Electronic Supplementary Information

Simultaneously Intensified Plasmonic and Charge Transfer Effects in Surface Enhanced Raman Scattering Sensors Using MXene-Blanketed Au Nanoparticles Assembly

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b а h‡ aplace pressure R R+g/2 d С 100 80 Counts (a.u.) 60 40 20 0 1 µm

S1. Interpretation of the deflection of surface-covered MXene layer by Laplace pressure

Fig. S1. (a), (b) Schematic illustration of the deflection of MXene by Laplace pressure. (c) AFM analysis of the surface-adsorbed MXene nanosheets on Si wafer, and (d) size distribution histogram of MXene nanosheets.

The Laplace pressure (P) within the meniscus shown in Fig. S1a can be given by the Young-Laplace equation as follow:

$$P = \gamma/r, \tag{S1}$$

where γ and r indicate the surface tension of the solvent (*i.e.*, water) and meniscus radius, respectively. Then, the meniscus force (*F*) can be obtained by product of the *P* by the meniscus area as follow: ^[S1]

$$F = 4\pi\gamma R\cos\theta \tag{S2}$$

where R and θ indicate the radius of Au NP and the contact angle of the liquid on the solid surface (*i.e.*, MXene), respectively. It can be assumed that the net force applied on the center of meniscus. Then the moment of force of MXene from 2 meniscus can be calculated as follow:

$$M = 2 \times \left(\frac{x}{2} 4\pi\gamma R\cos\theta\right) = 4\pi\gamma Rx\cos\theta$$
(S3)

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200 400 600 800 1000 MXene size (nm)

where x indicates the radius of the water stain on MXene (*i.e.*, meniscus). It should be noted that the meniscus is generated and force start exerting on MXene layer at the late stage (*i.e.*, x is smaller than R + g/2 (where g indicates gap distance)). Therefore, in this calculation x is simply assumed as x is equivalent to R + g/2 and moment of force can be defined as follow:

$$M = 4\pi\gamma R(R + \frac{g}{2})\cos\theta \tag{54}$$

The bending moment is defined as follows:

$$M = EIC = EI\frac{1}{R_C}$$
(S5)

where E, I, C and R_c indicate Young's modulus and second moment of inertia (*i.e.*, $bh^3/12$, b: width, h: thickness), curvature and corresponding radius of curvature, respectively. From the Equation (S4) and (S5), the radius of curvature (R_c) can be obtained as follow:

$$R_{c} = \frac{EI}{4\pi\gamma R(R + \frac{g}{2})\cos\theta}$$
(S6)

Relation between R_c and depth (d) can be obtained by geometrical calculation (Fig. S1b) as follows:

$$(R + R_c)^2 = (R + \frac{g}{2})^2 + (R + R_c - d)^2$$
(S7)

$$d = R + R_C - \left(\left(R + R_C \right)^2 - \left(R + \frac{g}{2} \right)^2 \right)^{0.5}$$
(S8)

Given R = 24 nm, g = 2 nm, E = 80 - 100 GPa,^[S2] b = 600 nm (*i.e.*, average flake width of MXene monolayer, shown in Fig. S1d), h = 1 nm,^[S3] $\gamma = 72.8$ mN m⁻¹,^[S4] and $\theta = 68.4^{\circ}$.^[S5] Using these values, the value of d can be estimated as $Ed = 8.1 \pm 0.5$ nm.

S2. Work function calculations of bare Au NPs and MXene-coated Au NPs assemblies



Fig. S2. Work function of bare Au NPs assembly and MXene-coated Au NPs assembly by AFM measurement: distribution (top) and histogram (bottom) image.

The work function was calculated with AFM measurement as follows. The conductive AFM tip was first calibrated with highly ordered pyrolytic graphite (HOPG, work function = 4.6 eV). When the approaching tip was attached on the sample surface (*e.g.* bare Au NPs or MXene-coated Au NPs assemblies), the electrons are transferred so as to have an identical Fermi levels between the sample and the tip. This Fermi level alignment induces an offset in the vacuum levels, which then generates the contact potential difference (V_{CPD}) between the tip and the sample. The relation between V_{CPD} , the work function of sample (Φ_s) and the work function of tip (Φ_t) can be given by:

$$V_{CPD} = \frac{\Phi_s - \Phi_t}{e} \tag{S9}$$

where e indicates the elemental charge and the V_{CPD} is measurable by AFM. From the equation of S9, the work functions of bare Au NPs and MXene-coated Au NPs assemblies are calculated.

S3. HOMO and LUMO level of MXene-Rhodamine B (RhB) complex



Fig. S3. Polarization curve of reduction (left) and oxidation (right) reaction measured by Linear sweep voltammetry (LSV) at 5.0 mV s⁻¹ in 1.0 M KOH. (Working electrode: MXene-RhB on carbon paper, reference electrode: Hg/HgO saturated with NaOH, counter electrode: Pt wire)

The HOMO-LUMO gap is estimated using the following equation:

$$HOMO - LUMO \ gap = 1e \times (E_{onset,ox} - E_{onset,red}).$$
(S10)

where $E_{onset,ox}$ and $E_{onset,red}$ indicate the onset potential of the oxidation and reduction, respectively. The $E_{onset,ox}$ and $E_{onset,red}$ values are obtained from Fig. S3 as 0.22 V and -0.23 V, respectively. Using these values, the HOMO-LUMO gap of MXene-RhB complex is calculated as 0.45 eV.

S4. Large area SEM image of Au NPs assembly



Fig. S4. Large area SEM image of Au NP assembly.

S5. Image analysis for calculating surface packing fraction of Au NPs assembly



Fig. S5. Procedure of image analysis for calculation surface packing fraction of random spots in Au NPs assembly.

S6. Surface packing fraction of hexagonally ideal arranged Au NPs assembly



Fig. S6. Schematic illustration of ideal arranged Au NPs assembly. R and g indicate the radius and gap, respectively.

From the Fig. S6, the area of unit cell (A_u) and area of particle in unit cell (A_p) can be calculated as follows:

$$A_{u} = \sqrt{3} \left(R + \frac{g}{2}\right)^{2}$$
(S11)
$$A_{p} = 3 \times \frac{1}{6} \pi R^{2} = \frac{\pi}{2} R^{2}$$
(S12)

Given R = 24 nm and g = 2 nm. Using these values, the A_u and A_p can be obtained as 1083 nm² and 905 nm², respectively. Then surface packing fraction is calculated as 83.6%.

S7. Radial distribution function



Fig. S7. (a) SEM image of Au NPs assembly with blue circle representing searched particle for image analysis and (b) corresponding radial distribution function.

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S8. Measurement of average diameter of Au NPs using TEM observations



Fig. S8. (a) TEM images of Au NPs and (b) the corresponding histogram of the diameter of Au NPs.

S9. Raman spectra and mapping image of RhB molecules



Fig. S9. (a) Raman spectra and (b) Raman mapping image of RhB molecules (10⁻⁷ M) from the surface of MXene-coated Au NPs assembly.

The characteristic peaks observed at 622 cm⁻¹, 1360 cm⁻¹, 1510 cm⁻¹ and 1649 cm⁻¹ correspond xanthene ring, aromatic C-C bending, aromatic C-H bending and aromatic C=C bending, respectively. The two peaks observed at 1203 cm⁻¹ and 1282 cm⁻¹ correspond both C-C bridge band stretching and aromatic C-H bending.^[S6]

S10. Raman spectra of RhB molecules with different concentration on bare Au NPs and MXene film



Fig. S10. Raman spectra of RhB molecules (from 10^{-10} to 10^{-7} M) from the surface of bare Au NPs assembly and RhB molecules (from 10^{-5} to 10^{-3} M) on the MXene film. Detection parameter: $\lambda_{\text{exitation}} = 532$ nm, accumulation time = 1 s, laser power = 5 mW.

S11. Raman intensities of RhB molecules from randomly selected spots



Fig. S11. Raman spectral intensities of RhB from randomly selected spots of the MXene-coated Au NPs assembly, bare Au NPs assembly and MXene film. (sample size of 1×1 cm²).

S12. Analytical enhancement factor (AEF) of MXene-coated Au NPs assembly, bare Au NPs assembly, MXene film



Fig. S12. Comparison of AEF of RhB from different SERS substrates (MXene-coated Au NPs assembly, bare Au NPs assembly and MXene film).

S13. Raman spectra of crystal violet molecules



Fig. S13. Raman spectra of crystal violet (10⁻⁷ M) from surfaces of bare Au NPs and the MXene-coated Au NPs assemblies. Detection parameter: $\lambda_{\text{exitation}} = 532$ nm, accumulation time = 1 s, laser power = 5 mW.

S14. SEM and AFM observation of MXene-coated Au NPs assembly



Fig. S14. SEM images and AFM observations (two-dimensional (top) and cross-sectional (bottom) images) of MXene-coated Au NPs assembly fabricated with different MXene concentration (*i.e.* 1.0 mg mL⁻¹ and 2.0 mg mL⁻¹). For AFM image, white line in top image corresponds to the cross-sections shown below.

S15. Image analysis for calculating coverage of MXene layer



Total area = 227097 px Packing Area = 169504 px Surface packing fraction = 74.63%

Fig. S15. Procedure of image analysis for calculation coverage of MXene over the Au NPs monolayer. The spin-casting concentration of MXene was 1 mg mL¹.

S16. Surface wrinkling period of MXene covered on Au NPs assembly



Fig. S16. Histogram of surface wrinkling period of MXene covered on Au NPs assembly with different concentration (from 0.5 mg mL⁻¹ to 5.0 mg mL⁻¹) of MXene suspension.

S17. Raman spectra of RhB on MXene-coated Au NPs assembly



Fig. S17. Representative Raman spectra at 1203, 1282, 1360, 1510, and 1649 cm⁻¹ of RhB molecules (10⁻⁷ M) from the surface of MXene-coated Au NPs assembly fabricated by spin-casting with different concentration (from 0.5 mg mL⁻¹ to 5.0 mg mL⁻¹) of MXene suspension.

S18. Cr(VI) Extraction process



Fig. S18. Schematic illustration of Cr(VI) extraction process

The Cr(VI) was extracted from arbitrary solution by procedure reported by Adam and Pribil.^[57] 40 mL of Arbitrary water solution was mixed with 10 mL of 1 M hydrochloric acid (HCl, Samchun Chemical, Republic of Korea). Then, the mixed aqueous solution was shaken with 5 mL of 10vol.% tri-n-octylamine (TOA, Sigma Aldrich, USA, 98%) solution in chloroform (CHCl3, Sigma Aldrich, USA, \geq 99%) for 5 minutes. In this process the Cr(VI) extracted by TOA due to the interfacial anion exchange mechanism as shown in the following reactions:

$$H^{+}_{(a)} + CI^{-}_{(a)} + R_{3}N_{(o)} \leftrightarrow R_{3}NH^{+}CI^{-}_{(o)}, \qquad (S13)$$

$$HCrO_{4}^{-}{}_{(a)} + R_{3}NH^{+}CI^{-}{}_{(o)} \leftrightarrow R_{3}NH^{+}HCrO_{4}^{-}{}_{(o)} + CI^{-}{}_{(a)},$$
(S14)

where (a) and (o) indicate aqueous phase and organic phase, respectively. After phase separation was finished, the organic phase was separated from aqueous phase. Then, for back-extraction process, separated organic phase was shaken with 5 mL of 0.3 M sodium hydroxide (NaOH, Samchun Chemical, Republic of Korea, 0.3 M) for 5 minutes. In this process, back-extraction is proceed as shown in below:

$$R_3NH^+HCrO_4^-_{(o)} + NaOH_{(a)} \leftrightarrow R_3NH^+OH^-_{(o)} + Na^+_{(a)} + HCrO_4^-_{(a)}.$$
 (S15)

Finally, the aqueous phase was transferred to empty flask, and then the Cr(VI) extraction was completed.

S19. Raman spectra observations of RhB for a short period (30 seconds)



Fig. S19. (a) Raman spectra of RhB on MXene-coated Au NPs assembly captured every 3 s for the initial 30 s. (b) Raman spectra intensity measured at 1649 cm⁻¹ in (a) according to time.

S20. Raman spectra for EDC-NHS reacted and non-reacted SERS substrate after the washing 5 times.



Fig. S20. Raman spectra of RhB molecules attached on the surface EDC-NHS reacted (left) and non-reacted (right) SERS substrate after washing 1–5 times.

S21. Raman spectra observations of RhB for a long period (3 days)



Fig. S21. (a) Raman spectra of RhB on MXene-coated Au NPs every 1 day for 3 days after first measurement. (b) Raman spectra intensity measured at 1649 cm⁻¹ in (a) according to time.

Bare Au NPs Bare Au NPs before washing after washing b а 5000 5000 4000 5 µm 4000 5 µm MXene-coated Au NPs MXene-coated Au NPs before washing after washing d 12000 12000 10000 10000 5 µm

S22. Raman mapping images of RhB on bare Au NPs and MXene-coated Au NPs assembly

Fig. S22. Comparative Raman mapping images of RhB on different substrate: (a, b) on bare Au NPs assembly before (a) and after surface washing (b), and (c, d) on MXene-coated Au NPs assembly before (c) and after surface washing (b). Although the reproducibility is retained for both substrates, the Raman signal contrast (e.g. sensitivity) is more intensified for MXene-coated Au NPs assembly (see increased scale in the colour bar).

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S23. Raman spectra and mapping image of RhB on random spots



Fig. S23. Raman spectra of RhB attached onto the random spot of MXene-coated Au NPs assembly, and the spot number corresponds to Fig. 4f.

S24. Raman spectra measurements of RhB on bare Au NPs assembly with different concentrations of Cr(VI) solution



Fig. S24. Raman spectra of RhB attached onto bare Au NPs assembly after react with triiodide solution produced by various concentration of Cr(VI) solution (from 5 μ g L⁻¹ to 1 mg L⁻¹)

- S1. B. Zhang, A. Nakajima, J. Colloid Interface Sci. 2002, 245, 215.
- S2. K. L. Firestein, J. E. von Treifeldt, D. G. Kvashnin, J. F. S. Fernando, C. Zhang, A. G. Kvashnin, E. V. Podryabinkin, A. V. Shapeev, D. P. Siriwardena, P. B. Sorokin, D. Golberg, *Nano Lett.* **2020**, *20*, 5900.
- S3. M. Ghidiu, M. R. Lukatskaya1, M.-Q. Zhao, Y. Gogotsi, M. W. Barsoum, Nature 2014, 516, 78.
- S4. R. Tuckermann, Atmos. Environ. 2007, 41, 6265.
- S5. Zukiene, G. Monastyreckis, S. Kilikevicius, M. Proch'azka, M. Micusik, M. Omastov'a, A. Aniskevich,
 D. Zeleniakiene, *Mater. Chem. Phys.* 2021, 257, 123820.
- S6. Lin, W. L. J. Hasi, X. Lin, S. Q. G. W. Han, X. T. Lou, F. Yang, D. Y. Lin, Z. W. Lu, Anal. Methods 2015, 7, 5289.
- S7. M. Chakraborty, Z. V. P. Murthy, C. Bhattacharya, S. Datta, Sep. Sci. Technol. 2005, 40, 2353.