrate and non-SERS substrate, I_{SERS} and I_{REF} are the Raman signal intensity at 612 cm^{-1} obtained from 10^{-8} M R6G on MG/AgNPs-PVP fiber and 10^{-3} M R6G solution in glass capillaries. Moreover, for SERS samples, about $5 \mu\text{l}(V_1)$ of $10^{-8} \text{ M}(C_1)$ R6G solution was absorbed on the surface of 2 mm^2 fiber (S_1), and then excited by a Raman's laser spot with a diameter about $5 \mu\text{m}$ (d).

Therefore, the N_{SERS} can be derived as:

$$N_{SERS} = \left(\frac{\pi d^2}{4 \times S_1} \right) \times V_1 \times C_1 \times N_A \quad S1-2$$

Similarly, since the laser can easily pass through the R6G solution ($C_2=10^{-3} \text{ M}$, depth approx. 2.5 mm), the illuminated volume (V_2) by Raman laser is about $6.25 \times 10^{-14} \text{ m}^3$. Therefore, the number of R6G molecules being illuminated in the glass capillaries was calculated as:

$$N_{REF} = V_2 \times C_2 \times N_A \quad S1-3$$

From this, the EF of MG/AgNPs-PVP fiber was derived as:

$$EF = \frac{(I_{SERS}/N_{SERS})}{(I_{REF}/N_{REF})} = 1.53 \times 10^{12} \quad S1-4$$

2. Establishment of standard color barcodes

The conversion from Raman spectra to color barcodes mainly includes the information of characteristic peak positions, relative intensities, and concentrations of analytes. First, the position of several characteristic peaks from SERS spectra were read to determine the relative distance of each rectangle in the barcodes.

The linewidth of the strongest characteristic peak was set as 1, and the linewidth of other characteristic peaks was determined by their relative intensities with the strongest one. Finally, the R/G/B values combined with the concentration fitting function were used to determine the color of barcodes. As a result, the color barcode can accurately and quickly screen the molecular species and concentration and can be used for electronic reading.

3. Supporting Tables

Table S1. Atomic percentage of pure MG and MG-Ox fibers.

MG fiber			MG-Ox fiber		
Region	BE (eV)	At %	Region	BE (eV)	At %
C 1s	284.80	13.95	C 1s	284.80	32.51
Ti 2p	454.08	42.19	Ti 2p	454.08	19.14
O 1s	529.08	19.90	O 1s	529.08	36.87
F 1s	684.08	23.96	F 1s	684.08	11.48

Table S2. XPS peak fitting results for pure MG and MG-Ox fibers.

MG fiber			MG-Ox fiber		
Region	BE (eV)	Assigned to	Region	BE (eV)	Assigned to
O 1s	529.65	-OH	O 1s	529.86	-OH
	531.46	C-O		531.43	C-O
	532.84	C=O		532.77	C=O
C 1s	284.80	C=C	C 1s	284.80	C=C
	285.83	CH/CO		285.86	CH/CO
	287.61	O=C-O		287.67	O=C-O

Table S3. EF of R6G molecules (10^{-8} M) on different MG/AgNPs fiber substrates.

Substrate	SERS Intensities (a.u)	EF
MG	$9.7 \times 10^2 \pm 18.3$	9.65×10^9
MG/AgNPs-Br ⁻	$5.4 \times 10^3 \pm 129.6$	5.16×10^{10}
MG/AgNPs-TSC	$8.1 \times 10^2 \pm 15.4$	9.31×10^{10}
MG/AgNPs-PVP	$5.2 \times 10^4 \pm 1241.3$	1.53×10^{12}
MG/AgNPs-CTAB	$3.4 \times 10^4 \pm 781.2$	8.78×10^{11}

Table S4. Comparison of SERS experimental peak position (cm^{-1}) and calculated peak position (cm^{-1}) of pesticide residues on fruit peels.

	Peach		Winter Jujube	
	Experimental	Calculation	Experimental	Calculation
Thiuram	644.03	672.68	1358.91	1259.76
Thiabendazole	1078.95	1021.73	/	/
Pymetrozine	/	/	273.06	291.03

4. Supporting Figures

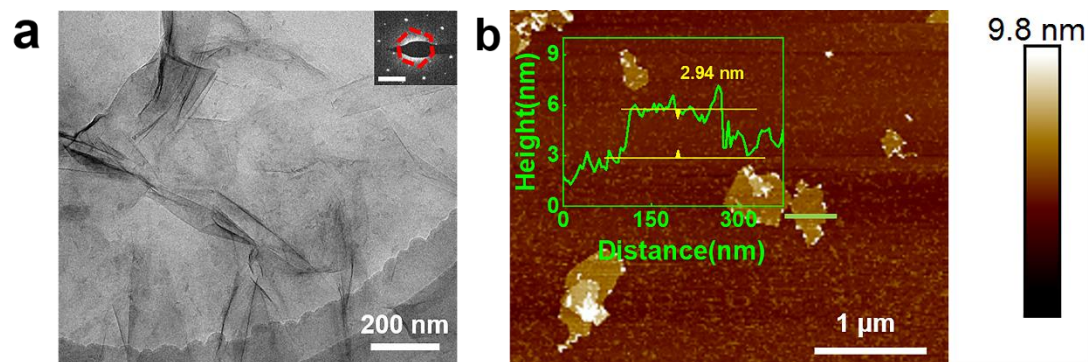


Figure S1. (a)TEM and (b) AFM images of MXene nanosheets.

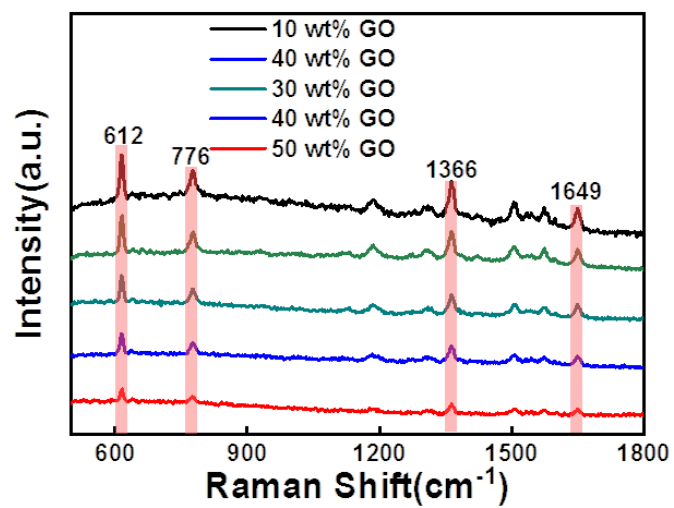


Figure S2. The SERS spectra of 10⁻⁴ M R6G collected from MG fibers with 10, 20, 30, 40 and 50 wt% GO contents.

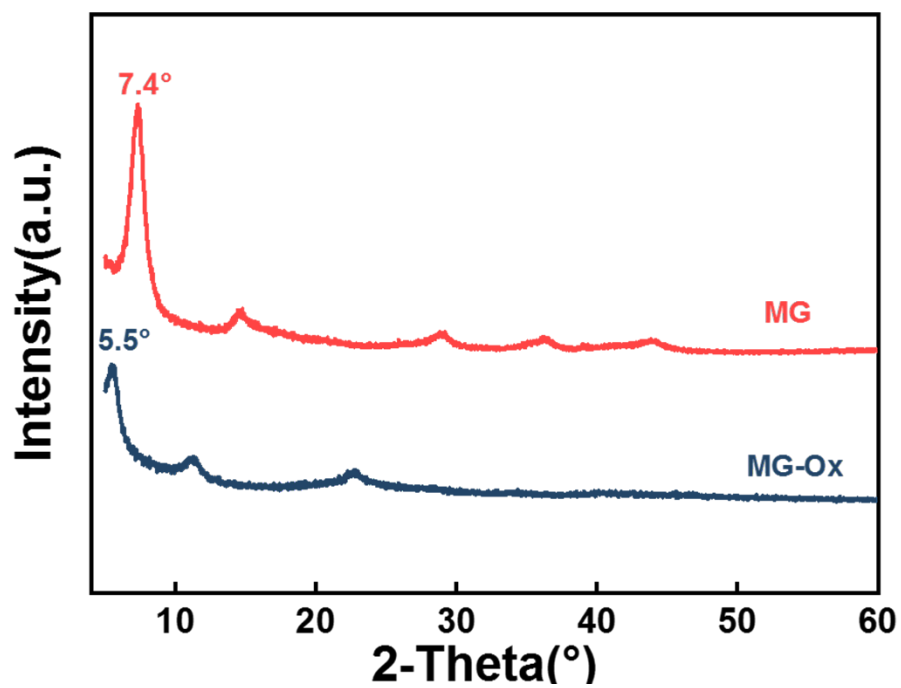


Figure S3. XRD patterns of MG and MG-Ox fibers.

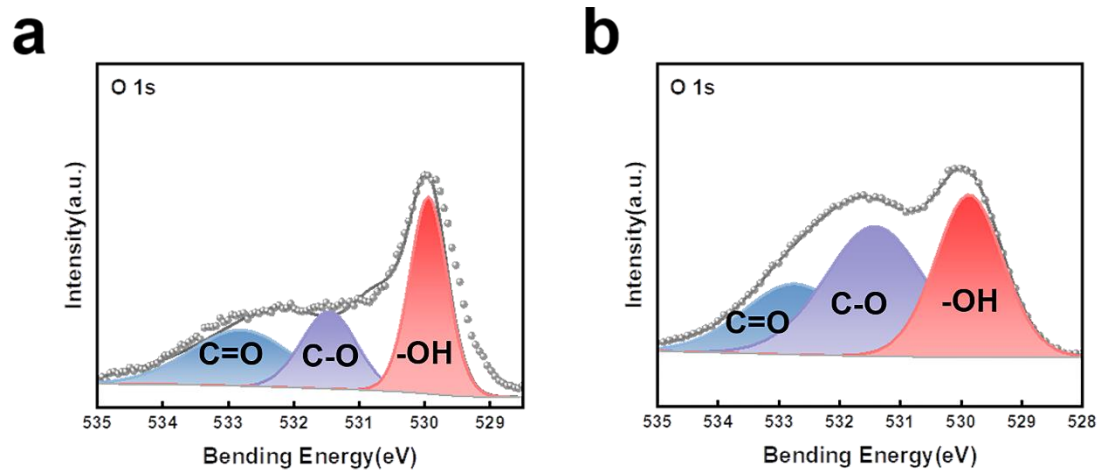


Figure S4. O1s high-resolution spectra of (a) MG and (b) MG-Ox fibers.

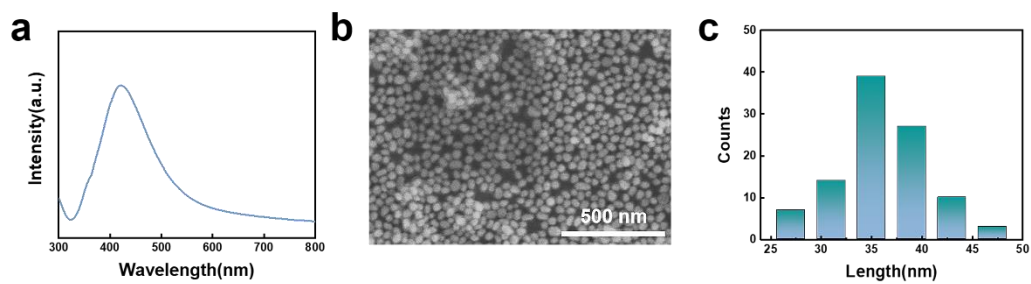


Figure S5. (a) UV-Vis spectra of AgNPs. (b) SEM image of the monolayer AgNPs assembled at the oil-water interface. (c) The size distribution of AgNPs (100 counts were performed).

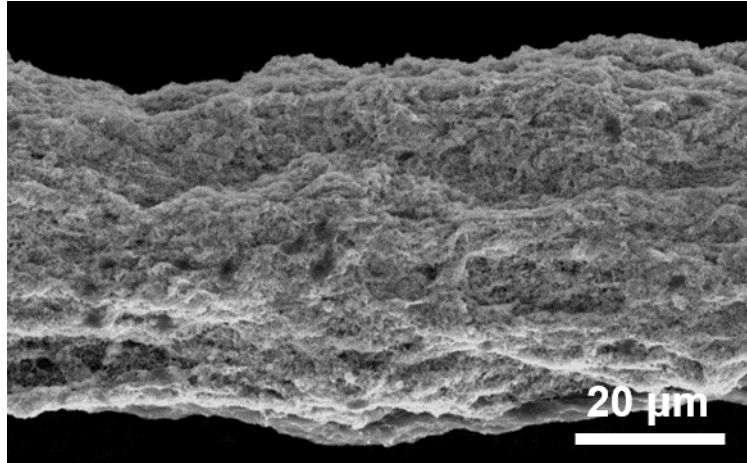


Figure S6. SEM image of full-covered AgNPs MG fibers.

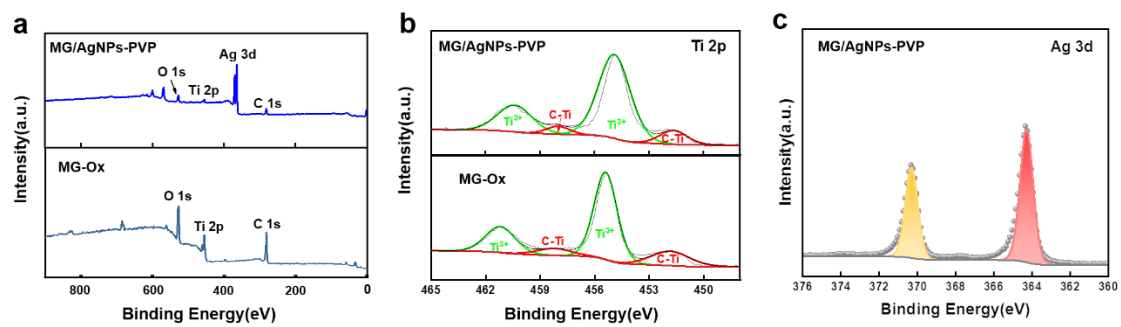


Figure S7. (a) The total XPS spectrum of MG/AgNPs-PVP and MG-Ox fibers. (b) The high-resolution spectrum of Ti 2p collected from MG/AgNPs-PVP and MG-Ox fibers. (c) The high-resolution spectrum of Ag 3d collected from MG/AgNPs-PVP fiber.

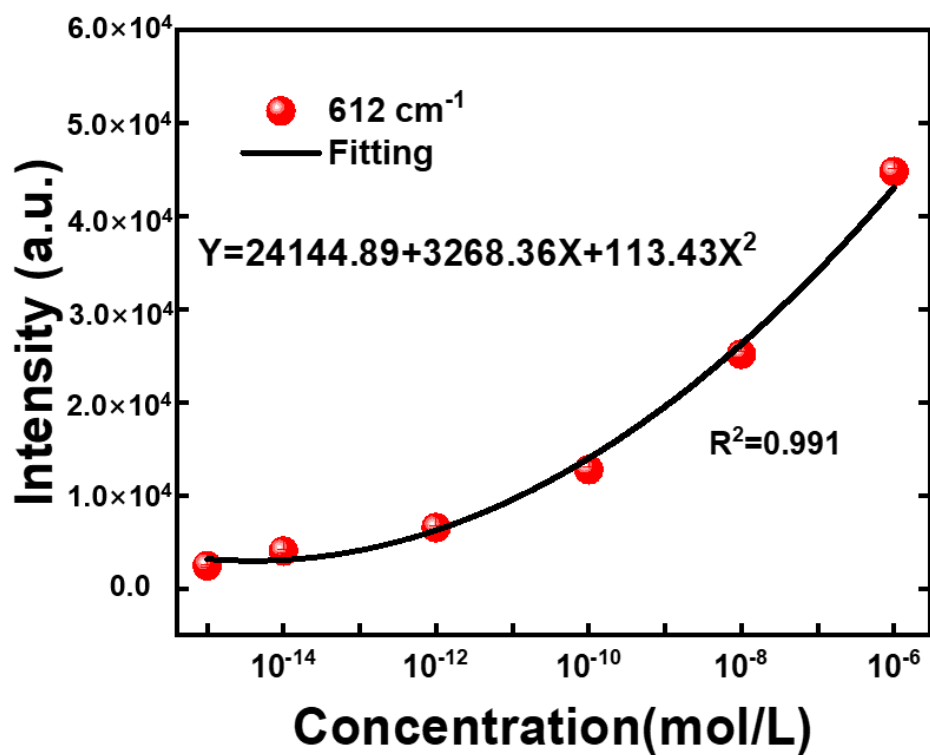


Figure S8. The relationship between intensity and concentration of R6G.

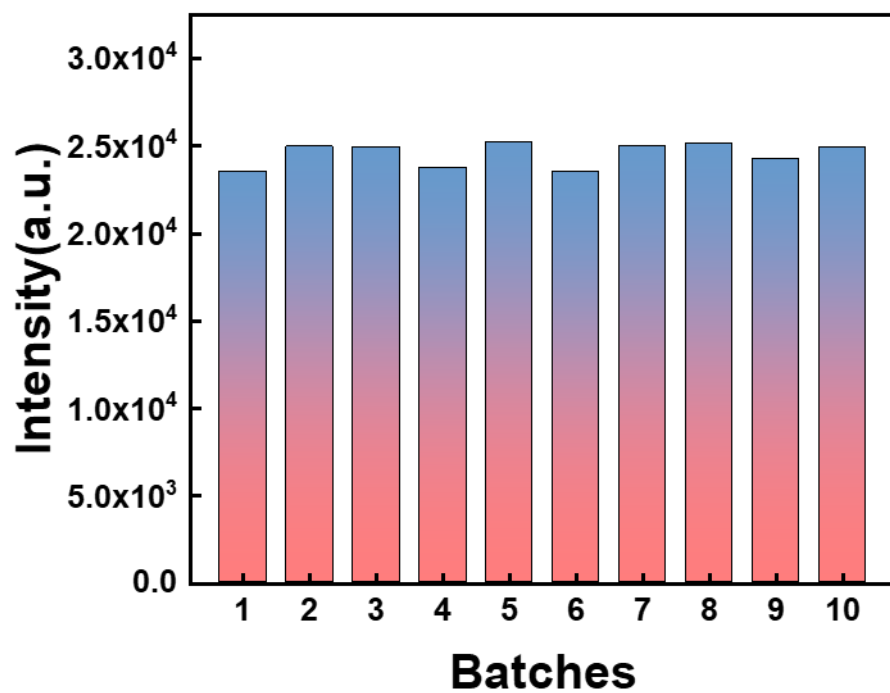


Figure S9. SERS intensity of 10^{-8} M R6G at 612 cm^{-1} on different batches.

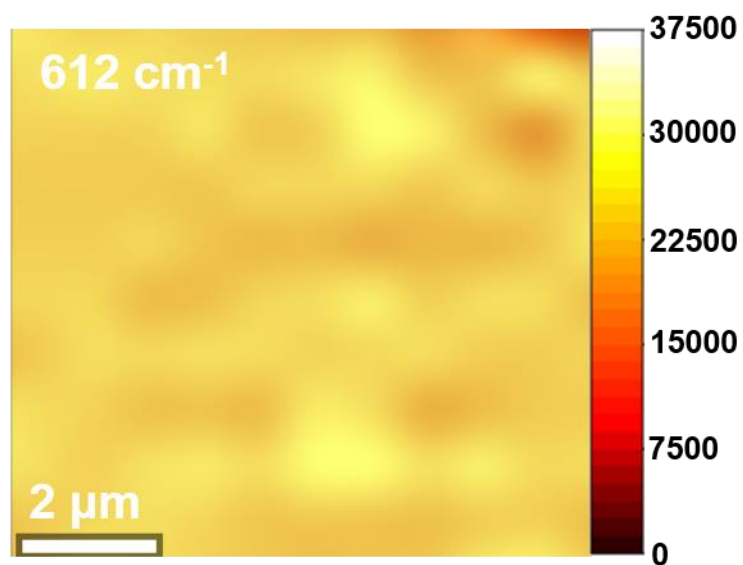


Figure S10. SERS mapping of 10^{-8} M R6G at 612 cm^{-1} on MG/AgNPs-PVP fiber in the $10 \times 10\ \mu\text{m}^2$ area.

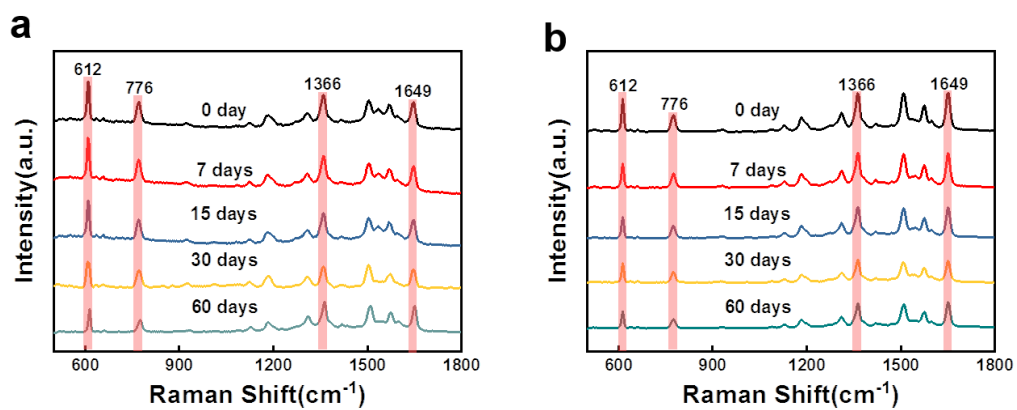


Figure S11. The SERS spectra of R6G collected from (a) MG/AgNPs-PVP fiber and (b) AgNPs colloids with different storage time in air.

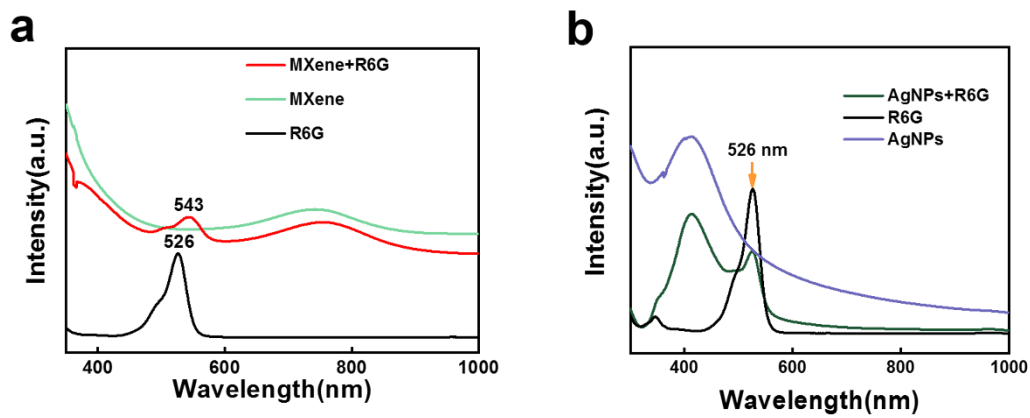


Figure S12. (a) UV-Vis spectra of R6G, MXene and the mixture of MXene and R6G.(b) UV-Vis spectra of AgNPs, R6G and the mixture of AgNPs and R6G.

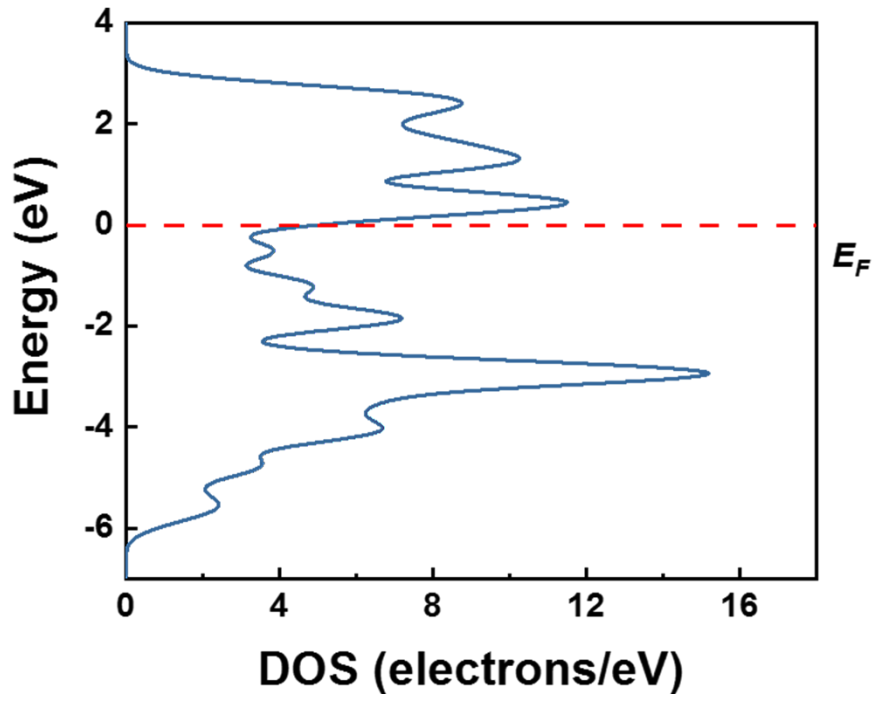


Figure S13. DOS of Ti₃C₂T_x MXene.

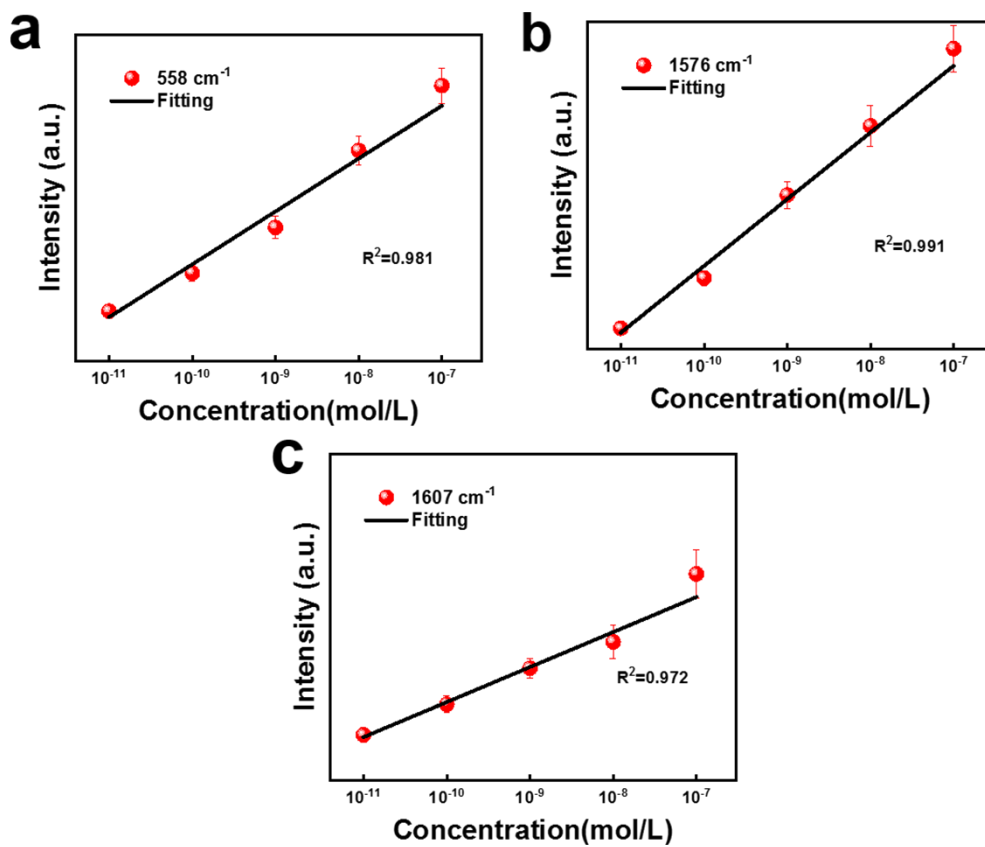


Figure S14. The relationship between intensity and concentration of (a) Thiuram, (b) Thiabendazole and (c) Pymetrozine.

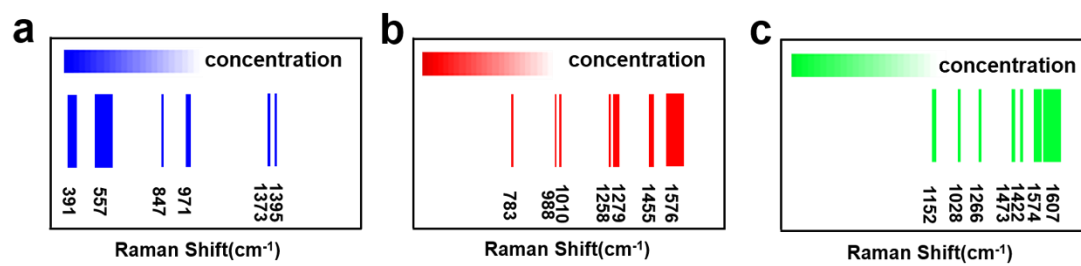


Figure S15. The chromatic barcodes of (a) thiuram, (b) thiabendazole and (c) pymetrozine molecules from 10⁻⁷ to 10⁻¹¹ M by MG/AgNPs-PVP fiber. Note: The color bar is from 10⁻⁷ to 10⁻¹¹ M, and the line width is set by the relative intensities between characteristic peaks.

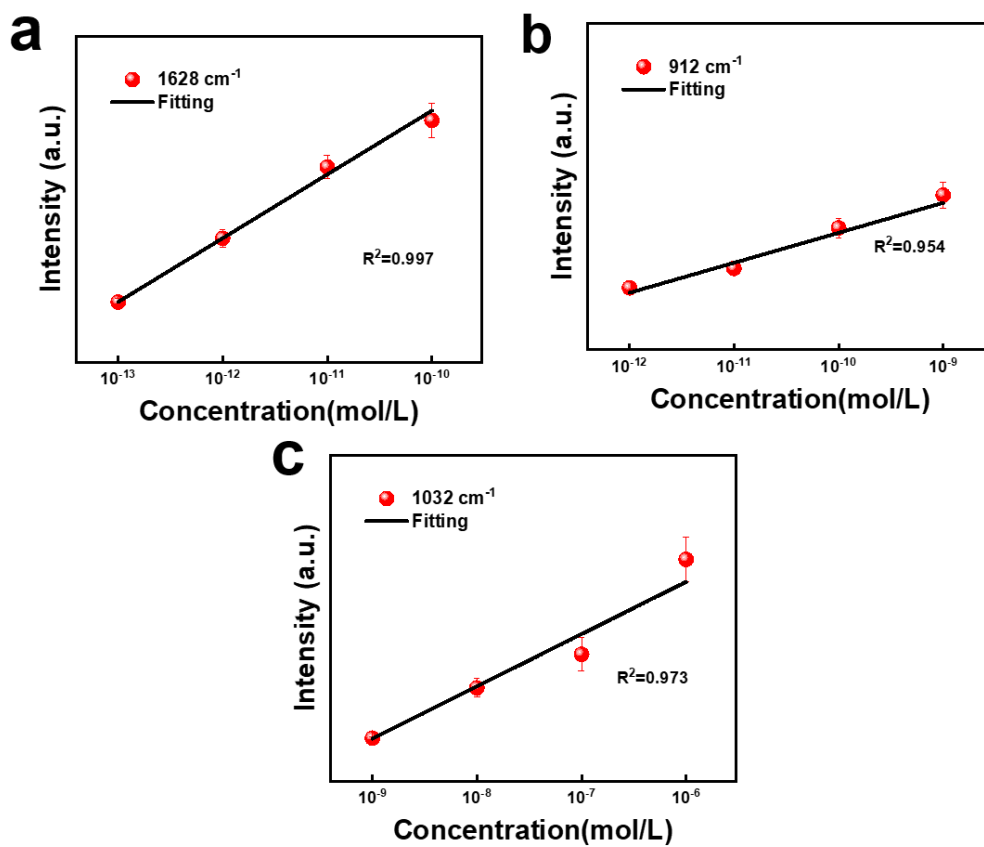


Figure S16. The relationship between intensity and concentration of (a) MB, (b) CV and (c) Nikethamide.