Electronic Supplementary Information

Entropic selectivity in air separation via a bilayer nanoporous graphene membrane

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1. Definition of the effective pore size (d)

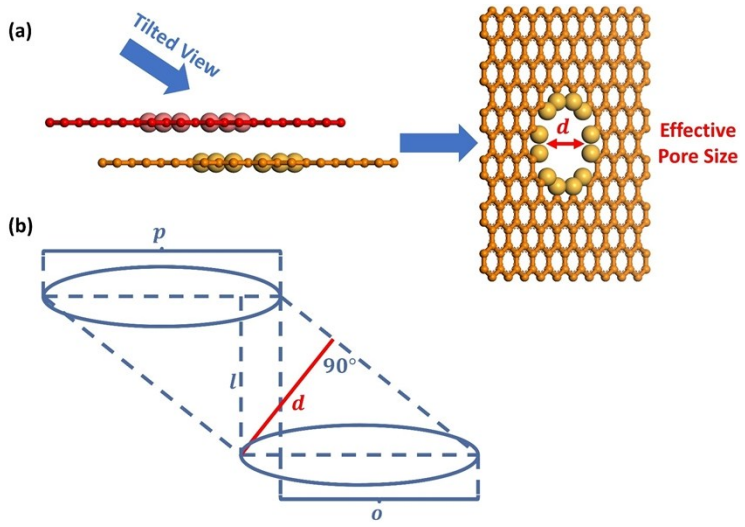

Fig. S1. (a) Side view and tilted view of bilayer nanoporous graphene membrane; (b) Schematic of cross section of pore (5.7 Å).

$$d = \frac{l}{\sqrt{l^2 + o^2}} \times p$$

l: the interlayer distance;

o: is the offset

p: single-layer pore size.

Table S1. Five numbers of offset used in this work and corresponding effective pore sizes.

p = **5.7 Å**, l = **3.4 Å**					
o/**Å**	4.16	4.26	4.36	4.46	4.56
d/**Å**	3.60	3.55	3.50	3.45	3.40

2. Comparison of flexible and frozen membranes for gas permeation.

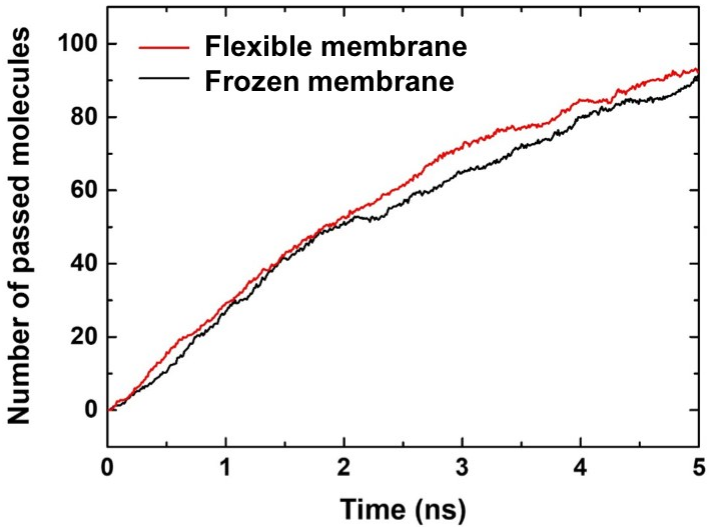

Fig. S2. Numbers of O_2 molecules passed through frozen (black) and flexible (red) bilayer nanoporous graphene membranes with the effective pore size of 3.60 Å. For the flexible membrane, all atoms of the membrane were allowed to move on the *xy* plane while the z coordinates as well as the center of mass of the bilayer membrane were constrained at their initial positions.

3. Calculation of vibrational amplitudes of O_2 and N_2 at 300 K

Following a previous study (E. J. Baran, *Zeitschrift für Naturforschung A*, 2003, **58**, 36-38), we have calculated the mean amplitudes of vibration of O_2 and N_2 by the following equations:

$$u_{XY}^2 = G_{XY} \cdot \nabla_1 \quad (1)$$

$$G_{XY} = \mu_X + \mu_Y \quad (2)$$

$$\nabla_1 = \left[h/8\pi^2 \nu_1\right] coth(h\nu_1/2kT) \quad (3)$$

where μ_X and μ_Y are the reduced masses of the atoms X and Y, in the current case being X=Y (O or N atom), and ν_1 is the characteristic vibrational frequency (ν_1) of the bond (1568 cm^{-1} for O_2 and 2446 cm^{-1} for N_2). Thus, at 300 K, the calculated mean amplitudes of vibration (∇_1) are 0.0367 Å for O_2 and 0.0314 Å for N_2.

4. Calculation of entropic selectivity

According to transition state theory of diffusion,[1, 2] the O_2/N_2 entropic diffusion selectivity can be written as:

$$\left(\frac{D_{O_2}}{D_{N_2}}\right)_{entropic} = \exp\left(\frac{S_{D,O_2} - S_{D,N_2}}{R}\right) = \frac{(F^{\neq}/F)_{O_2}}{(F^{\neq}/F)_{N_2}}$$

where D is diffusion, S is entropy, F is partition function for normal state, and $F^{\neq}$ is partition function for transition state. The partition function includes translational, rotational, and vibrational contributions, as shown below:

$$F = F_{trans} \cdot F_{rot} \cdot F_{vib},\ F_{trans} = \left(\frac{2\pi mkT}{h^2}\right)^{n/2} a^n,\ F_{rot} = \left(\frac{T}{\sigma\theta_r}\right)^{n/2},\ F_{vib} = \left[\frac{\exp\left(-\frac{\theta_v}{2T}\right)}{1 - \exp\left(-\frac{\theta_v}{T}\right)}\right]^n$$

where n is degree of freedom, m is mass of molecule, k is Boltzmann constant, h is Planck constant, a is cavity length (which is the difference between gas molecular width and the elliptical pore size[2]), σ is symmetry number of gas molecule, θ_r is characteristic rotational temperature, θ_v is characteristic vibrational temperature. In the transition state, all two rotational degrees of freedom of N_2 is suppressed, while O_2 still keeps one unconstrained rotational degrees of freedom. And in the transition state, both of N_2 and O_2 are believed to only have two translational degrees of freedom, since the factor $\frac{kT}{h}$ accounts for the translational degree of freedom in the direction of gas diffusion. The vibrational degrees of freedom of N_2 and O_2 are unrestricted in both normal and

transitional state.[1] Thus, the vibrational partition functions are cancelled out. Table S2 shows the parameters used in calculations. According to these functions and parameters, the O_2/N_2 entropy difference is 5.67 cal/K and entropic diffusion selectivity is 17.3 at 300 K.

Table S2. Parameters used in entropic selectivity calculation when effective pore size of 3.45 Å[1, 2]

	O_2	N_2
a for normal state / Å	100	100
a for transition state / Å	0.77 for short axis 2.85 for long axis	0.36 for short axis 2.01 for long axis
σ	2	2
θ_r	2.07	2.88

5. Force field parameters

5.1. Gas molecules

Table S3. Force field parameters for gas molecules[3]

O_2			
	ε (kcal/mol)	σ (Å)	q (e)
O	0.108	3.050	-0.1120
COM	0	0	0.2240
bonds	length (Å)		
O-O	1.21		
N_2			
	ε (K)	σ (Å)	q (e)
N	0.0728	3.318	-0.4048
COM	0	0	0.8096
bonds	length (Å)		
N-N	1.098		

5.2. Porous graphene

Table S4. Lennard-Jones parameters for the bilayer porous graphene membrane[4]

	ε (kcal/mol)	σ (Å)
C	0.086	3.400
H	0.015	2.450

Cartesian coordinates (Å) and partial atomic charges on the single-layer porous graphene

Rectangular unit cell: a=24.6076 Å, b=25.7308 Å

	q / e	x	y
C	-0.008	5.660565	7.186368
C	0.017	6.891031	7.901653
C	-0.021	8.121366	7.186365
C	0.084	9.351711	7.901561
C	0.091	10.582106	7.186303
C	-0.333	11.812498	7.901617
C	0.201	13.042896	7.186299
C	-0.333	14.273285	7.901627
C	0.090	15.503616	7.186307
C	0.085	16.733982	7.901628
C	-0.021	17.964414	7.186293
C	0.017	19.194780	7.901614
C	-0.008	20.425110	7.186295
C	0.005	21.655501	7.901623
C	0.000	22.885898	7.186305
C	0.000	24.116291	7.901618
C	0.000	0.739085	7.186360
C	0.000	1.969431	7.901556
C	0.001	3.199765	7.186269
C	0.004	4.430231	7.901553
C	-0.022	5.660566	11.474811
C	0.015	5.660565	10.045806
C	0.088	6.891030	12.190132
C	-0.332	8.121367	11.474808
C	-0.024	6.891032	9.330482
C	0.199	8.121364	10.045809
C	-0.331	9.351714	9.330574
C	-0.332	17.964414	11.474736

C	-0.331	16.733989	9.330507
C	0.200	17.964408	10.045881
C	0.088	19.194781	12.190093
C	-0.022	20.425110	11.474739
C	-0.025	19.194787	9.330521
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C	-0.008	4.430231	9.330582
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C	-0.022	5.660565	14.334252
C	-0.024	6.891031	16.478598
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C	0.088	6.891032	13.618961
C	-0.332	8.121364	14.334255
C	-0.331	9.351711	16.478504
C	-0.331	16.733982	16.478571
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