Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

CO_2-Selective Zeolitic Imidazolate Framework Membrane on Graphene Oxide Nanoribbons—Combined Experimental and Theoretical Studies

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Additional Experimental Section

Chemicals and materials: Zinc nitrate hexahydrate ($Zn(NO_3)\cdot 6H_2O$, 98%, Sigma-Aldrich) and 2-methylimidazole (99.0%, Sigma-Aldrich) were used as metal and ligand sources, respectively, to synthesize the ZIF-8 membranes. Multi-walled carbon nanotubes (MWCNTs, diameter = 15–25 nm, length = 20–100 μm, 7–12 layers, JenoTube 20A, JEIO, South Korea), sulfuric acid (H_2SO_4, 98%, Daejung), potassium permanganate ($KMnO_4$, Extra pure, Duksan), and hydrogen peroxide (H_2O_2, 35%, Daejung) were used for the synthesis of graphene oxide nanoribbons (GONRs). All the chemicals were used as-purchased without further purification.

GONR preparation: The GONRs were synthesized by a modified Hummer method wherein MWCNT powder (2 g) was added to 130 mL of H_2SO_4 solution, and 10.2 g of $KMnO_4$ was slowly added to the mixture. The MWCNT oxidation was maintained at 35 °C for 32 h in a water bath, and then 150 mL of deionized (DI) water was slowly added to the mixture in an ice bath. Then, 40 mL of H_2O_2 was added, and the solution containing the synthesized GONRs was vacuum filtered and repeatedly washed with DI water to remove any residual compounds such as H_2SO_4 solution, oxidizing chemicals, and potassium ions. The GONR solution was then prepared by dispersing the GONRs in 200 mL of DI water using a homogenizer.

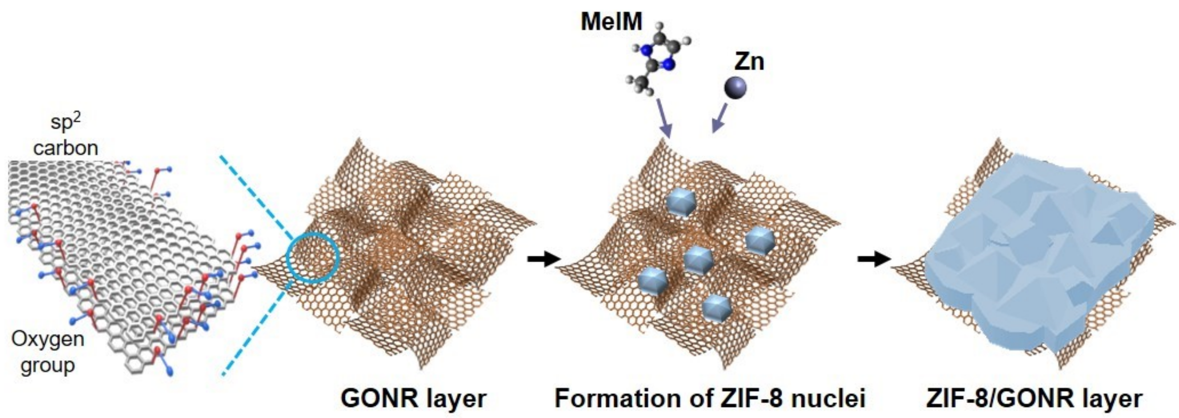


Figure S1. Schematics illustrating the crystal growth of ZIF-8 on GONR layer..

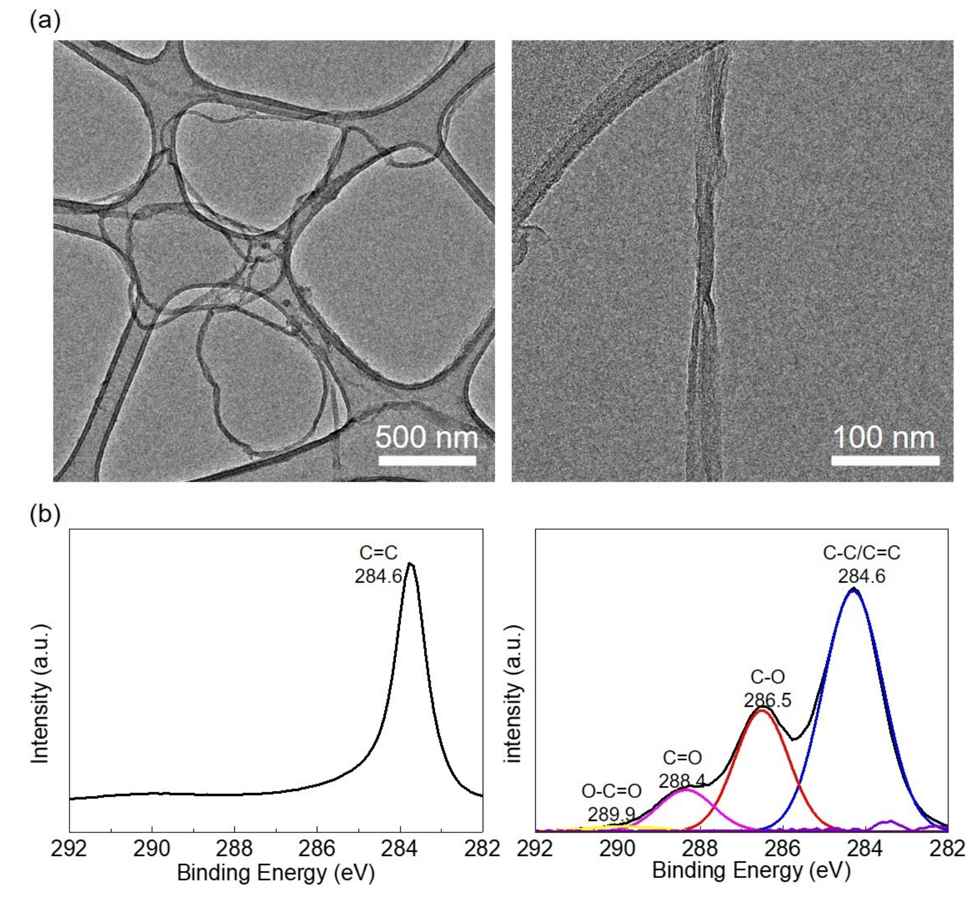


Figure S2. (a) TEM images of GONR at low-magnification and at high-magnification. **(b)** XPS C1s spectra of MWCNT and GONR.

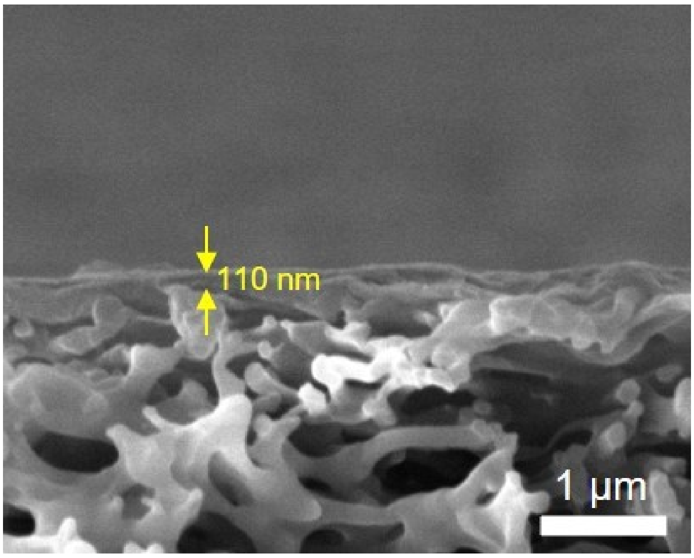


Figure S3. Cross-sectional SEM image of a GONR coated PES support.

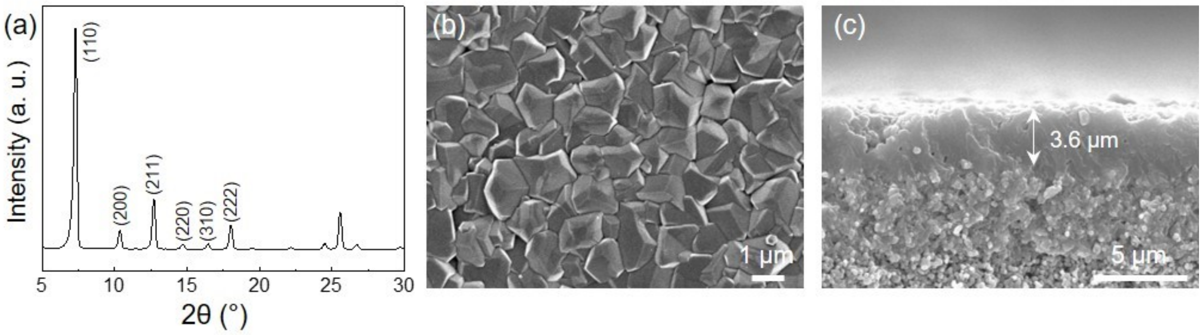


Figure S4. **(a)** XRD pattern of ZIF-8 coated on alumina support. **(b)** and **(c)** Top and cross-sectional SEM images of ZIF-8/alumina membrane.

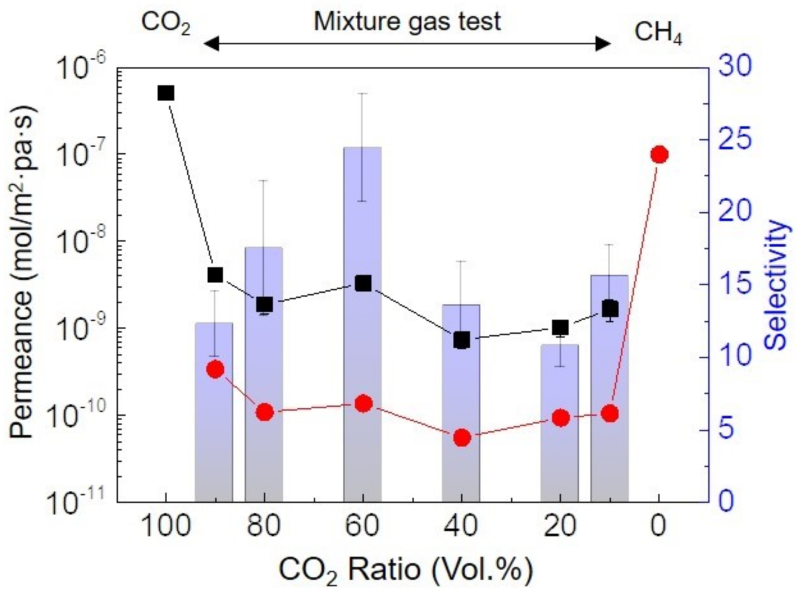


Figure S5. CO_2/CH_4 gas separation performance of ZIF-8/GONR/PES membrane depending on the ratio of CO_2 in the feed gas. Transmembrane pressure and temperature were 1 bar and 25 °C, respectively.

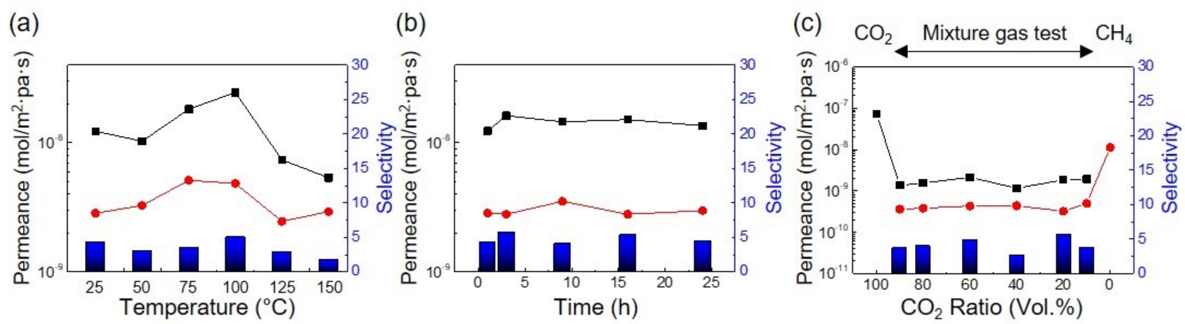


Figure S6. CO_2/CH_4 separation performance of ZIF-8/alumina membrane—as a function of **(a)** temperature, **(b)** time, and **(c)** feed composition. Binary mixture of CO_2 and CH_4 was used at 1 bar and room temperature.

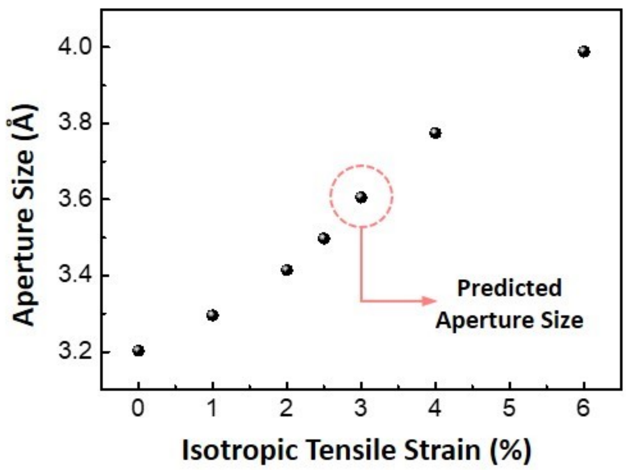


Figure S7. Calculated aperture size of ZIF-8 depending on isotropic tensile strain.

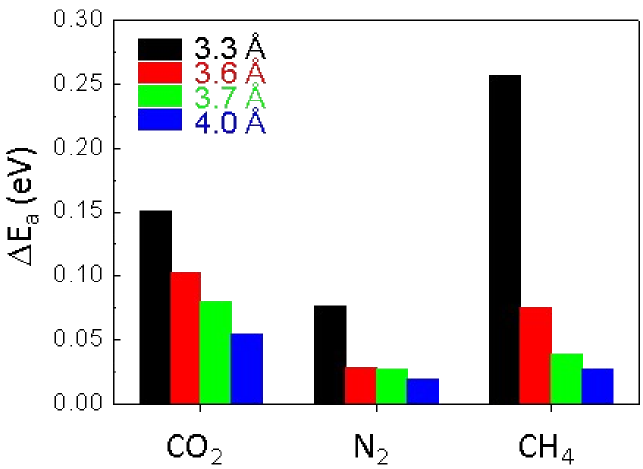


Figure S8. Calculated activation barrier of molecules depending on ZIF-8 aperture sizes.

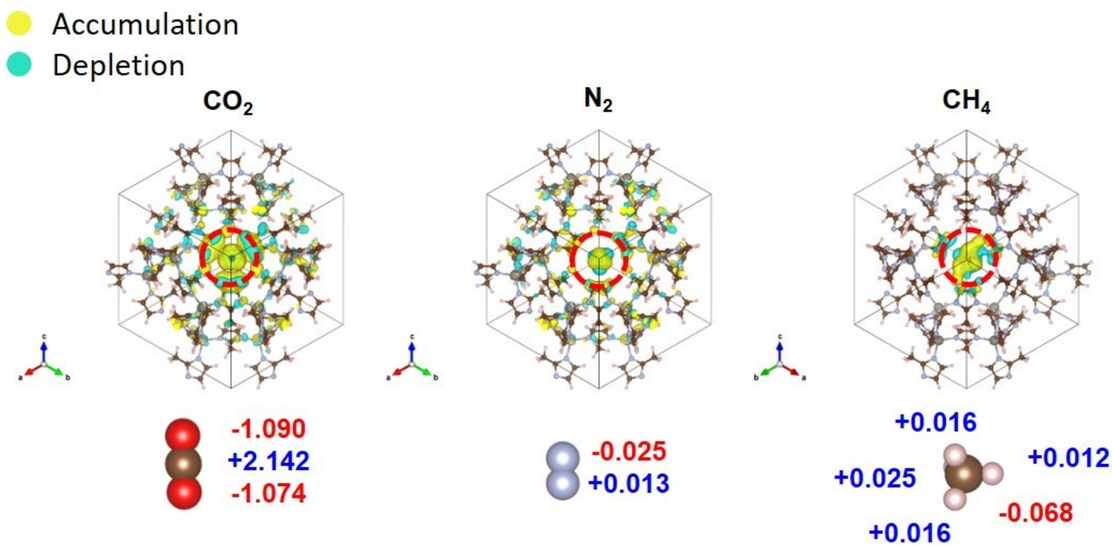
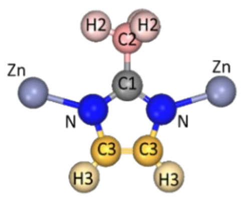


Figure S9. Calculated charge density difference (isosurface: 6×10^{-5} eV/Å^3) between the ZIF-8 cage and N_2/CO_2 and Bader charge analysis of CO_2/N_2/CH_4 interacting with ZIF-8 at the entrance of the pore. Cyan and yellow color represent charge depletion and accumulation, respectively. Silver, red, brown, and pink balls indicate N, O, C, and H respectively. The numbers in red and blue are the amount of charges gained and lost, as calculated from Bader charge analysis. The charge density difference ($\Delta\rho$) was calculated using the Equation S1:

$$\Delta\rho = \rho_{total} - \rho_{ZIF-8} - \rho_{gas} \qquad \text{(S1)}$$

where ρ_{total}, ρ_{ZIF-8}, and ρ_{gas}, are the charge densities of the total system, ZIF-8, and gas molecule, respectively.

Table S1. Lennard—Jones parameters, r_0 and D for gas molecules and non-bonded molecular pairs from simulations.



$$E(r) = D\left[\left(\frac{r_0}{r}\right)^{12} - 2\left(\frac{r_0}{r}\right)^{6}\right]$$

Compound	r_0 (Å)	D (kcal/mol)	Compound	r_0 (Å)	D (kcal/mol)
C (CO_2)	3.519913	0.187534	H(CH_4)-H3	2.97685467	0.01544798
O (CO_2)	3.125550	0.186062	H(CH_4)-H2	3.00085227	0.01509967
N(N_2)	3.309574	0.154984	H(CH_4)-C3	3.31285390	0.03861707
C(CH_4)	3.812529	0.099672	H(CH_4)-C1	3.31285390	0.03861707
H(CH_4)	2.883993	0.020936	H(CH_4)-C2	3.39189132	0.04077843
C(CO_2)-N(N_2)	3.215568	0.102497	H(CH_4)-N	3.79263659	0.05778014
O(CO_2)-N(N_2)	3.429603	0.122468	H(CH_4)-Zn	2.66843185	0.01379913
C(CO_2)-C(CH_4)	3.557130	0.129992	C(CH_4)-H3	3.28821216	0.03864026
C(CO_2)-H(CH_4)	2.896599	0.046990	C(CH_4)-H2	3.31471974	0.03776903
O(CO_2)-C(CH_4)	3.666833	0.160220	C(CH_4)-C3	3.86429188	0.09558047
O(CO_2)-H(CH_4)	2.726822	0.046167	C(CH_4)-C1	3.86429188	0.09558047
C(CH_4)-N(N_2)	3.649020	0.101186	C(CH_4)-C2	3.65711792	0.10199971
H(CH_4)-N(N_2)	2.832492	0.093500	C(CH_4)-N	4.12902779	0.12531556
C(CO_2)-O(CO_2)	3.022631	0.171421	C(CH_4)-Zn	2.93560504	0.03449225
C(CH_4)-H(CH_4)	3.048159	0.068338	C(CO_2)-H3	2.94849594	0.02960892
			C(CO_2)-H2	3.43102185	0.02917225
			C(CO_2)-C3	3.72380606	0.11335978
			C(CO_2)-C1	3.72380606	0.11335978
			C(CO_2)-C2	3.91830015	0.02734720
			C(CO_2)-N	4.40854878	0.06916831
			C(CO_2)-Zn	2.69014500	0.02650432
			O(CO_2)-H3	3.08120783	0.05009166
			O(CO_2)-H2	3.16588409	0.04896223
			O(CO_2)-C3	3.53972292	0.11039137
			O(CO_2)-C1	3.53972292	0.11039137
			O(CO_2)-C2	4.09202254	0.03577925
			O(CO_2)-N	4.53293364	0.04632141
			O(CO_2)-Zn	2.77234970	0.04333821

$N(N_2)$-H3	3.13235446	0.03439242
$N(N_2)$-H2	3.34803467	0.07658586
$N(N_2)$-C3	3.65907538	0.02365237
$N(N_2)$-C1	3.65907538	0.02365237
$N(N_2)$-C2	3.80576289	0.09541410
$N(N_2)$-N	4.70312861	0.07912765
$N(N_2)$-Zn	3.66664084	0.00366057

Table S2. Comparison of gas separation performances of ZIF-type membranes.

ZIF-type	CO_2 permeance (x 10^{-8} mol/m^2·pa·s)	System (Single or mixture)	Selectivity	Reference
ZIF-8	72.91	Single	6.8	1

ZIF-90	10.6	Single	1.5	2
ZIF-8	0.734	Single	14.6	3
ZIF-8	12.2	Single	2.92	4
ZIF-8	2	Single	2.98	5
ZIF-8	14.0	Single	1.79	6
ZIF-8	4.45	Single	3.34	7
ZIF-8	0.41	Single	2.05	8
ZIF-8	1.33	Single	2.77	9
ZIF-90	3.5	Single	2.2	10
ZIF-93	0.077	Mixture	16.9	11
ZIF-67	1.27	Mixture	47.27	12
ZIF-8	0.154	Mixture	6.1	13
ZIF-90	1.3	Mixture	4.7	14
ZIF-8	0.8	Mixture	12.9	15
ZIF-69	10	Mixture	4.56	16
ZIF-8	3.44	Mixture	7.1	17

Table S3. Self-diffusion coefficients of gas molecules in ZIF-8.

	Self-diffusion coefficients ($\times 10^{-5}$ cm^2/s)					
Aperture size	Pure gas			Mixed gas		
	CH_4	CO_2	N_2	CH_4 + CO_2	CO_2 + N_2	CH_4 + N_2

3.3 Å	0.0119	0.1143	0.0725	0.0044	0.1275	0.0879	0.0507	0.0624	0.0763
3.6 Å	0.2025	0.3855	0.2751	0.1502	0.5435	0.6776	0.3712	0.2933	0.2915
4.0 Å	2.8645	1.2940	2.3410	3.8630	1.6710	1.8035	2.7970	3.3365	2.1180

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