Supplementary Information

An atomically thin molecular aperture: two-dimensional gallium phosphate

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Out-of-phase Rotations in Bilayer Two-dimensional GaPO4

The rotations between neighboring GaO₄ and PO₄ tetrahedra in two-dimensional (2D) GaPO₄ bilayers can be mirrored in the two halves of the bilayer, producing in-phase rotations in the two layers when viewed from above as in **Figure 1** of the main text. Alternatively, the tetrahedra connected though the central 180° Ga–O–P can be rotated in opposite directions to produce the "out-of-phase" structure pictured below in **Figure S1** and reported previously. The in-phase structure was found to be \approx 1 meV per unit cell lower in energy in calculations performed with and without inclusion of long range van der Waals interactions.



Figure S1. (a) Top-down ball-and-stick model for out-of-phase GaPO₄, as reported in our previous study (side view inset). Red, yellow, and green represent oxygen, phosphorous, and gallium atoms. Lighter red halos represent the calculated atomic radius of oxygen in the upper layer, creating an effective pore size as noted by a blue circle. (b) Polyhedral representation of bilayer GaPO₄ with upper and lower tetrahedra rotated out-of-phase. Green and yellow triangles correspond to GaO₄ and PO₄ tetrahedra. Red spheres correspond to O in the upper layer, while the lighter red halos indicate the O ionic radii which forms an effective pore size denoted by a blue circle.

Isotropic Elastic Response of 2D GaPO₄

The anisotropy of the elastic response of 2D GaPO₄ was investigated by the response to uniaxial strain applied in orthogonal directions to a $(1 \times \sqrt{3})$ rectangular superstructure of the 2D bilayer GaPO₄ unit cell. The results are plotted in **Figure S2** below where "a" corresponds to the [10] primitive direction and "b" to the [11] direction. The slope of the line in **Figure S2a** indicates a Poisson ratio of 0.342. Meanwhile, the linearity of the plot of the differential strain energy versus strain for the two directions is indicative of an elastic response. All of the curves are independent of the applied strain direction indicating that the material behaves isotropically over the regime of interest.



Figure S2. Isotropic behavior of bilayer GaPO₄. (a) Strain in opposing axis when either the a-axis (black squares) or b-axis (red circles) is strained. (b) $dE/d\varepsilon$ in opposing axis when either the a-axis (black squares) or b-axis (red circles) is strained. (c) Energy per GaPO₄ unit when either the a-axis (black squares) or b-axis (red circles) is strained. Values are from PBE calculations, excluding van der Waals contributions.

Comparison of Differential Strain Curves for 2D AlPO₄ and GaPO₄

The strain relief mechanisms in 2D bilayer AlPO₄ and GaPO₄ were investigated by examining plots of the differential strain energy as a function of applied biaxial strain, as well as bond lengths and angles; the former are provided in **Figure S3**. The calculations were performed by proportionately increasing the two in-plane lattice constants of the 2D material by the biaxial strain and allowing all the atomic coordinates within the unit cell to relax to obtain the minimum energy configuration. The differential strain energies were computed from the residual forces acting on the lattice vectors. The single straight line for AlPO₄ is indicative of an elastic response with a single strain relief mechanism across the region of interest. Meanwhile the two straight lines with a change in slope near $\varepsilon = 5.0\%$ for GaPO₄ indicates two distinct elastic response regimes. As described in the main text, at lower strains the T_{III}O₄ tetrahedra rotate but do not distort producing a soft response in this regime. Near $\varepsilon = 5.0\%$, the tetrahedral rotations are eliminated and the material begins to respond strain by distorting the tetrahedra resulting in a slope similar to that of AlPO₄.



Figure S3. Derivative of the energy with respect to strain for AlPO₄ and GaPO₄. Connecting lines are best fits to the data regions.

Change in the Water Permeation Mechanism with Pore Size

As water adsorption energies on top of and at the center of 2D GaPO₄ bilayers were calculated as a function of pore size, systematic changes in the adsorption configuration on top and the permeation mechanism were observed as the pore size was reduced. At $\varepsilon = 0$ corresponding to a pore size of 1.70 Å, water molecules adsorbed on the top of the bilayer with the H atoms tilted down to form two H bonds with oxygens on the outer surface as shown in **Figure S4a**. To pass through to the center, the water molecule must flip to follow the lowest energy path as illustrated in the transition state configuration in **Figure S4a**. In contrast, for the 2.8 Å pores created by $\varepsilon =$ 5.0% tensile strain, the water molecules lie flat on the top surface then rotate to enter the pore O atom down as shown in **Figure S4b**.



Figure S4. Relaxed structures for H₂O transmission through 2D GaPO₄ for (a) $\varepsilon = 0$ and (b) $\varepsilon = 5.0\%$. White, red, yellow, and green represent H, O, P, and Ga atoms. O atoms in H₂O are shown in orange for clarity.

He/Ne selectivity ratios as a function of estimated He permeance

To facilitate easier comparison with future experimental and simulation studies, the full range of He/Ne selectivity ratios ($S_{He/Ne}$) are plotted against the estimated He permeance in **Figure S5**. Units of permeance are given in Barrer, which is a traditional unit for Robeson-style plots and is obtained by multiplying the standard permeance (in mol m⁻² s⁻¹ Pa⁻¹) by the film thickness (approximately 4.5 Å for 2D GaPO₄); 1 Barrer = 3.35×10^{-16} mol m⁻¹ s⁻¹ Pa⁻¹. The corresponding pore sizes are noted next to the data points.



Figure S5. He/Ne selectivity ratio ($S_{He/Ne}$) vs. estimated He permeance for GaPO₄. Data points are labeled with the corresponding pore size.

Support and Residual Stress Effects on Pressure Driven Pore Opening

The proposed device architecture involves affixing the 2D material to a porous support and applying a pressure differential across the structure to control the pore size. The effect of the radius of the support pores on the pressure differential required to achieve specific pore sizes was calculated with results provided in **Figure S6a**. In the main text we focused on 10 μ m radius holes as a compromise between the pressure required to trigger changes in the 2D GaPO₄ pore sizes and the required domain size of the 2D material.

As described in the main text, the deflection induced in a thin film during bulge testing depends on the residual stress in the film. The effect of residual stresses on the change in pore size as a function of pressure difference over 42 μ m support holes is provided in **Figure S6b**. The plot shows only a minor effect up to residual stresses on the order of 1.0 GPa.



Figure S6. Pore size vs. pressure curve for GaPO₄ suspended in a membrane test device as a function of (a) support hole size and (b) residual internal stress (σ_0). The values in (b) are computed assuming a 42 µm support hole size.

Kinetic Modeling of Transmission Through the 2D Membrane

Transmission through the 2D material was modeled as a sequential process involving adsorption on the membrane surface followed by passage to the center and then reemergence on either side of the 2D bilayer following the same kinetics. Adsorption, desorption and passage to the center were assumed to follow Langmuir kinetics with the activation energies for each step provided by the DFT calculations and assuming the same pre-exponential for all activated steps. The surface coverages and fractional occupation of the sites at the bilayer center were assumed to be in quasisteady state. Assuming a partial pressure of the gas of interest *P* on one side of the bilayer and zero pressure on the opposite side, the balance equations for the surface coverage θ and center site coverage θ_c are as follows:

(1)
$$\frac{d\theta}{dt} = 0 = k_{ad}P(1-\theta) + k_{ct}\theta_c(1-\theta) - k_d\theta - k_{tc}\theta(1-\theta_c)$$

(2) $\frac{d\theta_c}{dt} = 0 = k_{tc}\theta(1-\theta_c) - k_{ct}\theta_c(1-\theta) - k_{ct}\theta_c$

where k_{ad} is the adsorption rate constant which is given by

(3)
$$k_{ad} = \frac{s_0}{(2\pi m kT)^{1/2}}$$

with s_0 the initial sticking coefficient, *k* Boltzmann's constant, *m* the mass of the molecule and T the temperature. The remaining rate constants follow typical Arrhenius behavior:

(4)
$$k_d = v e^{-E_D/kT}$$

(5) $k_{tc} = v e^{-(E_{TS}+E_D)/kT}$
(6) $k_{ct} = \frac{1}{2} v e^{-(E_{TS}+E_C)/kT}$

where E_D , the desorption activation energy, is given by the absolute value of the calculated adsorption energies on the surface (see main text **Figure 3a**), E_{TS} is the energy of the transition state relative to the gas phase species (main text **Figure 3b**) and E_C the absolute value of the calculated adsorption energies for the molecule at the center of the bilayer (main text **Figure 3a**). The subscripts *tc* and *ct* denote motion from the top to the center of the bilayer and from the center to the top of the bilayer, respectively.

The two coupled equations can be solved numerically. For He and Ne at 300 K and any reasonable partial pressure, the coverages are vanishingly small ($<10^{-5}$); for water at 300 K, the coverages can be substantial and depend strongly on the partial pressure. Focusing on He and Ne, in the low coverage limit the coverage at the center reduces to:

(7)
$$\theta_C = \left(\frac{k_{ad}}{k_d}\right) \left(\frac{k_{tc}}{k_{ct}}\right) P$$

and the transmission rate to:

(8)
$$r = k_{ct}\theta_0$$

Substituting in the expressions for the rate constants yields:

(9)
$$r = \frac{s_0 P}{2(2\pi m kT)^{1/2}} e^{-E_{TS}/kT}$$

Thus, the barrier for the overall process becomes the energy of the transition state relative to the gas phase. The absolute He and Ne permeances were estimated by taking $s_0 = 1$ for atoms striking anywhere within the pore opening and zero elsewhere, and using a Maxwell distribution at standard conditions to model the transmission probability through a single pore. The non-exponential contribution to the permeance then becomes:

(10)
$$\frac{\epsilon}{2(2\pi mkT)^{1/2}}$$

where the porosity, ϵ , is taken as the area of the pore divided by the area of the primitive unit cell.