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Supplementary Information for

High-efficiency helium separation through inorganic graphenylene membrane: A theoretical study

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Supplementary Figures

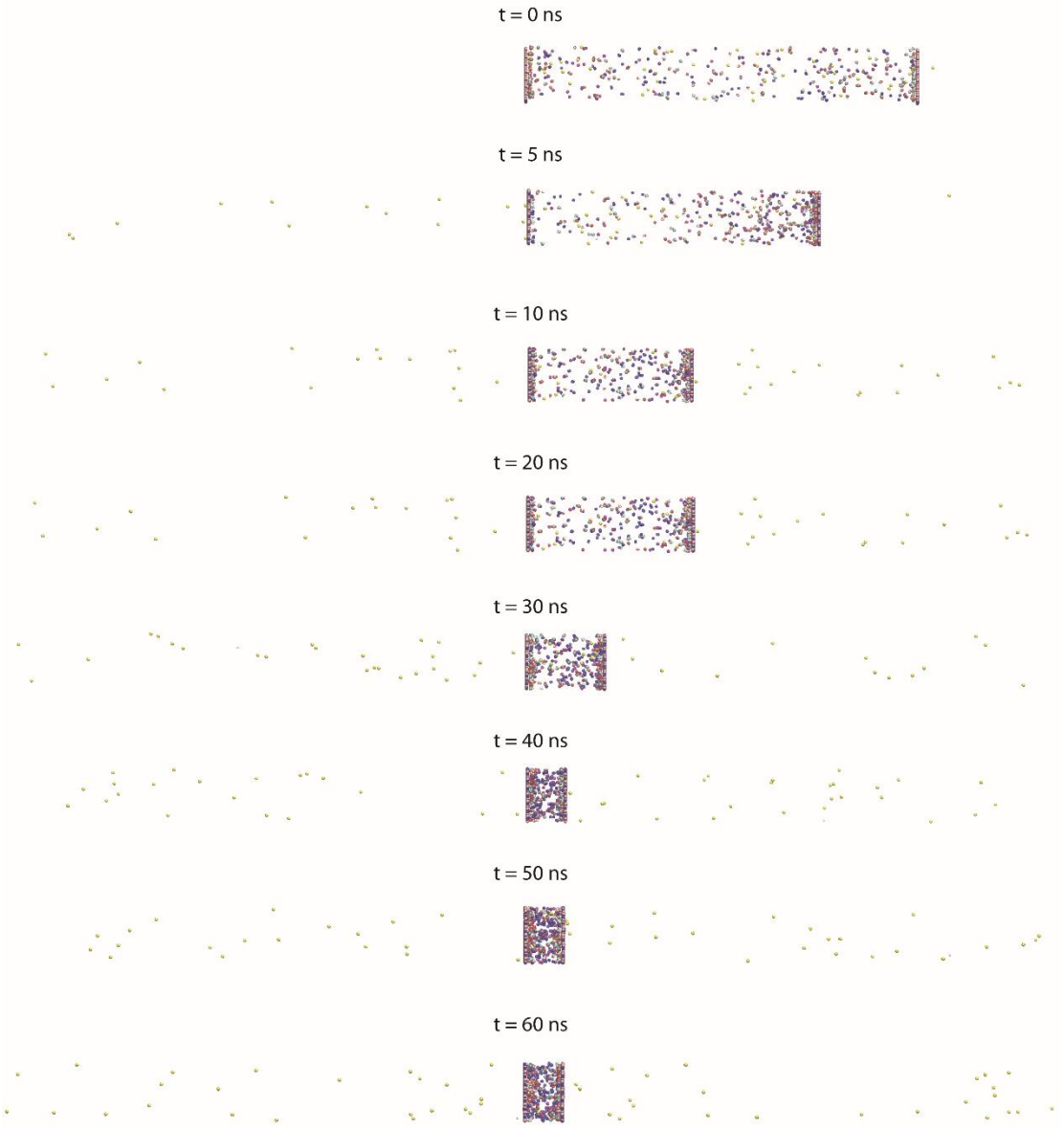


Figure S1 Trajectory snapshots of one representative simulation system under a constant pulling force of 140 kJ /mol /nm, corresponding to a pressure of 100 Bar.

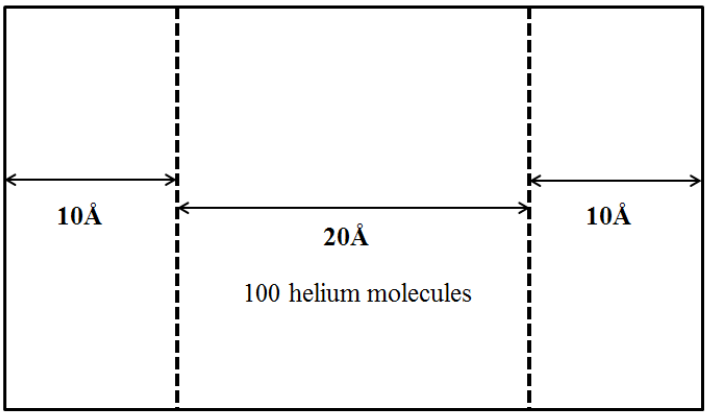


Figure S2 Molecular dynamics model for calculating permeance. Dashed line represents the positions of the IGP membranes.

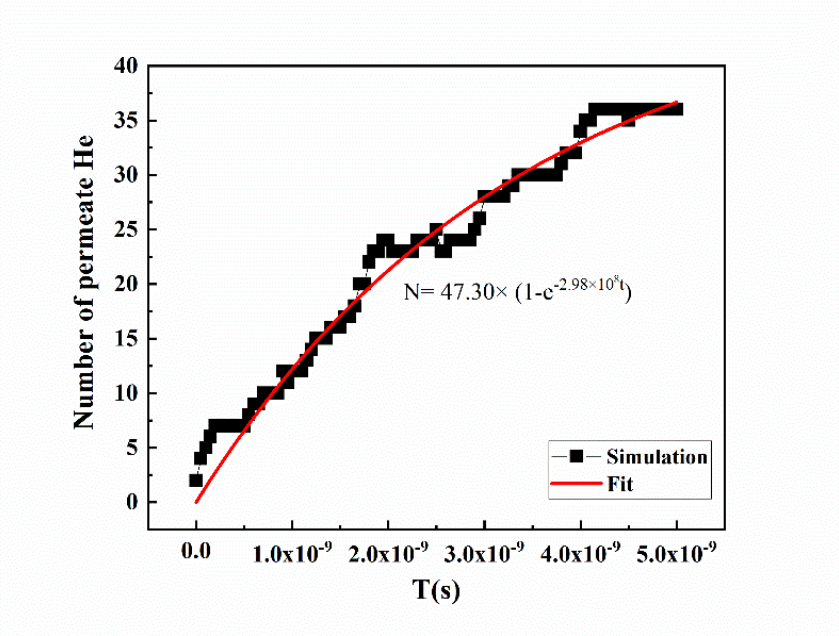


Figure S3 Number of permeated He molecules versus simulation time.

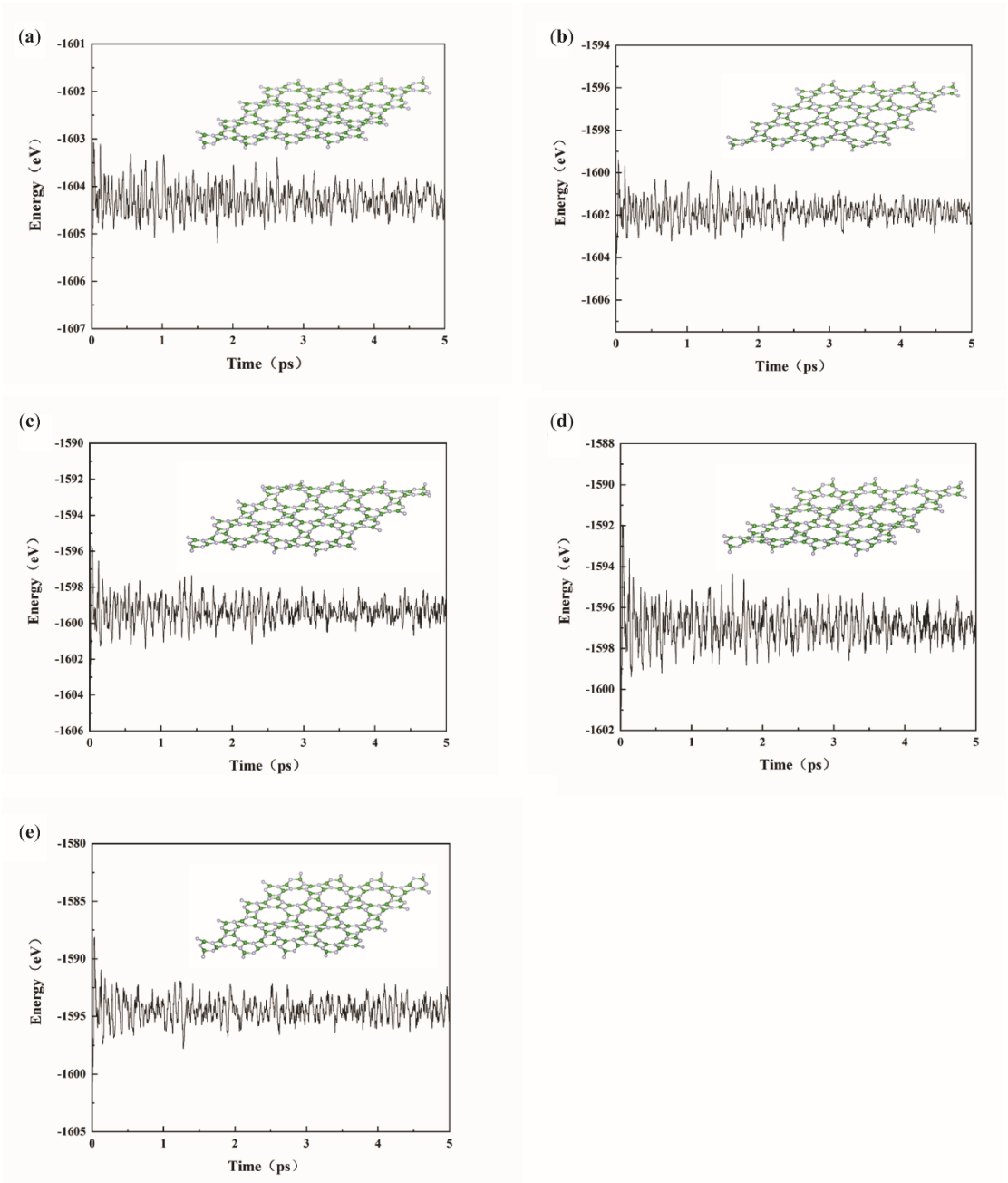


Figure S4. Thermal stability of IGP membrane by ab-initio quantum-mechanical molecular dynamics simulations. The energy fluctuation and the final structures of the 4X4 supercell of the IGP membrane at 100 K (a), 200 K (b), 300 K (c), 400 K (d), 500 K (e) are obtained for the 5 ps quantum-mechanical molecular dynamics simulations.

Supplementary Tables

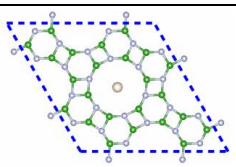
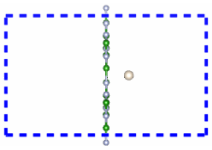
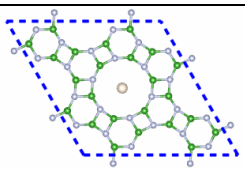
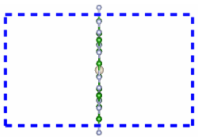
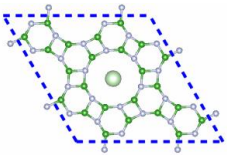
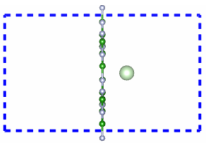
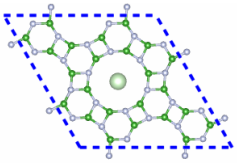
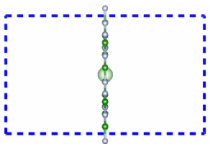
Table S1. Force field parameters (van der Waals terms and partial charges) for CO_2 and N_2.

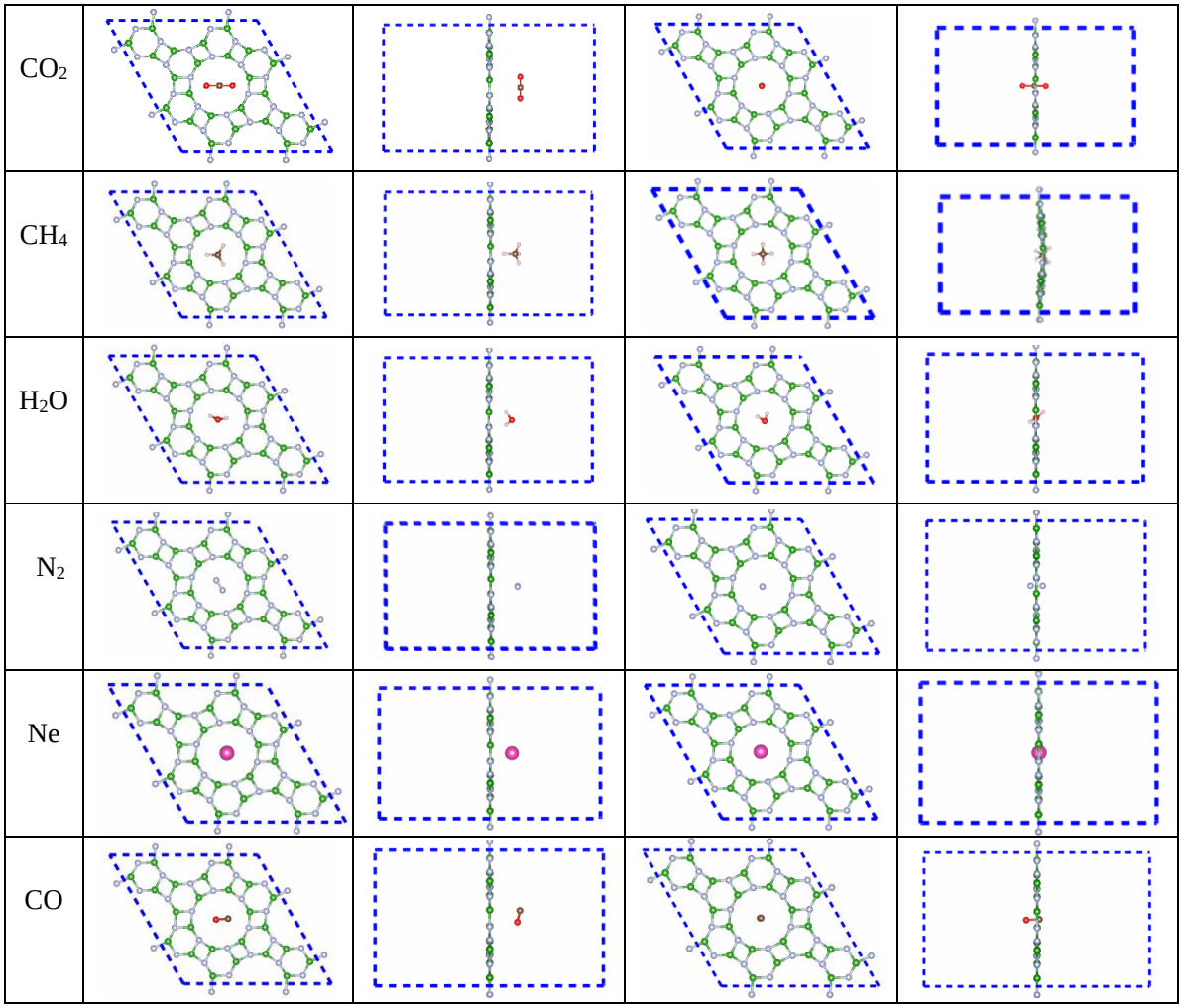
CO_2			
	ε (K)	σ(Å)	Q(e)
C	28.13	2.757	0.6512
O	80.51	3.033	-0.3256
bonds	length(Å)		
C-O	1.149		
N_2			
	ε (K)	σ(Å)	Q(e)
N	36.4	3.318	-0.4048
Center-Of-Mass	0	0	0.8096
bonds	length(Å)		
N-N	1.098		

Table S2. Atomic charges for the IGP membrane and gas molecules.

IGP membrane		CO		H_2O		CH_4	
	Q(e)		Q(e)		Q(e)		Q(e)
B	0.6512	C	0.0344	H	0.41	C	-0.3520
N	-0.3256	O	-0.0344	O	-0.82	H	0.0880

Table S3 Adsorption states and transition states for the gases passing through the IGP membrane.

	Adsorption State		Transition State	
	Top view	Side view	Top view	Side view
He				
Ar				



Supplementary Methods

Method for calculating permeance

In the simulation system, 100 helium molecules were placed randomly in the center of the simulation box sandwiched by two layers of IGP membranes, whose z-coordinates are frozen. The simulation box has a dimension of 4.781nm × 4.732nm × 40nm. The calculation model is shown in **Fig S2.** First, the permeability of helium through the membrane material was tested at 300K. The relationship between flux J (mol s^{-1}) and permeance S (mol s^{-1} m^{-2} Pa^{-1}) are defined by the following formula:[1-3]

$$J = \frac{1}{N_A}\frac{dN}{dt} = A_g \cdot \Delta P \cdot S \quad (1)$$

where A_g is the membrane area of IGP used in our MD simulations (A_g = 4.52×10^{-17}

m^2), ΔP is the pressure drop across the membrane, N is the number of permeated He molecules, t is the MD simulation time, and N_A is the Avogadro constant. ΔP is dependent on the molecular numbers N. The initial pressure is estimated to be 9.16×10^5 Pa based on ideal gas law. Therefore,

$$\Delta P = \frac{100-N_{ad}-2N}{100} \times 9.16 \times 10^5\ Pa \quad (2)$$

where N_{ad} stands for the average number of He molecules adsorbed on the IGP membrane. After integrating Eq. (1), we obtained

$$N = \frac{100-N_{ad}}{2} \times (1 - e^{-4.98\times10^{11}St}) \quad (3)$$

in which $B = 4.98\times10^{11}\ S$ is the exponent of time decay. Then, Eq. (3) is applied to fit the time-dependent number profiles of permeated He molecules (**Fig S3**). The fitted parameter $B = -4.98\times10^{11}\ S$ is calculated to be -2.98×10^8, and thus the He permeance (S) is found to be 6.0×10^{-4} mol s^{-1} m^{-2} Pa^{-1}. Likewise, we calculate the He permeance of IGP membrane at different temperatures.

Calculation details for adsorption energy

The pristine IGP membrane and gas molecules were optimized separately to obtain the energy of the pristine IGP membrane (E_{IGP}) and the energy of an isolated gas molecule (E_{gas}). Then, we placed one optimized gas molecule 3Å above the hole of the optimized IGP membrane. The whole system was then optimized again to obtain the total energies of the IGP membrane with an adsorbed gas molecule at the most stable adsorption state ($E_{IGP+gas}$) and the equilibrium heights (H_0). Finally, the formula $E_{ad} = E_{IGP+gas} - E_{IGP} - E_{gas}$ is used to calculate the adsorption energy E_{ad}.

Computational details for the quantum-mechanical molecular dynamics simulations

The quantum-mechanical molecular dynamics simulations were performed for the 4×4×1 supercell of the IGP membrane with Nose-Hoover thermostat at 100 K, 200 K, 300 K, 400 K and 500 K, respectively. K-point meshes of 1×1×1 were used in sampling the Brillouin zone. A total of 5 ps simulation was carried out for each temperature with a time step of 1.0 fs.

Reference

1. C. Sun, M. S. Boutilier, H. Au, P. Poesio, B. Bai, R. Karnik and N. G. Hadjiconstantinou, *Langmuir*, 2014, **30**, 675-682.
2. L. Zhu, Y. Jin, Q. Xue, X. Li, H. Zheng, T. Wu and C. Ling, *Journal of Materials Chemistry A*, 2016, **4**, 15015-15021.
3. B. Wen, C. Sun and B. Bai, *Phys Chem Chem Phys*, 2015, **17**, 23619-23626.