Electronic Supplementary Information

Surface-enhanced resonance Raman scattering of dye molecule adsorbed on two-dimensional titanium carbide $Ti_3C_2T_x$ (MXene) film

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Experimental section.

Chemicals and Apparatus.

Ultrasonicator (Bransonic M3800 Ultrasonic bath, 110 W and Frequency 40 kHz) was purchased from Branson Ultrasonics Corp., USA. The organic solvents (DMSO, methanol, ethanol, acetone, acetonitrile, isopropyl alcohol-IPA, isobutanol and THF) were purchased from the Sigma-Aldrich (USA). The Raman probe molecules such as crystal violet (CV), rose bengal (RB), rhodamine 6G (R6G), p-nitrothiophenol (*p*NTP), p-aminothiophenol (*p*ATP), *p*-hydroxy thiophenol (*p*HTP) and p-mercaptobenzoic acid (*p*MBA) were purchased from the Sigma-Aldrich (USA). All these chemicals were reagent grade and used as received.

Intercalation and delamination of $Ti_3C_2T_x$.

The $Ti_3C_2T_x$-MXene was prepared by soaking in hydrochloric acid (HCl) containing the fluoride salt (as a LiF) to etching out of Al elements from the Ti_3AlC_2 (MAX phase) at 35 °C for 24 h. For intercalation, a powder of $Ti_3C_2T_x$-MXene (0.3 g) was dispersed in 5 mL of various solvents (such as DMSO, methanol, ethanol, acetone, acetonitrile, isopropyl alcohol-IPA, isobutanol and THF) and stir for 24h at room temperature at 500 rpm. The unreacted solvents (non-intercalated solvent molecules) were removed from the mixture by centrifuged them at 3500 rpm for 5 min. For delamination step, the corresponding base solvents (150 mL) were used to produce $Ti_3C_2T_x$-MXene flakes, expect the DMSO. The deionized water (150 mL) was used only for the delamination of DMSO-intercalated $Ti_3C_2T_x$ sample to produce aqueous colloidal solution of $Ti_3C_2T_x$ flakes.

The above mixture was further bath sonicated for 10h with/without Ar gas bubbling (to avoid the mechanical oxidation of $Ti_3C_2T_x$ sample during the delamination step) at the given experimental condition (the temperature of the bath sonicator was kept at 32±5°C as constant). The supernatant solution of delaminated $Ti_3C_2T_x$ flakes (*d*-$Ti_3C_2T_x$) was then obtained by centrifuged at 3500 rpm for 1 h. The concentration

$Ti_3C_2T_x$ flakes in aqueous supernatant solution was found to be 1.25 mg/mL, which was estimated by freeze-dry method.

The transparent $Ti_3C_2T_x$-MXene film@glass.
The residual DMSO was removed in the *d*-$Ti_3C_2T_x$ solution by purging the Ar (gas) before the film deposition on glass substrate. The various thickness of the $Ti_3C_2T_x$ film was fabricated by repeating the number of spin-cast called as *run*. For each *run*, 200 μL volume of delaminated $Ti_3C_2T_x$-MXene (*d*-$Ti_3C_2T_x$*; 50 μg/ml*) aqueous suspension was spin-cast (200s, 1000 rpm) onto the glass substrate (18mm x 18mm; Area a=3.24 cm^2). This step was then repeated for three times (r_1=200μL*1; r_2=200μL*2 and r_3=200μL*3), which can ensure that uniform film deposition of $Ti_3C_2T_x$ flakes onto the glass substrate. Note: before the spin-cast, the glass substrate was pre-treated with the mixture solution containing 12.5 mL deionized water+2.5 mL 30wt% H_2O_2+2.5 mL of NH_4OH solution. The glass substrate was soaked in the above solution for 40 min at 70°C in fume-hood. All the glass substrate was removed from the mixture solution and then washed several times with distilled water, dried at N_2 gas before the spin-cast of $Ti_3C_2T_x$.

The SERS measurement.
The serious concentration of Raman dyes molecule (such as Crystal violet–CV; Rhodamine 6G–R6G and Rose Bengal–RB as a resonant molecule). The non-resonant Raman probe molecules such as para Nitrothiophenol–*p*NTP, para Amino thiophenol–*p*ATP, para hydroxy thiophenol–*p*HTP and para Mercapto benzoic acid–*p*MBA) were also prepared in ethanol solution with a stock concentration of ~1 mM. The enhancement factor (EF) is calculated using the equation $[I_{SERS}/C_{SERS}]/[I_{Normal}/C_{Bulk}]$ where I_{SERS} and I_{Normal} were the intensity of the surface-enhanced Raman scattering (SERS) (at 1619 cm^{-1} and normal Raman spectra of the probe molecule, respectively. C_{SERS} and C_{Bulk} are the concentration of probe molecule in the SERS and bulk samples, respectively.

Crystal violet (MW: 407.99 g/mol) stock:
0.001 M*407.99 g/mol *20 ml/1000 ml
=0.00815 g (actual weight taken= 0.0088 g in 20 ml C_2H_5OH)

Actual concentration of CV in C_2H_5OH:
0.0088 g in 20 mL C_2H_5OH (1.07845 mM)
0.0088 g*1000 = 8.8 mg/20 mL C_2H_5OH
Mg/L = ppm
8.8 mg/20 mL (20/1000=0.02), then,
8.8*0.02 = 0.176 mg/L or 0.176 ppm

Dilution _1:
100 μL of 0.176 mg/L was added in 8 mL C_2H_5OH (0.013480 mM)
0.1 ml*0.176 mg/L /8 mL of C_2H_5OH = 0.1*0.176/8 =0.0022 mg/L

Dilution _2
500 μL of 0.0022 mg/L (from dillution_1) dissolve in 8 mL C_2H_5OH (0.0008425 mM = 0.8425 μM = 842.5 nM)

0.5 ml*0.0022 mg/L /8 mL = 0.5*0.0022/8 =0.0001375 mg/L

300 µL of dilution_2 solution was deposited on glass (18 mm*18 mm, Area, a^2= 3.24 cm^2) substrate with/ without $Ti_3C_2T_x$ thin film@glass substrate,

300 µl*0.0001375 mg/l= 0.3 ml*0.0001375 mg/L
0.0003 L*0.0001375 mg/L = 0.0003*0.0001375 mg
0.00000004125 mg/3.24 cm^2.
0.04125 ng/3.24 cm^2.
0.04125/3.24 (ng/cm^2)
0.012732 ng/cm^2
12.732 pg/cm^2.

RG6 (MW: 479.01 g/mol) stock:
0.001 M*479.01 g/mol*20 ml/1000 ml
=0.00958 g (actual weight taken= 0.010 g in 20 ml C_2H_5OH)

Actual concentration of R6G in C_2H_5OH:
0.010 g in 20 mL C_2H_5OH (1.04382 mM)
0.010 g*1000 = 10 mg/20 mL C_2H_5OH
Mg/L = ppm
10 mg/20 mL (20/1000=0.02), then,
10*0.02 = 0.2 mg/L or 0.2 ppm

Dilution _1
100 µL of 0.2 mg/L dissolve in 8 mL C_2H_5OH (0.01305 mM)

0.1 ml*0.2 mg/L /8 mL = 0.1*0.2/8 =0.0025 mg/L

Dilution _02
500 µL of 0.0025 mg/L (from dillution_1) dissolve in 8 mL C_2H_5OH (8.1548e-4 mM = 0.81549 µM = 815.485 nM)

0.5 ml*0.0025 mg/L /8 mL = 0.5*0.0025/8 = 0.00015625 mg/L

300 µL of dilution_2 solution was deposited on glass (18 mm*18 mm, Area, a^2= 3.24 cm^2) substrate with/ without $Ti_3C_2T_x$ thin film@glass substrate,

300 µl*0.00015625 mg/l= 0.3 ml*0.00015625 mg/L
0.0003 L*0.00015625 mg/L = 0.0003*0.00015625 mg
0.000000046875 mg/3.24 cm^2.
0.046875 ng/3.24 cm^2.
0.046875/3.24 (ng/cm^2).
0.0144676 ng/cm^2.
14.4676 pg/cm^2.

Rose bengal (MW: 1017.64 g/mol) stock:
0.001 M*1017.64 g/mol*20 ml/1000 ml

=0.02035 g (actual weight taken= 0.0230 g in 20 ml C_2H_5OH)

Actual concentration of RB in C_2H_5OH:
0.0230 g in 20 mL C_2H_5OH (1.1301 mM)
0.0230 g*1000 = 23 mg/20 mL C_2H_5OH
Mg/L = ppm
23 mg/20 mL (20/1000=0.02), then,
23*0.02 = 0.46 mg/L or 0.46 ppm

Dilution _1
100 µL of 0.46 mg/L dissolve in 8 mL C_2H_5OH (0.01413 mM)
0.1 ml*0.46 mg/L /8 mL = 0.1*0.46/8 =0.00575 mg/L

Dilution _2
500 µL of 0.00575 mg/L (from dillution_1) dissolve in 8 mL C_2H_5OH (0.00088289 mM = 0.882890625 µM = 882.890625 nM)

0.5 ml*0.00575 mg/L /8 mL = 0.5*0.00575/8 = 0.000359375 mg/L

300 µL of dilution_2 solution was deposited on glass (18 mm*18 mm, Area, a^2= 3.24 cm^2) substrate with/ without $Ti_3C_2T_x$ thin film@glass substrate,

300 µl*0.000359375 mg/L = 0.3 ml*0.000359375 mg/L
0.0003 L*0.000359375 mg/L = 0.0003*0.000359375 mg
0.0000001078125 mg/3.24 cm^2.
0.1078125 ng/3.24 cm^2.
0.1078125/3.24 (ng/cm^2)
0.0332755 ng/cm^2
33.2755 pg/cm^2.

NIR-UV-Vis spectroscopy analysis of colloidal $Ti_3C_2T_x$ in various solvents.
The delaminated MXene (*d*-$Ti_3C_2T_x$) nanosheets were dispersed in a various solvent medium and the corresponding base solvent was used as reference.

NIR-UV-Vis and Raman spectroscopy analysis of $Ti_3C_2T_x$ film.
The various thickness of $Ti_3C_2T_x$ film (the colloidal nanosheets was obtained by sonication of DMSO-intercalated MXene in aqueous solution) were deposited onto the glass substrate ($Ti_3C_2T_x$@glass) based on number run, which is denotated as "r_n" where n is number of spin-cast (when n=1, 200 µL of colloidal $Ti_3C_2T_x$ solution (concentration = 50 µL/ml) was deposited on glass, which is referring to be r_1, and subsequent spin-casting are also referred to be r_2 and r_3). $Ti_3C_2T_x$@glass samples are dried at room temperature. The NIR-UV-Vis (UV-VIS-NIR Spectrophotometer V-670, JASCO Inc. USA with 1 cm optical path length cell) spectrum of each film was measured using bare glass as a reference background. The Raman probe molecules (CV, RB, R6G, *p*NTP, *p*ATP and *p*MBA) were drop cast onto the film and dried at room temperature. The NIR-UV-Vis spectra were measured for the all Raman probe molecules drop-cast films before the SERS. For normal Raman and SERS measurement, both were acquired using a confocal Micro-Raman spectrometer (HORIBA Jobin Yvon) with lasers at an excitation wavelength (λ_o) of 633 nm and 785

nm lasers (50×, 17 mW with the size of the laser spot was ~0.72 μm^2). The spectral acquisition time (t_{aq}) was 30s for all the samples with 2 accumulations averaged with the spectral resolution is about 0.4 cm^{-1} using CCD detector. Before Raman analysis, the wavenumber was calibrated using the Si peak at 520 cm^{-1} as a reference.

FE-SEM and TEM analysis.

The morphology of delaminated MXene film (*d*-$Ti_3C_2T_x$) on glass (without Pt deposition) were analyzed by both electron microscopy such as field emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM) analysis (HT7700, Hitachi, Tokyo, Japan).

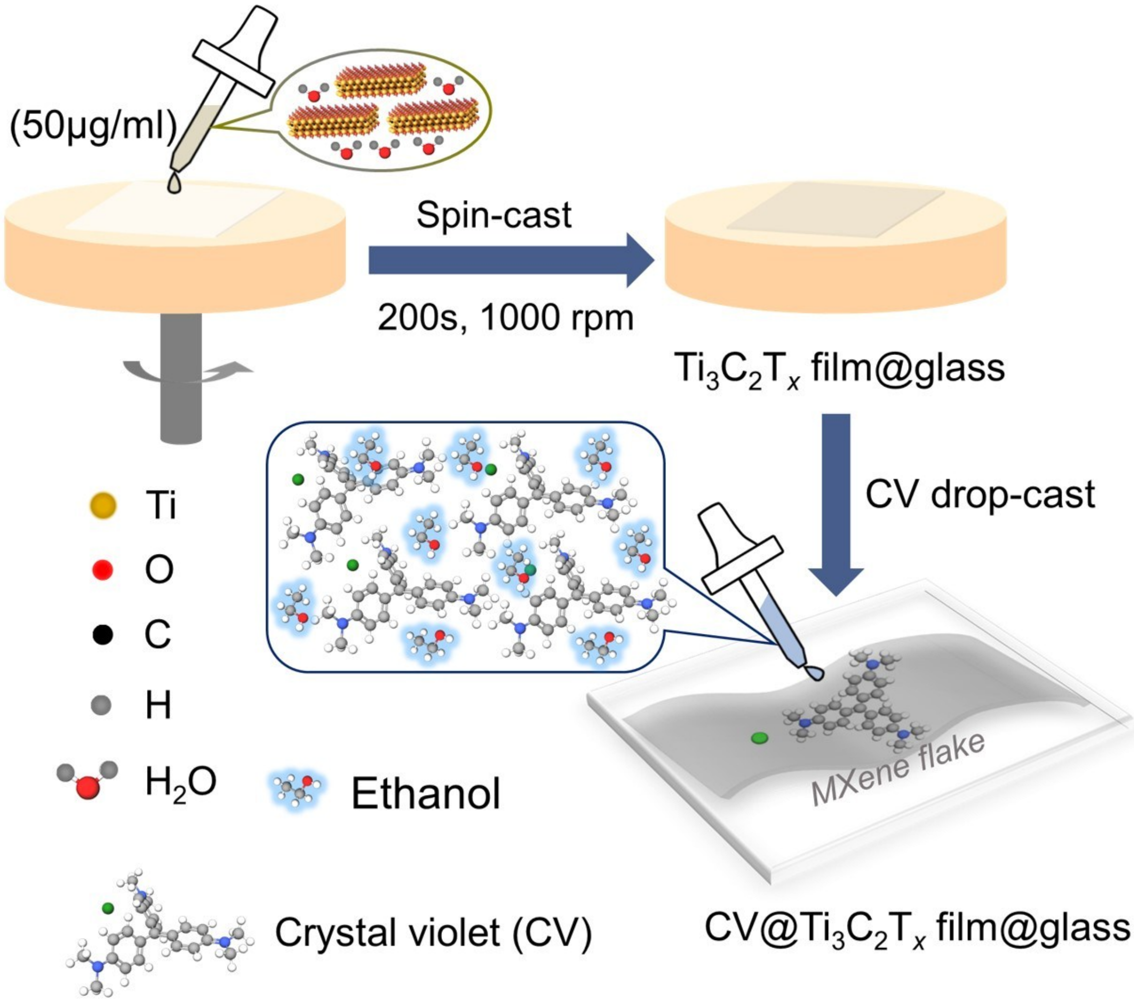

Figure S1. The graphical representation on fabrication of transparent SERS substrate based on thin film of $Ti_3C_2T_x$ prepared onto the glass by spin-coating. An aqueous solution of delaminated $Ti_3C_2T_x$-MXene (*d*-$Ti_3C_2T_x$) flakes was used for the fabrication of SERS substrate and subsequent drop-casting of both resonant (dyes: Crystal violet–CV; Rhodamine 6G–R6G and Rose Bengal–RB) and non-resonant Raman probe molecules (para Nitrothiophenol–*p*NTP, para Amino thiophenol–*p*ATP, para hydroxy thiophenol–*p*HTP and para Mercapto benzoic acid–*p*MBA).

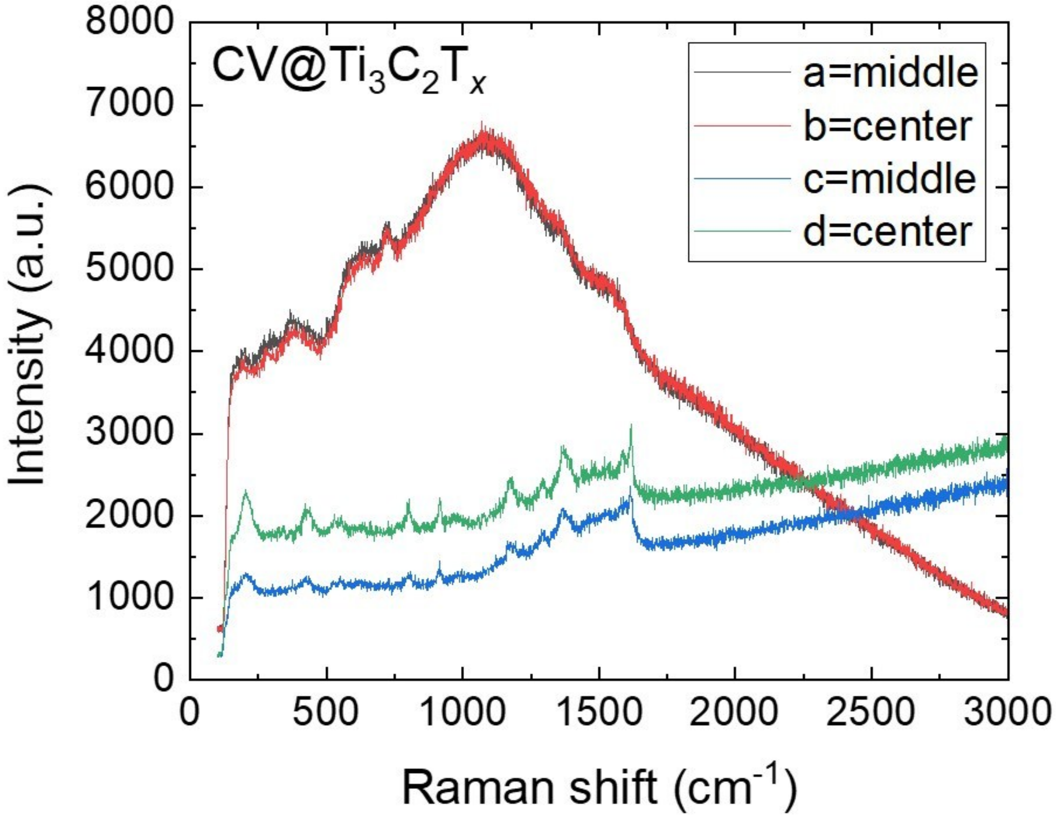

Figure S2. The SERS spectra of CV dye (*ca*. 12.732 ng/cm^2) on $Ti_3C_2T_x$ film (the spin-casted film prepared by r_{10} (a and b) and r_3 (c and d) using aqueous solution of *d*-$Ti_3C_2T_x$ flake with a concentration of 50 µg/ml). The SERS spectra were acquired from the center and middle of the substrate with excitation laser wavelength of 633 nm with 30 s with 2 accumulation averaged (50×, 17 mW with the size of the laser spot was ~0.72 µm^2).

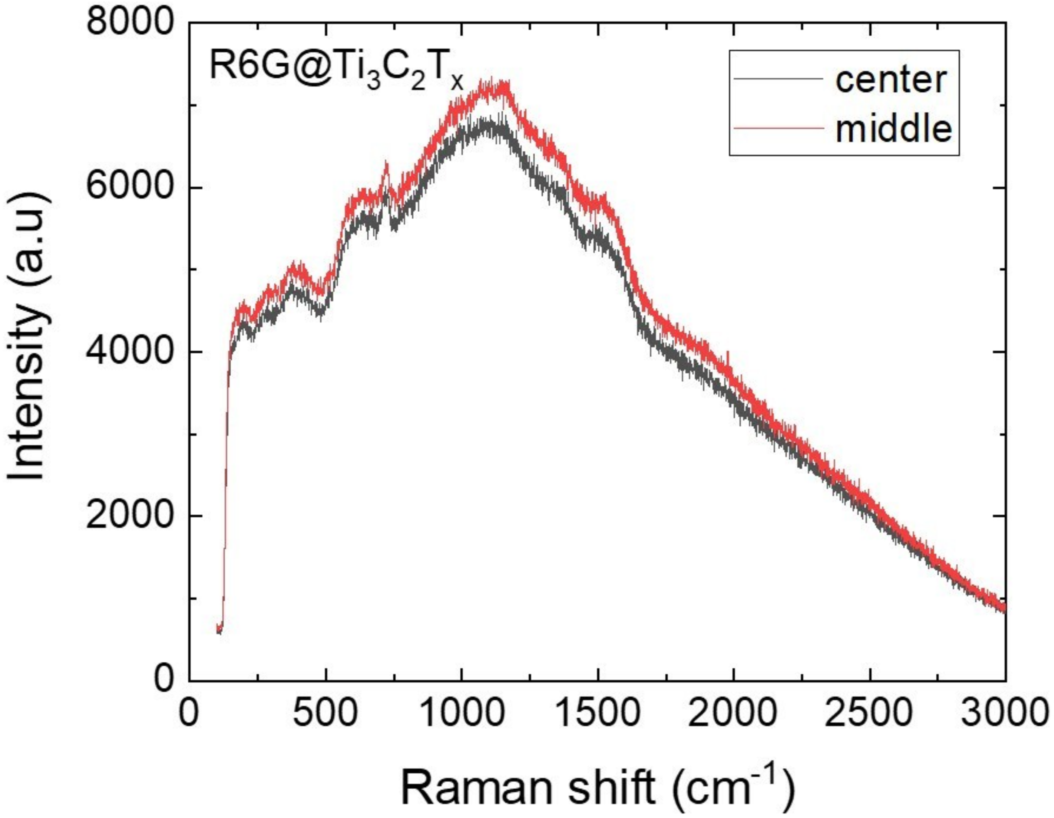

Figure S3. The SERS spectra of R6G dye (*ca*. 14.4676 ng/cm^2) on Ti$_3$C$_2$T$_x$ film (the spin-casted film prepared by r$_{10}$ using aqueous solution of *d*-Ti$_3$C$_2$T$_x$ flake with a concentration of 50µg/ml). The SERS spectra were acquired from the center and middle of the substrate with excitation laser wavelength of 785 nm with 30 s with 2 accumulation averaged.

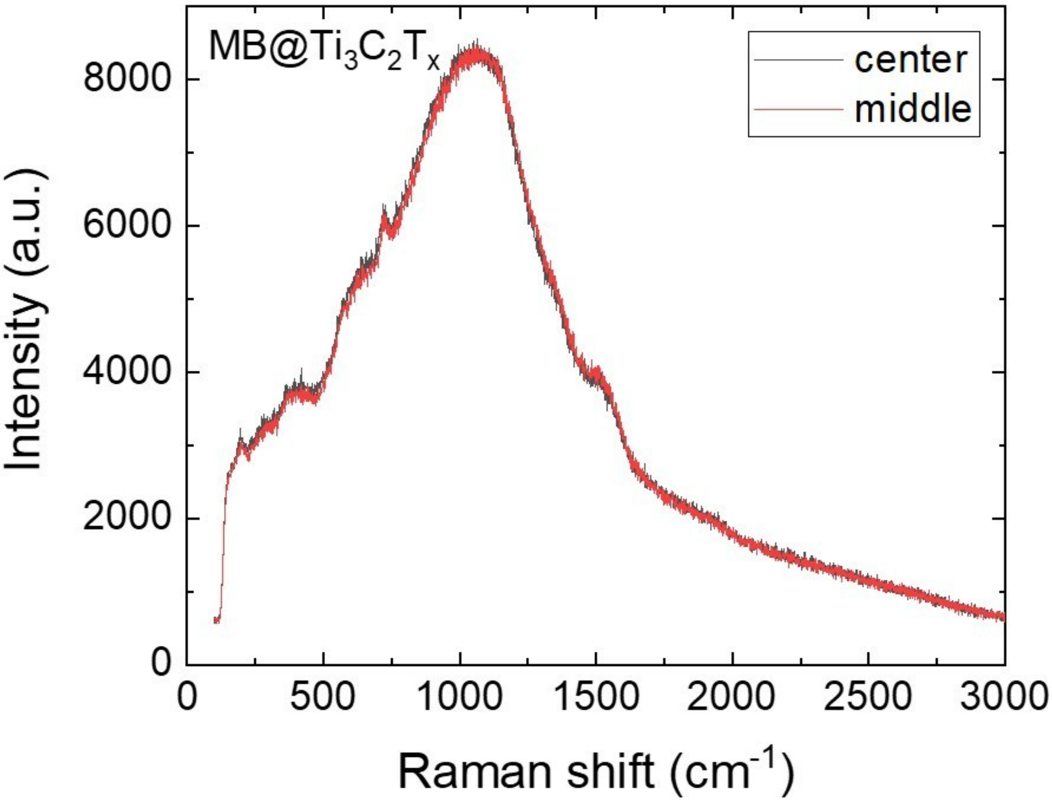

Figure S4. The SERS spectra of CV dye (*ca*. 33.2755 ng/cm^2) on $Ti_3C_2T_x$ film (the spin-casted film prepared by r$_{10}$ using aqueous solution of *d*-$Ti_3C_2T_x$ flake with a concentration of 50μg/ml). The SERS spectra were acquired from the center and middle of the substrate with excitation laser wavelength of 785 nm with 30 s with 2 accumulation averaged.

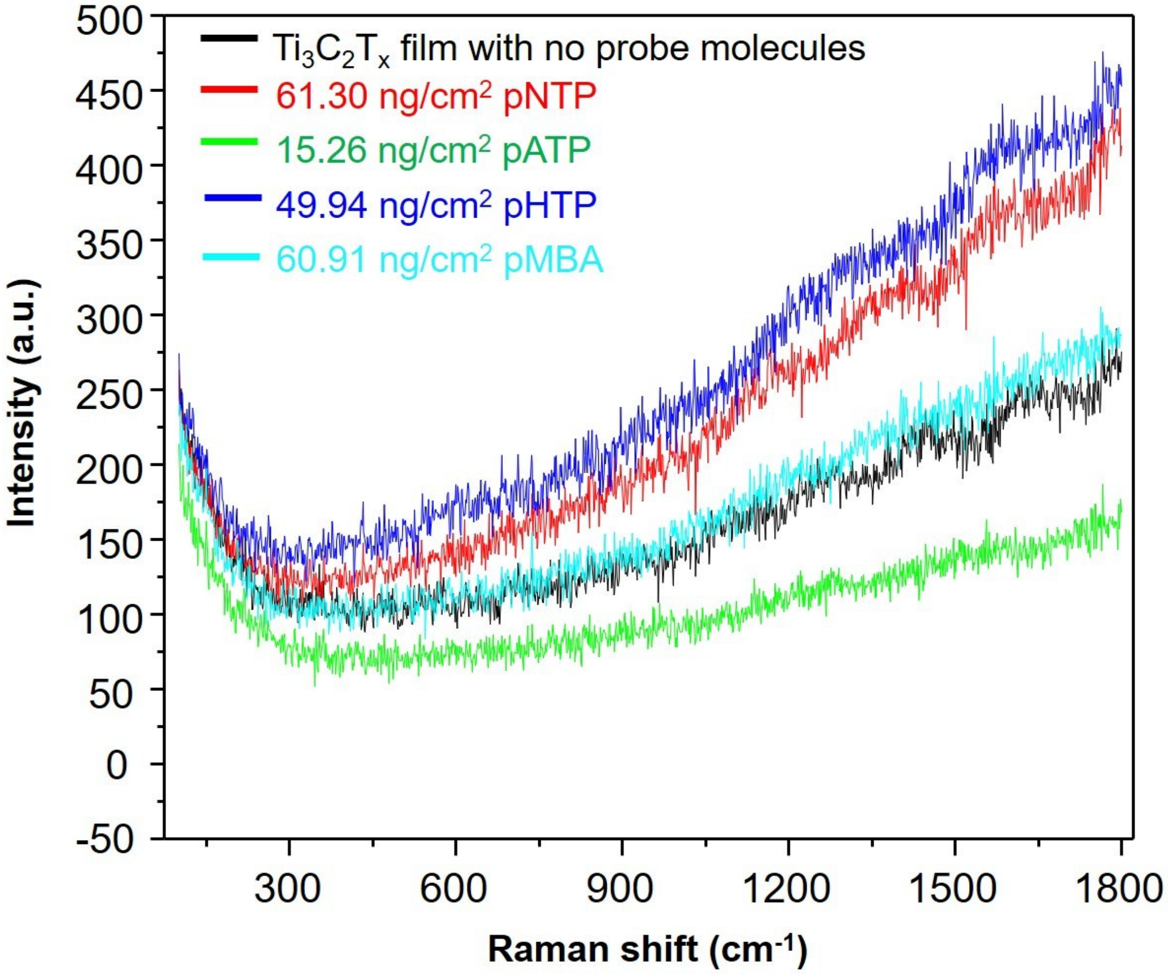

Figure S5. The SERS spectra non-resonant Raman probe molecules (Ethanol solution of para Nitrothiophenol–*p*NTP (ca. 61.30 ng/cm^2), para Amino thiophenol–*p*ATP (ca.15.26 ng/cm^2), para hydroxy thiophenol–*p*HTP (ca. 49.94 ng/cm^2) and para Mercapto benzoic acid–*p*MBA (ca. 49.94)) were drop-casted on $Ti_3C_2T_x$ film (the spin-casted film prepared by r*3* using aqueous solution of *d*-$Ti_3C_2T_x$ flake with a concentration of 50µg/ml). The SERS spectra is acquired with excitation wavelength of 633 nm laser with 30 s with 2 accumulation averaged (50×, 17 mW with the size of the laser spot was ~0.72 µm^2).

Table S1:

Vibrational mode, cm^{-1}	Assignment †
1619⊥	*a1* mode†
1583⊥	*e* mode†
1370	Asymmetric stretching ν_{as}(C–C_{center}C)/bending $\delta$$(CCC)_{ring}$/$\delta$(C–H)
1292	Asymmetric stretching ν_{as}(C–C_{center}C)/bending $\delta$$(CCC)_{ring}$/$\delta$(C–H)
1175⊥	Asymmetric stretching ν_{as}(CC_{center}C)
915⊥	Bending δ(C–C_{center}C)
800⊥	*e* mode†
553	Out-of-plane deformation γ(CCC)/ bending δ(C–N–C)/ bending δ(C–C_{center}C)
528	Bending δ(C–N–C)
436	Bending δ(C–N–C)
418	Bending δ(C–N–C)/ bending δ(C–C_{center}C)
341	Out-of-plane deformation γ(C–N–C)/ ρ_r(CH_3)
206	Torsion τ(CH_3) or A_{1g} vibration of Ti, C, O‡

† Maria Vega Can˜amares, Cat Chenal, Ronald L. Birke, and John R. Lombardi. DFT, SERS, and Single-Molecule SERS of Crystal Violet. J. Phys. Chem. C 2008, 112, 20295–20300.

‡ Pol Salles, Evan Quain, Narendra Kurra, Asia Sarycheva, Yury Gogotsi. Automated Scalpel Patterning of Solution Processed Thin Films for Fabrication of Transparent MXene Microsupercapacitors. Small 2018, 14, 1802864.

⊥ Vibrational modes for the single-molecules SERS (SM-SERS) detection of crystal violet molecules adsorbed on plasmonic substrate with excitation wavelength of 633 nm laser.