Supplementary Information

Direct writing of flexible two-dimensional MXene arrays for SERS sensing

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Fabrication of V_2C ink

V$_2$C MXene ink was prepared by selective etching of Al atomic layers from V$_2$AlC MAX phase powder. Typically, 1.0 g V$_2$AlC powder was slowly added to 25 mL of etching solution consisting of 10 mL of HF (40 wt%), 10 mL of 12 M HCl, and 5 mL deionized (DI) water. The mixed solution was stirred at 40 °C for 48 h. Afterward, the etched sample was washed several times with DI water until the pH reached 7. We collected the resulting multilayer sediment and stirred it with 25 mL of 5wt% tetramethylammonium hydroxide (TMAOH) for 6 h. Then, the sample was centrifuged at 8500 rpm for 5 min and washed three times with DI water to remove the residual TMAOH. After decanting the supernatant, the V$_2$C intercalated sediment was redispersed in 15 mL DI water and ultrasonic treatment for 30 min, followed by centrifugation at 3500 rpm for 10 min to obtain V$_2$C ink containing only delaminated nanosheets.

Fabrication of Mo_2C ink

Mo$_2$C MXene ink was prepared by selective etching of Ga atomic layers from Mo$_2$Ga$_2$C powder. Typically, 1.0 g Mo$_2$Ga$_2$C powder was slowly added to 10 mL of 49 wt% HF solution. The mixed solution was stirred at 55 °C for 120 h. Afterward, the etched sample was washed several times with DI water until the pH reached 7. We collected the resulting multilayer sediment and stirred it with 25 mL of 5 wt% TMAOH for 24 h at room temperature. Then, the sample was centrifuged at 6000 rpm for 5 min and washed three times with DI water to remove the residual TMAOH. After decanting

the supernatant, the Mo_2C intercalated sediment was redispersed in 15 mL DI water and ultrasonic treatment for 60 min, followed by centrifugation at 3500 rpm for 10 min to obtain Mo_2C ink containing only delaminated nanosheets.

Fabrication of Nb_2C ink

Nb_2C MXene ink was prepared by selective etching of Al atomic layers from Nb_2AlC powder. Typically, 1.0 g Nb_2AlC powder was slowly added to 15 mL of 49 wt% HF solution. The mixed solution was stirred at 50 ^oC for 72 h. Afterward, the etched sample was washed several times with DI water until the pH reached 7. We collected the resulting multilayer sediment and stirred it with 25 mL of 20 wt% TMAOH for 24 h at room temperature. Then, the sample was centrifuged at 8000 rpm for 5 min and washed three times with DI water to remove the residual TMAOH. After decanting the supernatant, the Nb_2C intercalated sediment was redispersed in 15 mL DI water and ultrasonic treatment for 30 min, followed by centrifugation at 3500 rpm for 10 min to obtain Nb_2C ink containing only delaminated nanosheets.

Fabrication of Ag substrates

Ag substrates were prepared on Si (100) by porous anodic aluminum oxide (AAO) template-assisted evaporation method. The Ag nanoarray was prepared by E-beam evaporation, and the evaporation rate, film thickness and evaporation vacuum were 1 Å/s, 60 nm, and 4×10^{-4} Pa, respectively. Afterwards, the AAO membrane was peeled off from the substrate with tape, leaving patterned Ag nanoarray on the substrate.

Calculation of the Raman enhancement factors

The Raman enhancement factors (EFs) of the samples could be calculated using the equation below:[1,2]

$$EF = (I_{SERS}/N_{SERS}) / (I_{normal}/N_{normal}) \quad\quad (S1)$$

$$N_{SERS} = CVN_A A_{Raman}/A_{Sub} \quad\quad (S2)$$

$$N_{normal} = \rho h A_{Raman} N_A/M \quad\quad (S3)$$

where I_{SERS} and I_{normal} are the intensities of the selected Raman peak in the SERS and non-SERS spectra, respectively. N_{SERS} and N_{normal} are the average number of molecules in scattering area for SERS and non-SERS measurement. The data of bulk R6G is used as non-SERS-active reference. C is the molar concentration of R6G solution and V is the volume of the droplet (10 μL). N_A is Avogadro constant (6.023 × 10^{23} mol^{-1}). A_{Raman} is the laser spot area. A_{Sub} is the effective area of the substrate, which is approximately $9\,\pi$ mm². The confocal depth h of the laser beam is ~21 μm. The molecular weight M of R6G is 479 g mol^{-1} and density ρ of bulk R6G is 1.15 g cm^{-3}.

Simulation of the electromagnetic field distribution

The finite element method (FEM) simulations are carried out on COMSOL. The modes are excited by a plane wave source with incident direction perpendicular to the plane of structure, the incident light wavelength is 532 nm, and its electric field intensity is 1V/m. The refractive index of Ti_2C under 532 nm laser irradiation are set as n (Ti_2C) = 1.701 + i 1.753. According to the results of SEM, TEM, and XRD, Ti_2C geometric mode is set as follows: 20 layers Ti_2C MXene with a diameter of 1.0 μm, layer thickness of 0.23 nm and inter-layer distance of 1.37 nm.
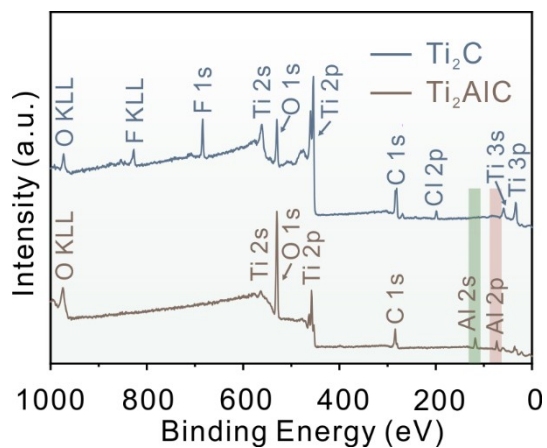
Figures

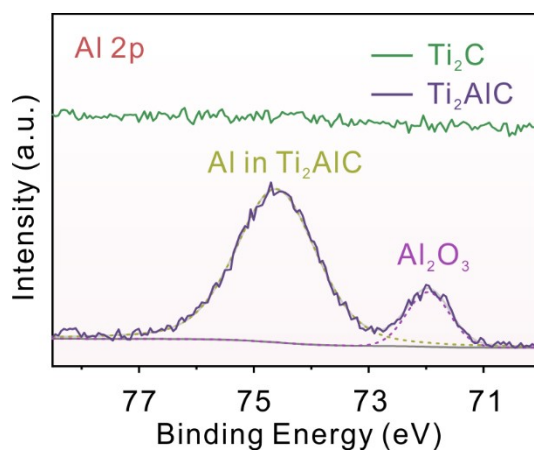**Fig. S1** Survey XPS spectra of Ti$_2$AlC and Ti$_2$C MXene.
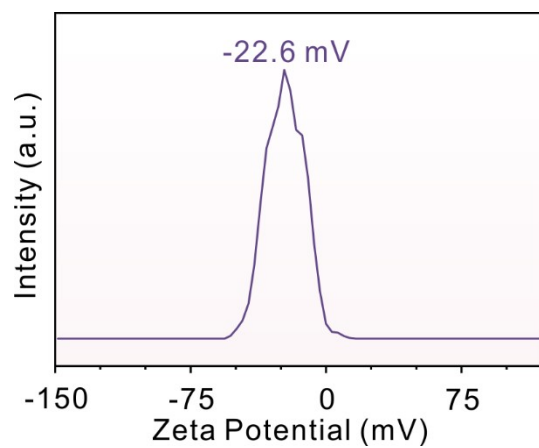

Fig. S2 Al 2p spectra of Ti$_2$AlC and Ti$_2$C MXene.

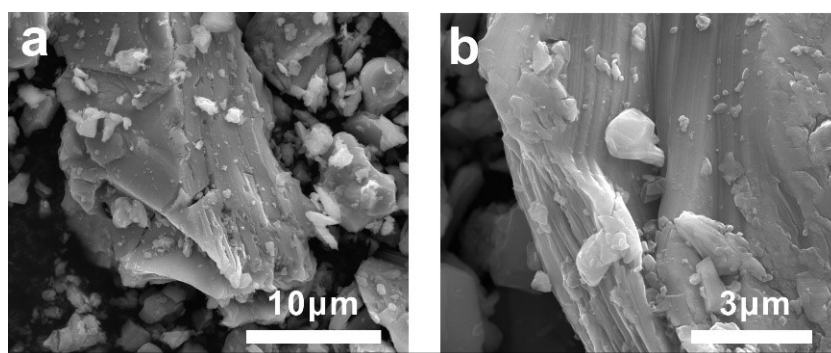**Fig. S3** Zeta potential distribution curve of Ti$_2$C suspension.

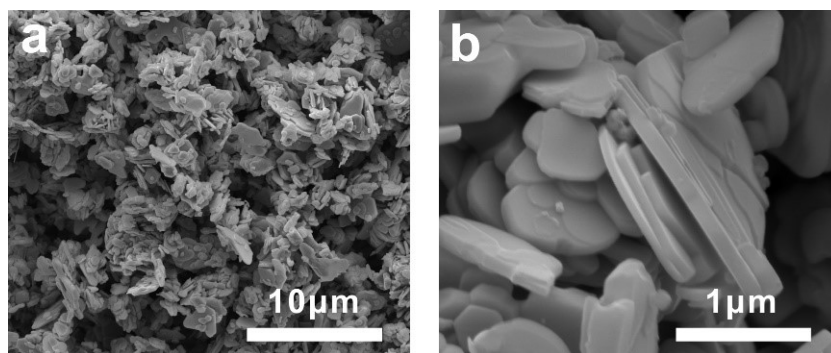**Fig. S4** SEM images of V$_2$AlC powder.

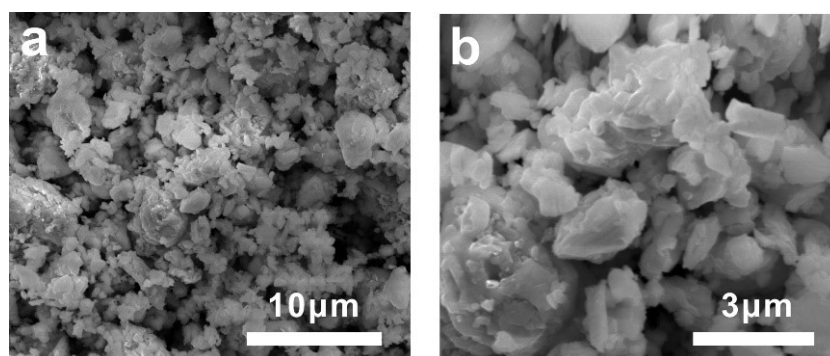**Fig. S5** SEM images of Mo$_2$GaC powder.

Fig. S6 SEM images of Nb$_2$AlC powder.
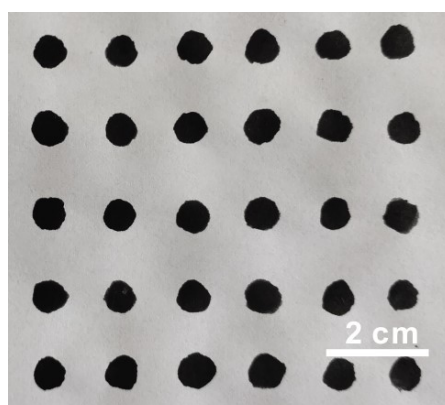
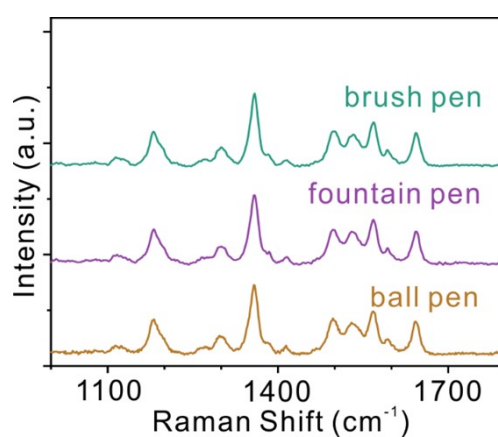**Fig. S7** The photographs of as-drawn arrays on paper by using Nb$_2$C MXene ink.

Fig. S8 Raman spectra of R6G (1 × 10^{-5} M) adsorbed on the handwritten Ti$_2$C substrates

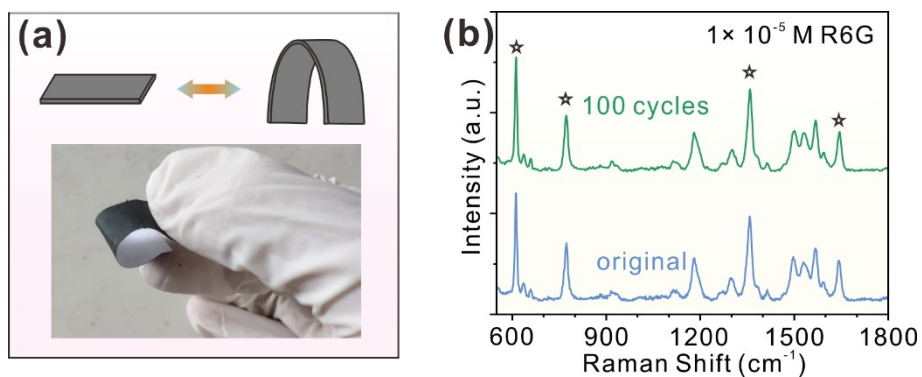using ball pen, fountain pen, and brush pen.

Fig. S9 (a) Schematic illustration of the bending deformation. (b) Raman spectra of R6G (1×10^{-5} M) absorbed on the flexible MXene substrate after 100 cycles of bending-releasing.
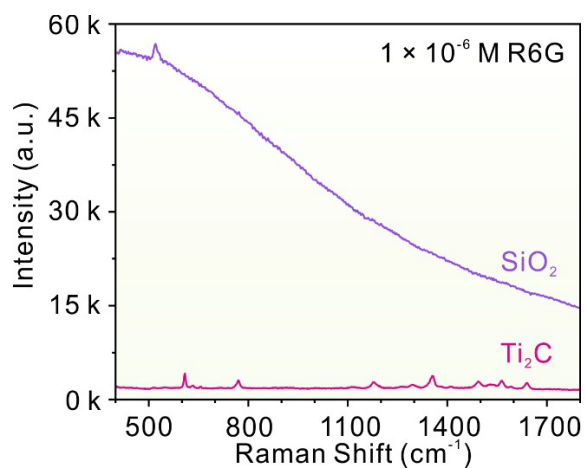

Fig. S10 Raman spectra of R6G (1×10^{-6} M) adsorbed on SiO_2 and Ti_2C MXene without baseline correction.
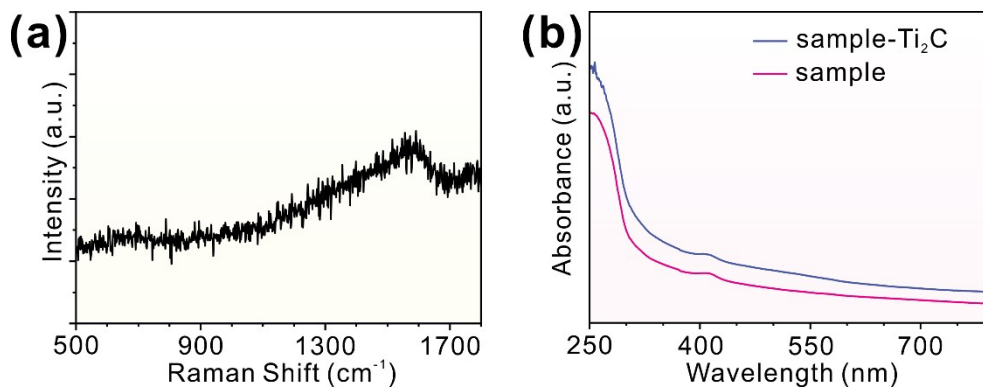
Fig. S11 (a) SERS spectrum of fish skin without immersion treatment of fish drugs. (b) (b) UV-vis absorption spectra of the sample from fish skin and the samsple-Ti_2C MXene.
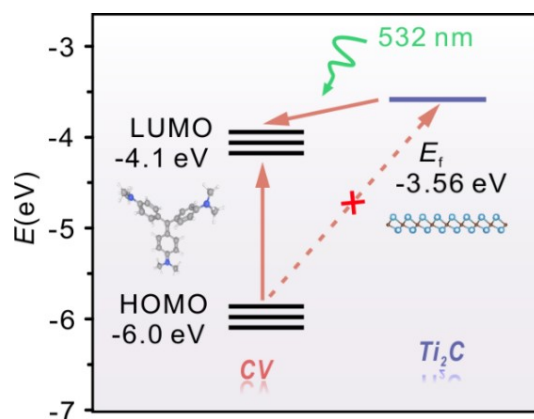

Fig. S12 Energy level diagrams and charge transfer routes in CV-Ti_2C complex.
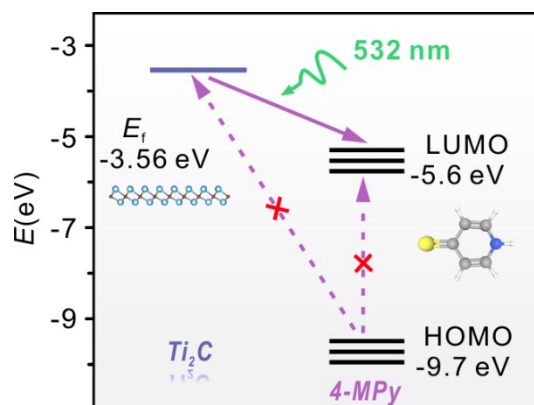

Fig. S13 Energy level diagrams and charge transfer routes in Ti_2C-4-MPy complex.

References

1 X. Fan, M. Li, Q. Hao, M. Zhu, X. Hou, H. Huang, L. Ma, O. G. Schmidt, and T. Qiu, *Adv. Mater. Interfaces*, 2019, **6**, 1901133.

2 S. Cong, Y. Yuan, Z. Chen, J. Hou, M. Yang, Y. Su, Y. Zhang, L. Li, Q. Li, F. Geng, and Z. Zhao, *Nat. Commun.*, 2015, **6**, 7800.