Supplemental Material

Multilayer Graphene Sheet with Conical Nanopore as a Membrane for High-Permeance Molecular Separation

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Content

1. Pore structure

The conical graphene nanopore (Pore-CO) is consisted of three-layer graphene with a central-located pore. The pores have different sizes and the pore-rim unsaturated carbon atoms are all passivated with hydrogen atoms. To establish the conical graphene nanopore, the central line of the three pores in each layer is basically co-axial and the three pores are arranged from smallest size to largest size in turn. The graphene sheet with the smallest pore faces toward the permeate side while the graphene sheet with the largest pore faces toward the feed side. The structures of pores in each graphene sheet are clearly shown in **Figure S1**. The pore diameters of these three pores are 0.677, 0.977 and 1.426 nm, respectively, which are estimated by circularly fitting the coordinates of the pore-rim hydrogen atoms. The atomic models of Pore-S and Pore-CY from different viewing angles are also shown in **Figure S1**.
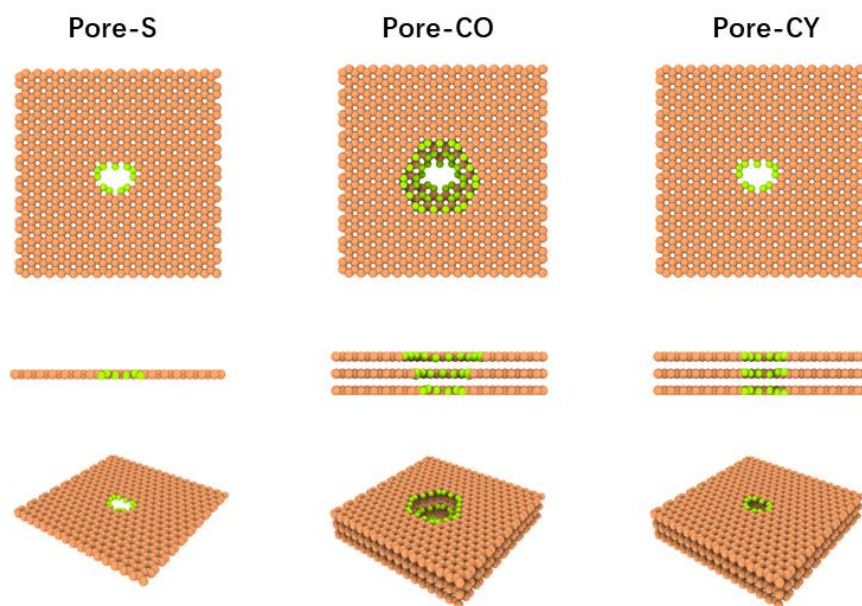

Figure S1 Pore structures of Pore-S, Pore-CO and Pore-CY.

2. Simulation model

2.1 MD simulation system

The MD simulations evaluating the molecular permeation through graphene nanopores are performed in a non-equilibrium system. The gas molecules are originally arranged in one side (feed side) of graphene, over time the permeating molecules can move to the other side (permeate side). Based on the time-variation of the number of permeated molecules, the molecular permeance of graphene nanopores can be obtained. The graphene sheet separates the cubic simulation box with a height of 140 nm into two chambers with equal volume. To restrict the molecules in the simulation box, reflect wall boundary conditions are applied in the direction perpendicular to the graphene sheet while periodic boundary conditions are applied in the direction parallel to the graphene sheet. To simulate the porous graphene sheet with a reasonable pore density, the area of graphene sheet is determined as 4×4 nm^2 and the corresponding pore density is 6.25×10^{12} cm^{-2}, which is comparable to that of experimentally fabricated graphene membranes [1]. To better evaluate the effects of pore shape and structure on the molecular permeation, the graphene sheet is fixed during the simulation except the passivated hydrogen atoms on the pore rim. The simulation system is equilibrated at 350 K and the time step is set as 1 fs. The simulations run for 25000000 timesteps. In the simulation box, the molecular number of each gas species is 500 and the initial gas pressure in the feed side is estimated as 21.1 bar based on the ideal gas kinetic equation.
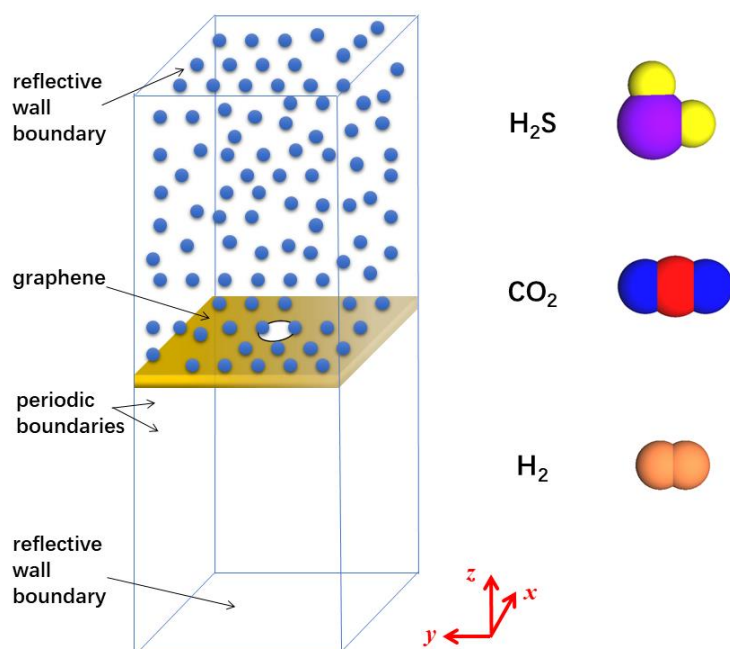
Figure S2 Simulation system and atomic models of gas molecules.

2.2 Potential models

Several different atomic species are involved in the all-atomic MD simulations, thus the hybrid atomic pair interactions are applied. The C and H atoms in the graphene sheet and H_2 molecules are modeled by the AIREBO potential model; while the CO_2 and H_2S molecules are modeled by the Lennard-Jones (L-J) potential model coupling with a Coulombic term, which considers both the Van der Waals and electrostatic interactions. For the gas molecules, the bond interactions including bond stretch and bond angle deformation are also considered by the Harmonic potential model.

The L-J potential model with a polar term is shown as follows:

$$\phi(r_{ij}) = \begin{cases} 4\varepsilon\left[\left(\dfrac{\sigma}{r_{ij}}\right)^{12} - \left(\dfrac{\sigma}{r_{ij}}\right)^{6}\right] + \dfrac{Cq_iq_j}{\chi r_{ij}} & (r_{ij} < r_{cut}) \\ 0 & (r_{ij} \geq r_{cut}) \end{cases} \tag{1}$$

where ε is energy parameter, σ is length parameter, q_i and q_j are charges on atom i and j, C is electrostatic constant, χ is dielectric constant. The parameters in AIREBO potential model can be found in the work by Stuart et al. [2], and the L-J potential parameters for the other atomic pairs and the atomic charges are listed in **Table S1**.

Table S1 L-J potential parameters of molecules and atomic charges.

	ε /eV	σ /Å	charge /e
	CO_2 [3]		
C-C	2.424×10^{-3}	2.757	0.6512
C-O	4.101×10^{-3}	2.895	/
O-O	6.938×10^{-3}	3.033	-0.3256
	H_2S [4]		
H-H	0.336×10^{-3}	0.98	0.124
H-S	2.691×10^{-3}	2.35	/
S-S	21.545×10^{-3}	3.72	-0.248

The parameters in L-J potential models for the crossing atoms are obtained by the Lorentz-Berthelot mixing rule. To obtain these crossing parameters, the benchmark parameters for C-C and H-H are needed, as follows: C-C: $\sigma = 3.40$ Å, $\varepsilon = 2.413\times10^{-3}$ eV; [5] H-H: $\sigma = 2.50$ Å, $\varepsilon = 1.300\times10^{-3}$ eV. [6]

For the bond stretch and bond angle deformation in a single molecule, the Harmonic model is applied. The Harmonic model for bond stretch energy E_r is:

$$E_r = K_r(r - r_0)^2 \qquad (2)$$

where r_0 is equilibrium bond length, K_r is bond parameter. The Harmonic model for bond angle deformation energy E_θ is:

$$E_\theta = K_\theta(\theta - \theta_0)^2 \qquad (3)$$

where θ_0 is equilibrium bond angle, K_θ is angle deformation parameter. The bond information for H_2 molecules is considered in AIREBO potential model; for the other molecules, they are modeled by Harmonic model and the parameters are listed in **Table S2**.

Table S2 Bond and angle Harmonic potential parameters of molecules.

	E_r	
	K_r /eV·Å^{-2}	r_0 /Å
C-O (CO_2) [7]	6.158	1.160
H-S (H_2S) [7]	2.021	1.365
	E_θ	
	K_θ /eV·rad^{-2}	θ_0 /°
O-C-O (CO_2) [8]	6.416	180
H-S-H (H_2S) [9]	1.110	91.5

3. Calculation of permeance

The molecular permeance is calculated basically based on the relationship between the number of permeated molecules N and time t. Based on our early work [10], a theoretical correlation $N = f(t)$ is derived as follows:

$$N = (250 - N_{al}/2) \times (1 - e^{-8.24 \times 10^{10} Pt})$$ (4)

where N_{al} is average number of molecules adsorbed on both sides of graphene, P is molecular permeance, and the constant 250 is related to the molecular number 500 in the simulation box. Employing this correlation, the curves of molecular number N versus time t shown in **Figure S3** are fitted. Then, the molecular permeance P is easily obtained, as displayed in **Figure S4**.
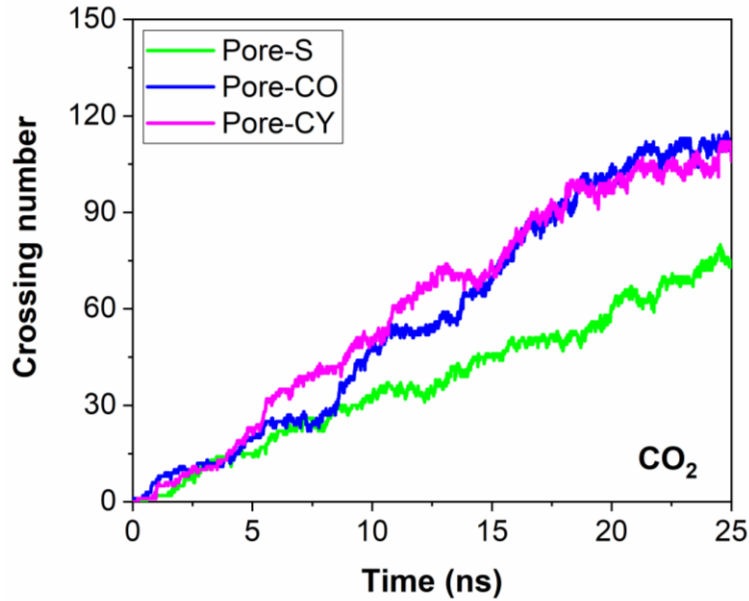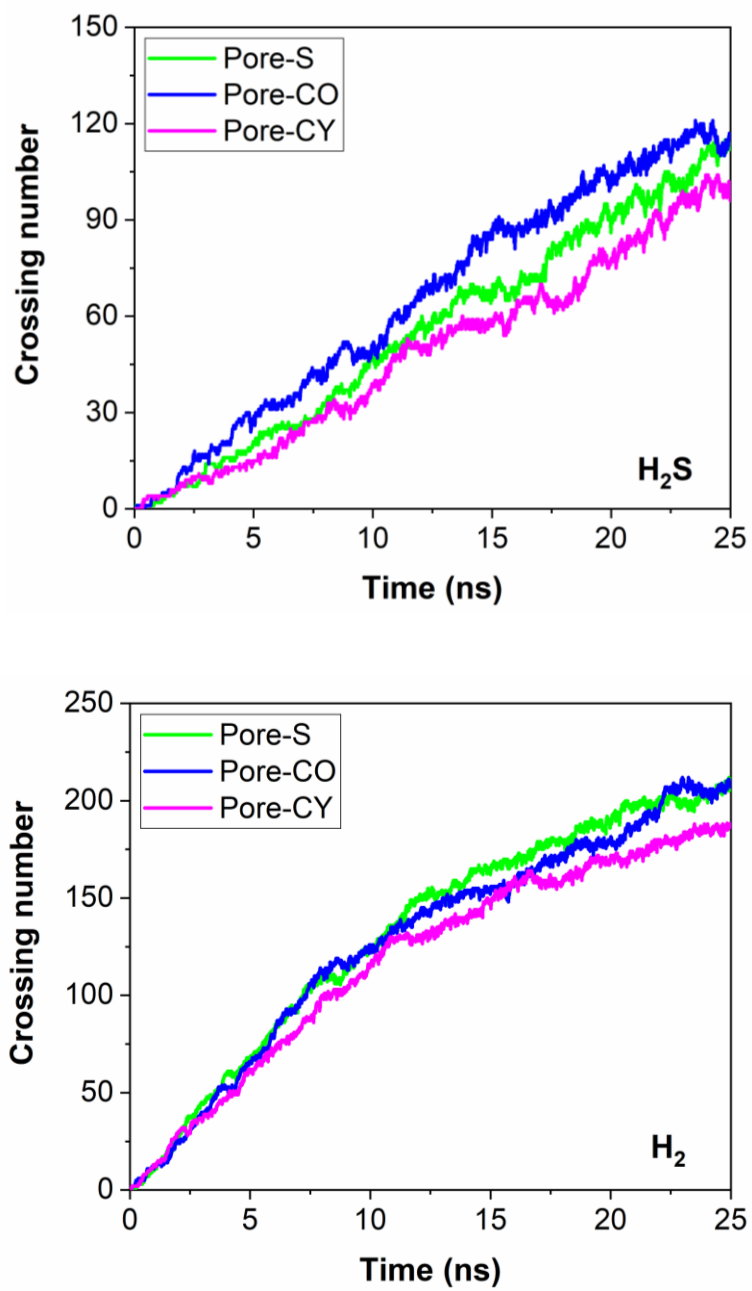
Figure S3 Time-varying number of permeated molecules for the three different molecules.
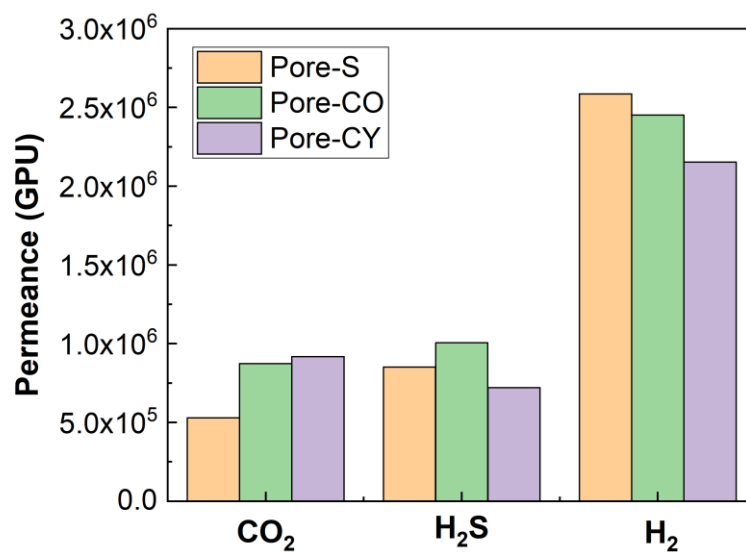
Figure S4 Calculated molecular permeance for the three pores.

4. Molecular trajectory in nanopores

Molecular trajectories in the nanopores during the permeation process through the three pores are shown in **Figure S5**. The CO_2, H_2S and H_2 molecules are shown separately. It is noted that the time interval is 0.5 ps for CO_2 and H_2S while 0.1 ps for H_2.
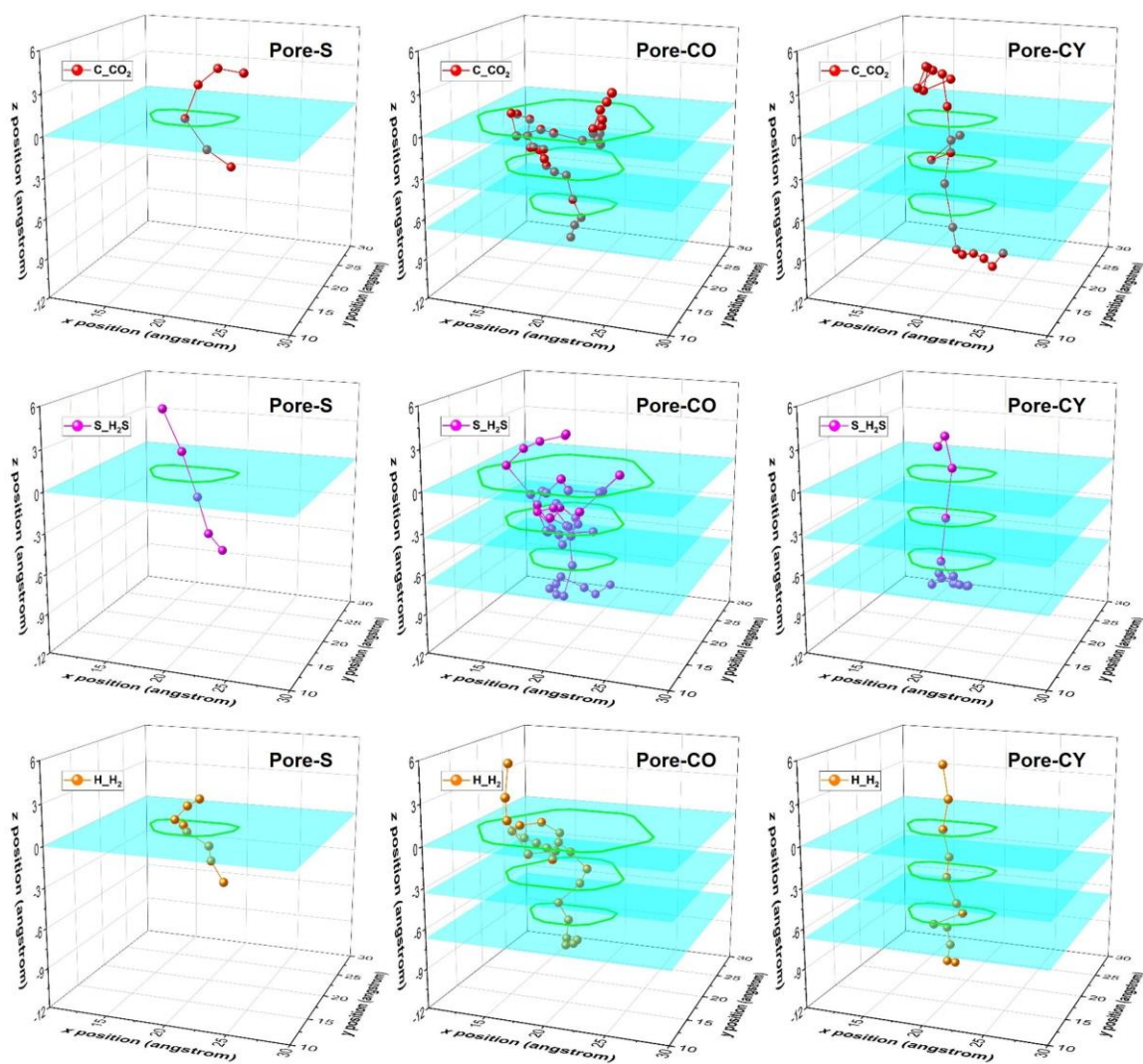
Figure S5 Molecular trajectories in the three pores for different gas molecules.

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