Supplementary Information

Inhibition of Non-permeating Component on Gas Permeability of Nanoporous Graphene Membrane

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1 Interaction potential

1.1 Lennard-Jones potential

The interactions for C and H atoms were modeled by the AREABO potential, of which the parameters can be found in the Ref. 1. For the N\(_2\) and its related interactions, the standard 12-6 Lennard-Jones (L-J) potential model was adopted, as follows:

\[
E = 4\varepsilon \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6}, \quad r < r_c
\]

where \(r_c\) is the cutoff radius, \(\varepsilon\) is the depth of the potential well, \(\sigma\) is the finite distance at which the inter-particle potential is zero. Potential parameters between crossing atoms were obtained using the Lorentz-Berthelot mixing rule. The L-J potential parameters related to the nitrogen atom are listed in Table S1.

Table S1 Lennard-Jones potential parameters.\(^2,3\)

<table>
<thead>
<tr>
<th></th>
<th>(\varepsilon) (eV)</th>
<th>(\sigma) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-N</td>
<td>(3.126 \times 10^{-3})</td>
<td>3.297</td>
</tr>
<tr>
<td>N-H</td>
<td>(2.156 \times 10^{-3})</td>
<td>2.974</td>
</tr>
<tr>
<td>C-N</td>
<td>(2.746 \times 10^{-3})</td>
<td>3.349</td>
</tr>
</tbody>
</table>

1.2 Harmonic bond potential

The internal bond interaction of the N\(_2\) molecules was modeled by the harmonic bond potential,

\[
E = K(r - r_0)^2
\]

where \(K\) is the bond coefficient and \(r_0\) is the equilibrium bond distance. For molecular nitrogen, \(r_0 = 1.112\) Å and \(K = 1.426\) eV·Å\(^{-2}\).\(^4\)

2 Calculation of Permeance
By analyzing the molecular motions, we can obtain the number of permeated molecules versus time in all cases, as shown in Fig. S1-S2. As seen from the figures, the H$_2$ and N$_2$ molecules permeate rapidly through the nanopore while the CH$_4$ molecules hardly pass through it.

Fig. S1. Number of permeated CH$_4$ and H$_2$ molecules versus time in Case 1-4.
According to the Eq. (3) of the time-dependent of permeated molecular number \(N\), we can fit the curves of Fig. S1-S2 and obtain the permeances. For example, Fig. S3 shows the variation of \(N\) of the \(N_2\) molecules versus time and the fitting curve by Eq. (3) in Case 5. Based on the fitted parameter \(B\), we can obtain the permeances of molecules in all cases. Table S2 lists the values of permeances and their fitting standard errors.

![Fig. S3. Fitting curve of the permeated number of the \(N_2\) molecules versus time in Case 5.](image)

**Table S2.** Permeances and fitting standard errors of the \(H_2\), \(N_2\) and \(CH_4\) molecules in all cases.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Case</th>
<th>Permeance (mol·s⁻¹·m⁻²·Pa⁻¹)</th>
<th>Standard error (mol·s⁻¹·m⁻²·Pa⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_2)</td>
<td>Case 1</td>
<td>(2.09\times10^{-3})</td>
<td>±(1.496\times10^{-5})</td>
</tr>
<tr>
<td>(H_2)</td>
<td>Case 2</td>
<td>(1.50\times10^{-3})</td>
<td>±(1.898\times10^{-5})</td>
</tr>
<tr>
<td>(H_2)</td>
<td>Case 3</td>
<td>(1.83\times10^{-3})</td>
<td>±(1.900\times10^{-5})</td>
</tr>
<tr>
<td>(H_2)</td>
<td>Case 4</td>
<td>(1.71\times10^{-3})</td>
<td>±(1.897\times10^{-5})</td>
</tr>
<tr>
<td>(N_2)</td>
<td>Case 5</td>
<td>(2.08\times10^{-4})</td>
<td>±(4.420\times10^{-7})</td>
</tr>
<tr>
<td>(N_2)</td>
<td>Case 6</td>
<td>(1.04\times10^{-4})</td>
<td>±(2.217\times10^{-7})</td>
</tr>
<tr>
<td>(N_2)</td>
<td>Case 7</td>
<td>(7.39\times10^{-5})</td>
<td>±(2.364\times10^{-7})</td>
</tr>
<tr>
<td>(N_2)</td>
<td>Case 8</td>
<td>(1.37\times10^{-4})</td>
<td>±(2.365\times10^{-7})</td>
</tr>
<tr>
<td>(CH_4)</td>
<td>Case 2</td>
<td>(4.85\times10^{-6})</td>
<td>±(2.287\times10^{-8})</td>
</tr>
<tr>
<td>(CH_4)</td>
<td>Case 3</td>
<td>(5.67\times10^{-6})</td>
<td>±(2.754\times10^{-8})</td>
</tr>
<tr>
<td>CH₄</td>
<td>Case 4</td>
<td>5.35×10⁻⁶</td>
<td>±3.121×10⁻⁸</td>
</tr>
<tr>
<td>------</td>
<td>--------</td>
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<td>-------------</td>
</tr>
<tr>
<td>CH₄</td>
<td>Case 6</td>
<td>6.25×10⁻⁶</td>
<td>±2.329×10⁻⁸</td>
</tr>
<tr>
<td>CH₄</td>
<td>Case 7</td>
<td>5.78×10⁻⁶</td>
<td>±2.802×10⁻⁸</td>
</tr>
<tr>
<td>CH₄</td>
<td>Case 8</td>
<td>5.23×10⁻⁶</td>
<td>±2.311×10⁻⁸</td>
</tr>
</tbody>
</table>

### 3 Selectivity

#### 3.1 Simulated selectivity

The selectivity of this nanopore for two kinds of gas molecules can be obtained by

\[
F_{A/B} = \frac{S_A}{S_B}
\]

In our simulations, only one or two CH₄ molecules can permeate through the nanopore, no crossing events even occur in Case 2. In order to calculate the selectivity, the permeated number of the CH₄ molecules is assumed to be 1 in Case 2. The selectivities of all cases are shown in Fig. S4.

![Selectivity Graph](image)

Fig. S4. Selectivities of H₂ over CH₄ and N₂ over CH₄ in Case 2-4 and Case 6-8.

#### 3.2 Estimation of selectivity using interaction energy

The selectivity \((F)\) of the NPG membranes can be estimated from interaction energy by using the Arrhenius equation for diffusion.

\[
F_{H₂/CH₄} = \frac{D_{H₂}}{D_{CH₄}} = \frac{A_{H₂} e^{-E_{H₂}/RT}}{A_{CH₄} e^{-E_{CH₄}/RT}}
\]

(S3)
\begin{equation}
F_{N_2/CH_4} = \frac{D_{N_2}}{D_{CH_4}} = \frac{A_{N_2}}{A_{CH_4}} \frac{e^{-E_{N_2}/RT}}{e^{-E_{CH_4}/RT}}
\end{equation}

where $F$ is the selectivity, $D$ is the diffusion rate, $A$ is the prefactor and $E$ is the diffusion barrier. Diffusion barrier is the difference between the highest and the lowest value of the interaction energy profile, as shown in Figure 8. In this paper, the room temperature $T = 300$ K and we assumed that the prefactors of the two kinds of gases are in the same magnitude. Thus, $A_{H_2} / A_{CH_4} \approx 1$ and $A_{N_2} / A_{CH_4} \approx 1$ according to the work by Jiang et al.\textsuperscript{5}

3.3 Comparison of the relative barrier heights

In our calculations of the interaction energy using the density functional theory, the geometry of the nanopore was fully frozen. To be more confident on the calculation, we compare the diffusion barriers in our study and those for the Pore A and Pore B in the study by Hauser and Schwerdtfeger,\textsuperscript{6} as shown in Fig. S5. It can be seen that the diffusion barriers of the CH$_4$, N$_2$ and H$_2$ molecules in our study are generally lower than those for Pore A while higher than those for Pore B.

![Fig. S5. The comparison between our results and those of the previous study.\textsuperscript{6}](image)

The size of the nanopore we used is larger than that of the pore A, which makes it easier for gas molecules to permeate. Thus, the relative barrier heights in our study are
lower than that of the pore A. Moreover, pore modifications have a significant influence on the gas permeability and selectivity. For the pore B modified by N atoms and H atoms, the stronger attractive van der Waals interactions between N atoms and molecules make the gas molecules permeate easier. Therefore, the relative barrier heights of pore B are lower than those in our study. This comparison demonstrates that our calculation of the diffusion barriers is reliable.

References