Supporting Information

Selective gas diffusion in two-dimensional MXene lamellar membranes: insights from molecular dynamics simulations

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The Calculation of the Water Contact Angle (WCA) of the MXene Nanosheet.

We have calculated the water contact angle of MXene nanosheet in this work. The result, $55.0^{\circ}\pm0.5^{\circ}$, is quite close to the experimental value, 59.5° .¹ We just briefly describe the calculation procedure as follows, and interested readers could refer to our previous publications²⁻³ for more details.

The size of simulation box is 11.85 nm×6.36 nm×8.00 nm, containing 1630 water molecules and a single-layer MXene nanosheet (see Fig. S2a). First, the system was energy-minimized by the steepest descent method. Then a 5 ns NVT (T = 300 K) equilibration simulation was performed. Finally, the production simulation was carried out in the NVT (T = 300 K) ensemble for 60 ns. For the water wetting of MoS₂, the last 40 ns of a whole trajectory (60 ns) was averaged to yield the wetting configurations and contact angle. Density map of water droplet was obtained by distribution probability of water molecules along the x-z plane, see Fig. S2b. The coordinates of water along the contour line can be used to calculate the contact angle (Fig. S2c): the data points at the contour line were fitted to a circle equation by the method of least squares. The regression equation was $(x-a)^2 + (z-b)^2 = R^2$. Taking into account the height of MXene, z_0 , the contact angle can be calculated by the following equation S(1):

$$\theta = 90^{\circ} + \arcsin(\frac{b - z_0}{R}) \tag{S1},$$

where θ is the water contact angle, *b* is the coordinate of the circle center (along z direction, note $b < z_0$) and *R* is the radius of the circle; *b* and *R* are calculated from the aforementioned regression equation. The simulation was repeated three times, and the average contact angle is $55.0^{\circ} \pm 0.5^{\circ}$.



Fig. S1. Two types of 2D material-based membranes: nanosheet membranes (a, b) and lamellar membranes (c). Green ball represents gas molecules, red arrow or dash line represents the transportation path of gas molecules.



Fig. S2. (a) A snapshot of the simulation system for studying the water contact angle on a MXene nanosheet. Atoms Ti, C, O, and H are drawn as pink, cyan, red, and white balls, respectively. (b) Density map of the water droplet along x-z plane on MXene nanosheet. (c) The contact angle θ for water droplet on MXene nanosheet.



Fig. S3. (a) xy-RDF of 6 He atoms diffusing in d = 14 Å (olive), 6 Å (red) MXene nanogallery and RDF of 6 He atoms in vacuum (blue); simulations with the number of He atoms ranging from 2 to 12 yield very similar results; we did not calculate RDF for 1 He atom simulations; we only used the x,y coordinates of He atoms for xy-RDF calculation when they were diffusing in a 2D nanogallery; the RDF's are smoothed. The He-He xy-RDF's in nanogallery are close to 1, which is similar to the RDF in vacuum. Taking to account the volume element of $2\pi r d\delta r$ (nanogallery, d is the interlayer spacing, r is the radial distance) or $4\pi r^2 \delta r$ (vacuum), the probability of He-He distance grows with the He-He distance. Thus the aggregation of He atoms in the MXene nanogallery is negligible. (b) The distribution frequency of He-He (d = 14 Å, blue), He-MXene (d= 6 Å, red; 14 Å, olive) interaction energy. Most He-He interaction energy (magnitude), |INTE_{He-He}|, is essentially 0 (93.50%<10⁻¹⁴, 97.38%<0.001,99.06%<0.01 KJ/mol, see Table S1 for more details), while He-MXene interaction energy (magnitude) is much greater (when d = 14 Å, 66.3% > 0.1; d = 6 Å, 99.5% > 0.1 KJ/mol, see Table S1). The He-He, He-MXene interaction energies are mainly Lennard-Jones interaction (L-J), which decays with (1/r)⁶ (when He-He, He-MXene distances are not too small and L-J is negative, as shown in Fig. S3b). Thus, He-MXene (d = 14 Å, olive) interaction is much smaller than He-MXene (d = 6 Å, red) interaction. He-He interaction is even tiny because 1. He-He distance is quite large most of the time (Fig. S3a); 2, the density of He atoms (gas) is much smaller than that of MXene.



Fig. S4. Diffusion coefficient, *D*, of different number of He molecules diffusing in d = 14 Å MXene nanogallery (black); or in vacuum without MXene nanosheets (red); *D's* in vacuum were divided by 10 so that they could be put in the same plot as *D's* in MXene. The 1 He molecule diffusivity in vacuum could not be simulated because the interaction between He and other atoms is absent (note the cut-off for Lennar-Jones interaction is less than one half of the simulation box size). Thus it was estimated from the average of $D_{D_2-H_2}$ 1.22 and D_{H_2-He} 1.49 cm² s⁻¹; in comparison, D_{He-Ne} is 1.07 cm² s⁻¹, and the self-diffusivity of He, D_{He} should be larger; D_{A-B} refers to the binary diffusion coefficient of the A-B Equimolar Mixture at 293.15K and 101.325 KPa (*CRC hand book of Chemistry and Physics*, 84th ed. pp1165-1166). Other diffusivities (either in MXene or in vacuum) were calculated from MD simulations with the Einstein relation (see the 'MODELS AND METHODS' section of main text). The number of gas molecules affects *D* in vacuum (red) as the Gilliland's equation predicts, but affects *D* in MXene nanogallery (black) insignificantly.



Fig. S5. Diffusion coefficient, *D*, of different gases in anhydrous MXene (a) or MXene (b) with varying interlayer distance, *d*. *D*'s are plotted with respect to the kinetic diameters of gas, where 2.6, 2.89, 3.3, 3.64 and 3.8 Å refer to He, H₂, CO₂, N₂ and CH₄, respectively. At small interlayer distance, *D* decreases with kinetic diameter increases, and there is a sharp cutoff between H₂ (2.89 Å) and CO₂ (3.3 Å). D_{CO_2} is usually smaller than D_{N_2} , which would be explain in the 'Influence of Gas-MXene interaction' section of main text.



Fig. S6. Interaction energy of gas molecules with MXene in anhydrous MXene (a) or MXene (b) nanogalleries with different d values. The interaction energy in MXene nanogalleries is less negative than anhydrous MXene because the intercalating water prevents gas molecules from approaching the MXene wall.



Fig. S7. Diffusion coefficient, *D*, of different gases in anhydrous MXene (a) or MXene (b) with varying interlayer distance, *d*. *D*'s are plotted with respect to the molecular mass of gas (m), where 2, 4, 16.04, 28.01 and 44.01 amu refer to H₂, He, CH₄, N₂ and CO₂, respectively. At large interlayer distance (d > 10 Å), *D* scales with m^{-1/2}. D_{CO_2} is quite smaller than the m^{-1/2} prediction, which would be explained in the 'Influence of Gas-MXene interaction' section of main text. In d = 10 Å MXene, *D*'s of big gas molecules (CH₄, N₂ and CO₂) are also smaller than m^{-1/2} prediction, because intercalating water enhances the molecular sieving effect (see the 'Effect of Intercalating Water ' section of main text).



Fig. S8. The time series of a helium molecule's z coordinate (blue, enlarged and shifted), interaction energy with MXene sheets (red), which diffuses in an anhydrous MXene nanogallery with interlayer distance, d = 14 Å. Most of the time, the He molecule is in the middle of the nanogallery ($z \sim 1.5$ nm), with He-MXene interaction energy close to 0. When He collides with MXene ($z \sim 1.0$ or 2.0 nm), the He-MXene interaction energy reach a local minimum or maximum.



Fig. S9. The time series of a helium molecule's *z* coordinate (red), x,y,z velocities (green, blue, pink), which diffuses in an anhydrous MXene nanogallery with interlayer distance, d = 14 Å. The x,y,z velocities change violetly when He collides with MXene ($z \sim 1.0$ or 2.0 nm), due to the strong He-MXene interaction (Fig. S8).



Fig. S10. The time series of a helium molecule's *z* coordinate (blue), interaction energy with MXene (red), interaction energy with all other He atoms (olive), which diffuses in an anhydrous MXene nanogallery with interlayer distance, d = 14 Å. The He-MXene collision frequency was estimated to be ~5*10¹¹ s⁻¹ per molecule from the oscillation of the He atom's z coordinate. When the He atom is far away from other He atoms, its interaction energy with them is 0. When there is a collision event, there would be a peak or valley in the time series of He-other He atoms interaction energy, because the interaction becomes non-negligible. The He-He collision frequency could be estimated from the number of peak or valley in the time series of He-other He atoms interaction energy.



Fig. S11. Diffusion coefficient, *D*, of CH₄ or CO₂ in anhydrous MXene or MXene with interlayer distance, *d*, varying from 5 to 24 Å. D keeps increasing with d increases, though it vary slowly at large interlayer distance (d > 10 Å). See more explanations in the 'Effect of Interlayer Distance' section of main text.



Fig. S12. The ratio of diffusion coefficient in anhydrous MXene to that in hydrous MXene for the same interlayer distance, *d*. The ratio, or the effect of intercalating water on gas diffusion, is large for small interlayer distances or gas molecules with big kinetic diameters. See more explanations in the 'Intercalating Water' section of main text.



Fig. S13. (a) In (hydrous) MXene nanogallery with small interlayer distance, d, the intercalating water molecule blocked the gas diffusion so severely that, a gas molecule can no longer push itself through the space between water and MXene wall. (b) In (hydrous) MXene nanogallery with large interlayer distance, gas molecules could diffuse through the space between water and MXene wall, and water molecules roughen the potential surface for gas diffusion. Thus the effect of intercalating water on gas diffusion becomes more significant for MXene nanogallery with small d, as Fig. S12 shows.



Fig. S14. (a) The diffusion coefficient, *D*, of CO₂ (black) or H₂ (blue) in MXene nanogallery with different intercalating water content, at d = 7 Å (a) or 14 Å (b). The diffusion coefficients increase, or approach *D*'s of anhydrous MXene nanogalleries, with water content decreasing. This indicates the effect of intercalating water on *D* becomes minor for less water content.



Fig. S15. The selectivity, $S_{\text{gas/N}_2}$, for large d (*e.g.* 10 Å) anhydrous MXene nanogallery are quite close to those in recent studies on graphene⁴ or MoS₂⁵ membranes (with some minor deviations though). *S* of graphene or MoS₂ with $d \ge 10$ Å are shown. When $d \ge 10$ Å, $S_{\text{gas/N}_2}$ in anhydrous MXene nanogallery do not change with *d*, thus only d = 10 Å data are shown. $S_{\text{gas/N}_2}$ is plotted with respect to the molecular mass of gas: 2, 4, 16.04, 28.01 and 44.01 amu refer to H₂, He, CH₄, N₂ and CO₂, respectively. $S_{\text{gas/N}_2}$ of MoS₂ usually follow the m^{-1/2} prediction, while S_{CO_2/N_2} of MXene is lower, which would be explained in the 'Effect of Gas-MXene Interaction' section of the main text.



Fig. S16. The selectivity of H₂ (a) or He (b) over other gases for MXene nanogallery. The simulation results of d = 6 Å (red) or 7 Å (blue) are quite close to the experimental data (black, d = 6.8 Å).⁶

He-He interaction energy		He-MXene interaction energy		He-MXene interaction energy	
(d = 14 Å)		(d = 14 Å)		$(d = 6\text{\AA})$	
Range(KJ/mol)	frequency	range(KJ/mol)	frequency	range(KJ/mol)	frequency
$0 \sim +\infty$	0.03%	$0 \sim +\infty$	2.01%	$0 \sim +\infty$	5.13%
-10 ⁻¹⁴ ~0	93.50%				
-0.001~-10 ⁻¹⁴	3.88%	-0.1~0	33.69%	-0.1~0	0.45%
-0.01~-0.001	1.68%				
-0.1~-0.01	0.68%				
-0.2~-0.1	0.16%	-0.2~-0.1	12.00%	-0.2~-0.1	0.46%
-0.3~-0.2	0.07%	-0.3~-0.2	7.44%	-0.3~-0.2	0.55%
-0.4~-0.3	0	-0.4~-0.3	5.47%	-0.4~-0.3	0.63%
-∞~-0.4	0	-∞~-0.4	39.40%	-∞ ~-0.4	92.77%

Table S1. The normalized distribution of He-He (d = 14 Å)[†], He-MXene (d = 6 or 14 Å) interaction energy (these data are also shown in Fig. S3b)

[†] The distribution frequency of He-He interaction energy (d = 6 Å) is quite similar, thus was not shown.

1. J. Liu, H. B. Zhang, R. Sun, Y. Liu, Z. Liu, A. Zhou and Z. Z. Yu, *Adv. Mater.* **2017**, *29* (38), 1702367.

2. H. Chen, L. Li, T. Zhang, Z. Qiao, J. Tang and J. Zhou, J. Phys. Chem. C 2018, 122 (4), 2070-2080.

3. G. Cheng, M. Liao, D. Zhao and J. Zhou, *Langmuir* **2017**, *33* (7), 1732-1741.

4. S. Jiao and Z. Xu, ACS Appl. Mater. Interfaces 2015, 7 (17), 9052-9059.

5. D. Wang, Z. Wang, L. Wang, L. Hu and J. Jin, *Nanoscale* **2015**, *7* (42), 17649-17652.

6. L. Ding, Y. Wei, L. Li, T. Zhang, H. Wang, J. Xue, L. X. Ding, S. Wang, J. Caro and Y. Gogotsi, *Nat. Commun.* **2018**, *9*, 155.

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