Supporting information

Solvent-free Crystallization of Zeolitic Imidazolate Framework Membrane via Layer-by-Layer Deposition

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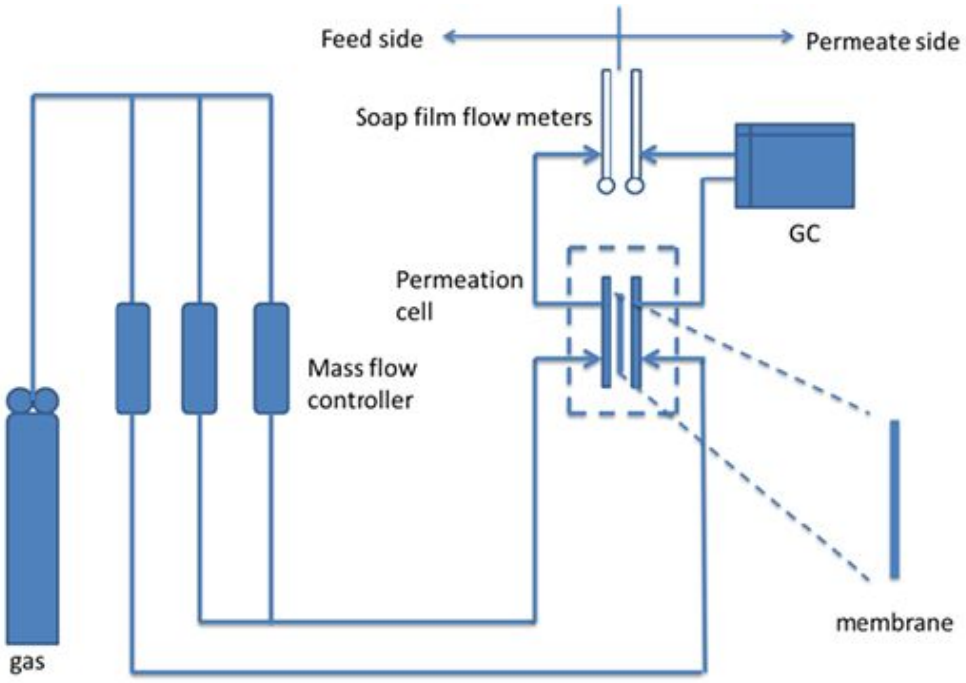

Figure S1. Schematic diagram of gas separation test device.

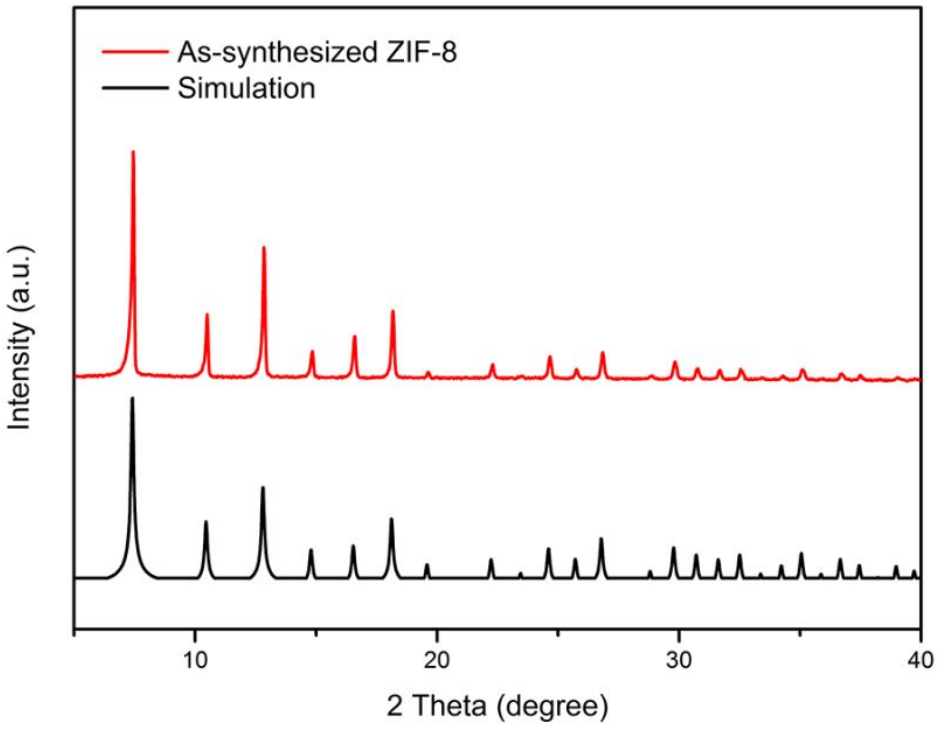

Figure S2. PXRD patterns of the simulated ZIF-8 material (black) and the as-synthesized ZIF-8 powder (red).

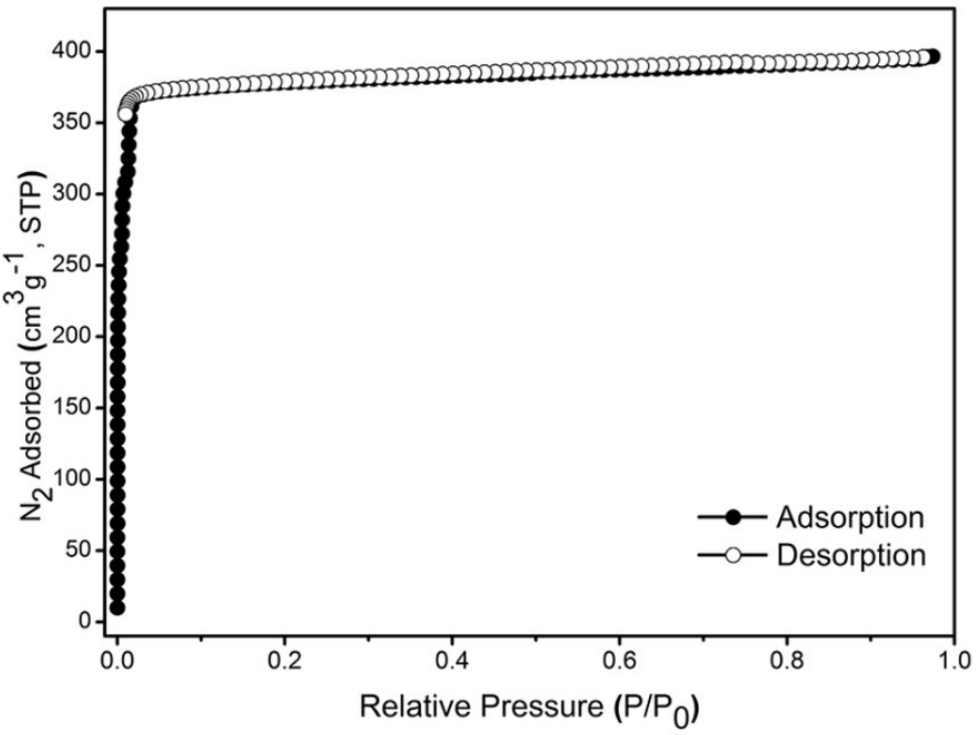

Figure S3. Nitrogen adsorption–desorption isotherm of the formed ZIF-8 sample at 77 K.

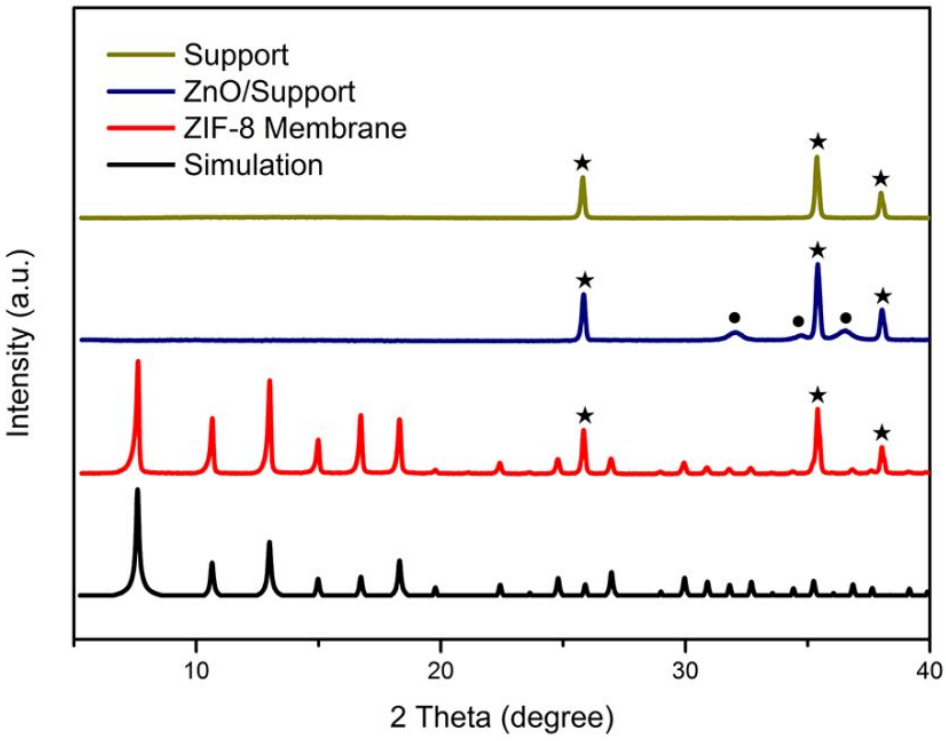

Figure S4. PXRD patterns of the bare Al_2O_3 support (dark yellow), the ZnO-coated Al_2O_3

support (blue), the as-synthesized ZIF-8 membrane (red), the simulated ZIF-8 material (black).(★Al_2O_3 ●ZnO)

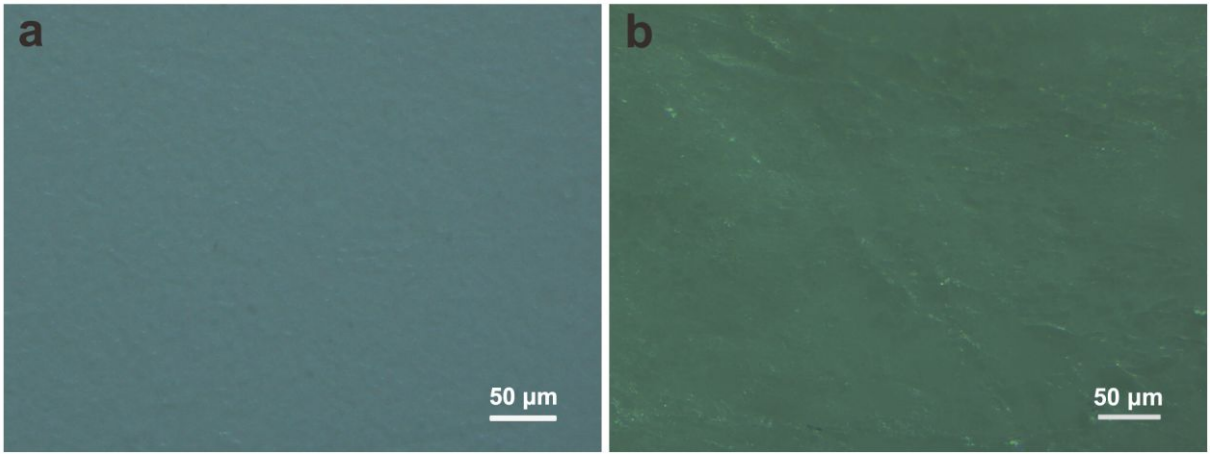

Figure S5. Leica Optic micrographs for the ZnO-coated layer (a) and Hmim layer (b) on the Al_2O_3 support.

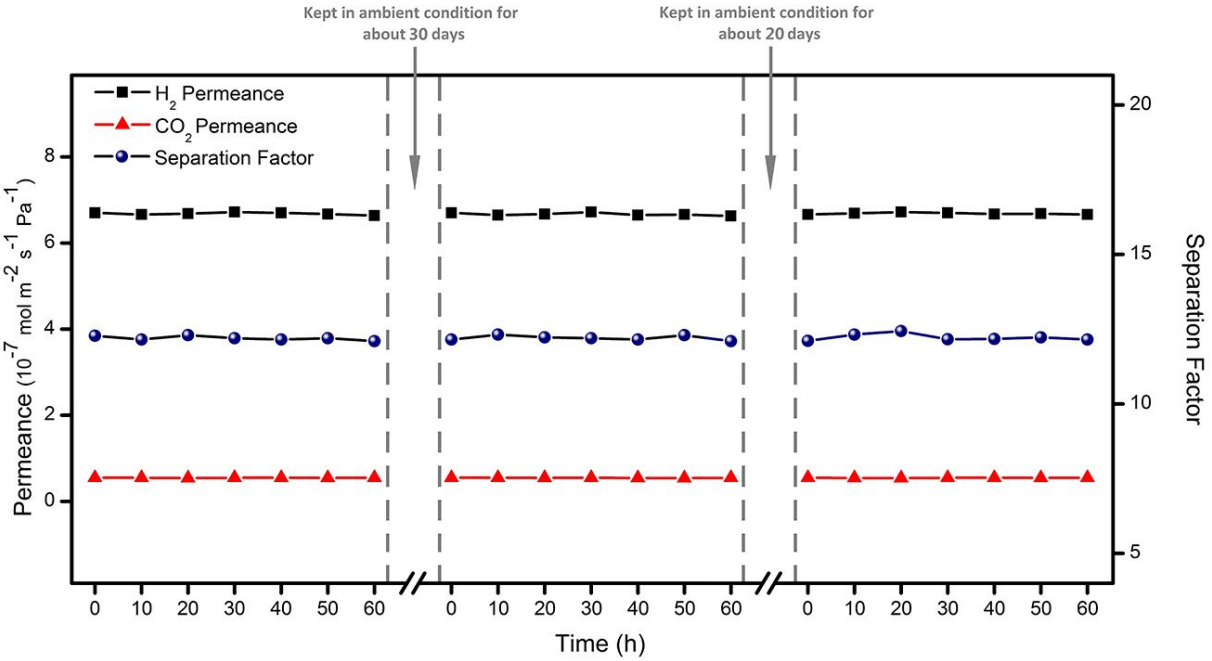

Figure S6. Long-term stability and recyclability measurement of the ZIF-8 membrane prepared by solvent-free method. Equimolar H2/CO2 mixture was used as feed gas. Experiment was conducted at 25°C under 1 bar.

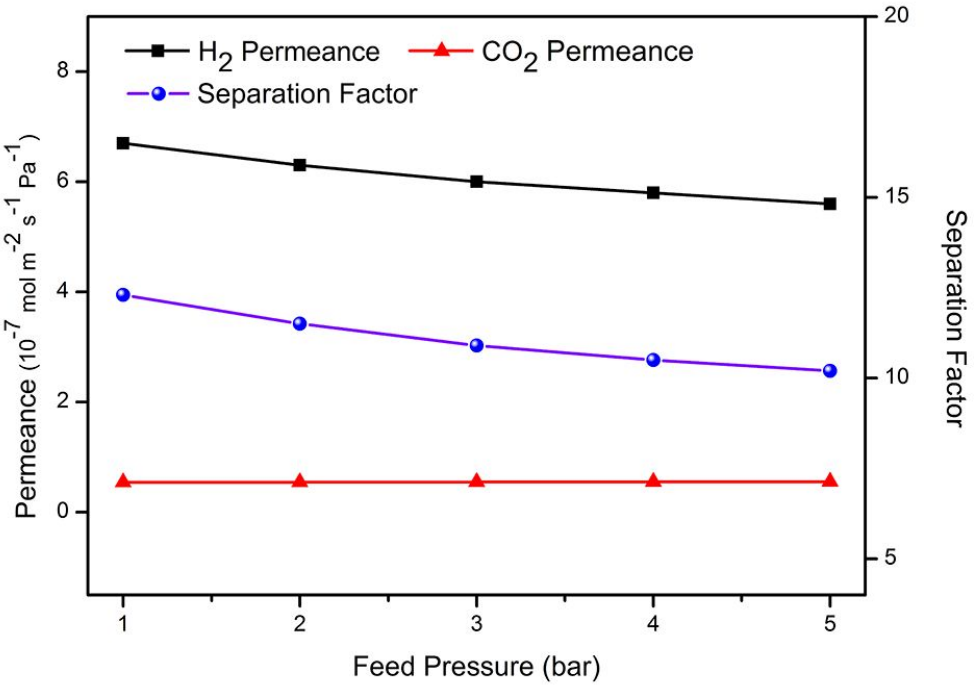

Figure S7. Separation performance of as-prepared ZIF-8 membrane as a function of feed pressure at room temperature.

Table S1. Mixture gas permeances (10^{-7} mol m^{-2} s^{-1} Pa^{-1}) and separation factors (H_2 versus other gases) of the ZIF-8 membranes at 25°C and 1bar.

Gas(i/j)	Permeance(i)	Permeance(j)	Knudsen content	Separation factor
H_2/CO_2	6.70	0.55	4.69	12.28
H_2/N_2	7.10	0.95	3.74	7.48
H_2/CH_4	7.20	0.83	2.83	8.70

Table S2. Mix gas permeances and separation factors of three ZIF-8 membranes were tested at 25 ^{0}C and 1 bar.

Sample	Permeance (H_2) (10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1})	Separation factor (H_2/CO_2)
M1	6.70	12.28
M2	6.67	12.24
M3	6.75	12.31

Table S3. Comparison of gas permeation properties (H_2 permeance and H_2/CO_2 selectivity) of ZIF-8 membranes reported previously.

Support	Synthesis Method	Thickness (μm)	Permeance (H_2) (10^{-7}mol·m^{-2}·s^{-1}·Pa^{-1})	Selectivity (H_2/CO_2)	Refs
Titania	Microwave-Assisted Solvothermal Synthesis	30μm	0.6	4.54[a]	19
α-Al_2O_3	Liquid phase epitaxy	1.5μm	0.19	4.63[a]	20
Al_2O_3 Hollow fiber	Repeated growth	6μm	1.7	7.1	40
γ-Al_2O_3	LDH buffer layer modification and solvothermal growth	20μm	1.4	4.2	46
α-Al_2O_3	Activation of ZnO Nanorods and solvothermal growth	6μm	1.6	4.6	47
PAN HF	Surface chemical modification and solvothermal growth	1μm	3.05	6.85	48
γ-Al_2O_3	Growth of LDH membrane and then solvothermal treatment	2μm	0.35	4.2	49
PVDF	Chemical modification of support and solvothermal growth	30μm	19.03	12.42	50
α-Al_2O_3 tube	Activation of ZnO layer and then solvothermal growth	8μm	2.75	3.39	51
AAO	Electrophoretic nuclei assembly	0.5μm	83	7.3[a]	52
PVDF Hollow fiber	Hydrothermal sol-gel coating of TiO2 layer on modified support and then solvothermal growth	1μm	201	7.04[a]	53

BBPO	Simultaneous Surface chemistry and pore structure modification	0.2μm	20.5	12.8[a]	54
α-Al_2O_3 tube	APTES monolayer modification and cycling precursors	2μm	4.3	3.54[a]	55
α-Al_2O_3	Surface chemical modification	12μm	1.7	3.3[a]	56
α-Al_2O_3	Solvent-free crystallization	7μm	6.7	12.28	This work

[a]Ideal separation factor