# Electronic Supplementary Material

## Mechanism of ethanol/water separation through functional graphene membrane: a molecular simulation investigation

Quan Liu[1,2], Xian Wang[1], Yanan Guo[2,*], Gongping Liu[2,*], Kai-Ge Zhou[3]

[1] School of Chemical Engineering, Analytical and Testing Center, Anhui University of Science and Technology, Huainan 232001, China

[2] State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, 30 Puzhu Road (S), Nanjing 211816, China

[3] Haihe Laboratory of Sustainable Chemical Transformations, Tianjin 300192, China

*Corresponding authors: guoyn@njtech.edu.cn (Dr. Y. Guo); gpliu@njtech.edu.cn (Prof. G. Liu)

### 1. The criterion for the diameter definition of nanopores

Fig. S1 shows the criterion for the diameter definition of nanopores. Taking the PG_D3.6Å as an example, the pore size is defined as the diameter of an inserted sphere that is inserted in the pores without contact with membrane atoms [1, 2].

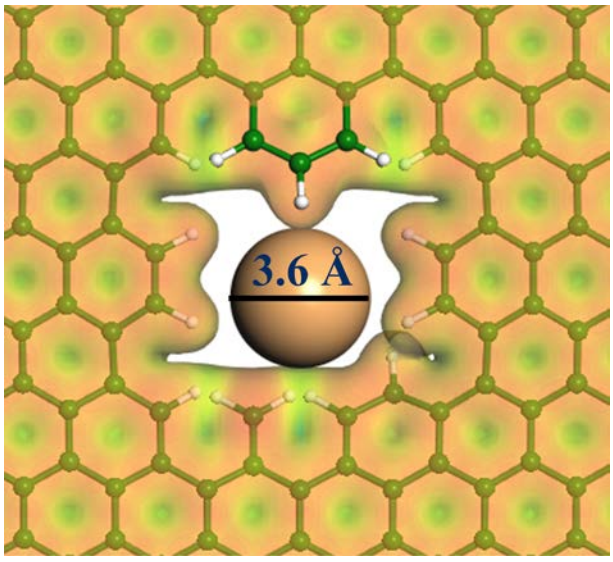


**Fig. S1.** The criterion for the diameter definition of the nanopore in PG_D3.6Å.

### 2. Comparison of pervaporation performance

The reversed separation performance of our designed membrane is compared with both polymeric and inorganic membranes. In Table S1, all fluxes are normalized by the transmembrane pressure as per previous studies [2,3]. The designed PG_D3.8Å shows promising performance for ethanol/water separation with ethanol permeance and its separation factor up to $11.5\times10^3$ GPU (i.e., 69.3 $kg\cdot m^{-2}\cdot h^{-1}\cdot bar^{-1}$) and 34, which is comparable to previous experiments.

**Table S1** Performance comparison. $S_{e/w}$ is the separation factor of ethanol over water, and $F_e$ and $P_e$ are ethanol contents in the feed and permeate sides, respectively.

| **Membrane** | **Temp. ( °C)** | **$F_e$ (wt%)** | **Total flux ($kg\cdot m^{-2}\cdot h^{-1}$)** | **$S_{e/w}$** | **$P_e$ (wt%)** | **Ethanol permeance (GPU)** | **Ref.** |
|---|---|---|---|---|---|---|---|
| PDVB/PDMS | 60 | 6 | 1.423 | 10.0 | 39.0 | 1885.8 | [4] |
| BTESO/silicalite-1 | 60 | 5 | 6.84 | 24.6 | 56.4 | 15442.9 | [5] |
| W-MFI zeolite | 60 | 5 | 2.81 | 32.0 | 62.7 | 7055.2 | [6] |
| ZIF-91/PDMS-20 | 55 | 5 | 0.846 | 15.8 | 45.4 | 1950.5 | [7] |
| AZIF-8@PDMS | 40 | 5 | 0.5856 | 17.7 | 48.2 | 3093.1 | [8] |
| PDMS/ZIF-8@GO | 40 | 5 | 0.4438 | 22.2 | 53.9 | 2619.0 | [9] |
| ZIF-8@PDMS | 40 | 5 | 1.778 | 12.1 | 38.9 | 7576.1 | [10] |
| ODPA-ZIF-8(4)@ZIF-8/PDMS | 30 | 5 | 0.64 | 17.4 | 47.8 | 5877.4 | [11] |
| silicalite-1 | 50 | 10 | 4.47 | 66.0 | 88.0 | 14021.6 | [12] |
| PTMSP | 40 | 10 | 0.19 | 8.3 | 48.0 | 545.1 | [13] |
| PDMS/PVDF | 30 | 10 | 0.085 | 6.0 | 40.0 | 355.1 | [14] |
| PG_D3.8Å | 27 | 10 | 87.6 | 34.0 | 79.0 | 11542.8 | **This work** |

## References


1. Liu J, Kong X, Jiang J. Solvent nanofiltration through polybenzimidazole membranes: Unravelling the role of pore size from molecular simulations. Journal of Membrane Science, 2018, 564: 782-787
2. Liu Q, Zhu H, Liu G, Jin W. Efficient separation of ($C_1$–$C_2$) alcohol solutions by graphyne membranes: A molecular simulation study. Journal of Membrane Science, 2022, 644: 120139
3. Liang F, Zheng J, He M, Mao Y, Liu G, Zhao J, Jin W. Exclusive and fast water channels in

zwitterionic graphene oxide membrane for efficient water–ethanol separation. AIChE Journal, 2021, 67(7): e17215

4. He X, Wang T, Huang J, Chen J, Li J. Fabrication and characterization of superhydrophobic PDMS composite membranes for efficient ethanol recovery via pervaporation. Separation and Purification Technology, 2020, 241: 116675
5. Ren X, Yu H, Guo M, Xu R, Zhong J. Long alkyl chain-containing organosilica/silicalite-1 composite membranes for alcohol recovery. Microporous and Mesoporous Materials, 2022, 338: 111947
6. Peng L, Wu Z, Wang B, Liu H, Zhang C, Gu X. Fabrication of high-stability W-MFI zeolite membranes for ethanol/water mixture separation. Journal of Membrane Science, 2022, 659: 120729
7. Pan Y, Yu X. Preparation of zeolitic imidazolate framework-91 and its modeling for pervaporation separation of water/ethanol mixtures. Separation and Purification Technology, 2020, 237: 116330
8. Zhu T, Yu X, Yi M, Wang Y. Facile covalent crosslinking of zeolitic imidazolate framework/polydimethylsiloxane mixed matrix membrane for enhanced ethanol/water separation performance. ACS Sustainable Chemistry & Engineering, 2020, 8(33): 12664-12676
9. Zhu T, Xu S, Yu F, Yu X, Wang Y. ZIF-8@GO composites incorporated polydimethylsiloxane membrane with prominent separation performance for ethanol recovery. Journal of Membrane Science, 2020, 598: 117681
10. Mao H, Zhen H G, Ahmad A, Zhang A S, Zhao Z P. In situ fabrication of MOF nanoparticles in PDMS membrane via interfacial synthesis for enhanced ethanol permselective pervaporation. Journal of Membrane Science, 2019, 573: 344-358
11. Pan Y, Zhu T, Xia Q, Yu X, Wang Y. Constructing superhydrophobic ZIF-8 layer with bud-like surface morphology on PDMS composite membrane for highly efficient ethanol/water separation. Journal of Environmental Chemical Engineering, 2021, 9(1): 104977
12. Ueno K, Negishi H, Okuno T, Saito T, Tawarayama H, Ishikawa S, Miyamoto M, Uemiya S, Sawada Y, Oumi Y. A simple secondary growth method for the preparation of silicalite-1 membrane on a tubular silica support via gel-free steam-assisted conversion. Journal of Membrane Science, 2017, 542: 150-158
13. Cheng X Q, Konstas K, Doherty C M, Wood C D, Mulet X, Xie Z, Ng D, Hill M R, Lau C H, Shao L. Organic microporous nanofillers with unique alcohol affinity for superior ethanol recovery toward sustainable biofuels. ChemSusChem, 2017, 10(9): 1887-1891
14. Ahmed I, Pa N F C, Nawawi M G M, Rahman W A W A. Modified polydimethylsiloxane/polystyrene blended IPN pervaporation membrane for ethanol/water separation. Journal of Applied Polymer Science, 2011, 122(4): 2666-2679