Electronic Supplementary Information (ESI)

Rapid synthesis of ultrathin defect-free ZIF-8 membranes via chemical vapour modification of polymeric support

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Materials

BPPO was kindly supplied by Tianwei Membrane Co. Ltd., Shandong of China. Zinc acetate dihydrate $(Zn(CH_3COO)_2.2H_2O, 98\%)$, 2-methylimidazole (Hmim, C₄H₆N₂, 99%), ethylenediamine (EDA, 99.5%) and ammonium hydroxide solution (NH₃, 28–30% aqueous solution) were purchased from Sigma-Aldrich, Australia and used as received. Methanol (absolute) was purchased from Merck, Australia.

Synthesis of BPPO membrane and its EDA-vapour modification

The flat sheet BPPO support ultrafiltration membranes were fabricated via non-solvent induced phase inversion (also known as the immersion precipitation technique). Dope solution was prepared by dissolving 18 wt% of BPPO in NMP at around 25 °C for 24 h with mechanical stirring at 200 rpm. The homogenous solution was left stagnant until no bubbles were observed. Subsequently, the polymer solution was cast on a cleaned glass plate using a casting knife (Paul N. Gardner Co., Inc. USA) with a gap of 150 μ m at room temperature (21–23 °C) and 30-35 % humidity and immediately immersed in a coagulation bath of deionized water (Fig. S1 (a)). After peeling off from the glass plate, the membranes were removed from the coagulation bath, washed and kept in water bath for at least one day to thoroughly remove the residual solvents. The thickness of the prepared membrane was about 70 μ m.

The vapour-phase EDA modification was conducted in a custom-made container as illustrated in Fig. S1 (b). 20 mL of EDA was allowed to vaporize, and stabilized for 1 h. Based on the Antoine equation,¹ the EDA vapour pressure at 25 °C was estimated to be 12.0 mm of Hg and the air of the closed chamber consists of 1.6 % v/v EDA vapour. The support membranes were quickly placed inside the containment with the top layer exposed and

suspended above the EDA solution. After surface modification at room temperature for 4-16 h, the surface modified membranes were removed from the containment and immediately washed with pure water to completely remove the residual EDA. The resultant membranes were denoted as MBPPO-4, MBPPO-10, and MBPPO-16, where numbers show EDA exposure time.



Figure S1. (a) Schematic diagram of UF membrane fabrication via phase inversion, (b) Experimental setup of vapour-phase EDA modification process.

Growth of ZIF-8 Thin Film on modified BPPO Supports

Modified BPPO supports were immersed vertically in the solution of zinc acetate dehydrate (0.22) in 9.6 g methanol and sonicated for 3 min to fix the Zn^{2+} . A solution of Hmim (0.164 g) in 9.6 g methanol was added to the above solution followed by dropwise addition of ammonia hydroxide solution (0.12 g) and the mixture was then ultrasonically treated for another 3 min. After crystallization, the composite membranes were washed with methanol and dried. The

ZIF-8 nanocrystals were also separated from the solution by centrifugation and washed several times with methanol, and dried at 60 °C overnight. For comparison, BPPO was also used for ZIF-8 membrane growth under the same condition.

Pure water flux and molecular weight cut off (MWCO) measurements

Pure water flux of the membranes was determined at room temperature (21–23 °C) using a Sterlitech HP4750 dead-end stirred cell (Sterlitech Corporation, USA) with an inner diameter of 49 mm and an effective membrane area of 14.6 cm². The cell has a volume capacity of 300 ml and is attached to a 5.0 L dispensing vessel. To attain stable flux data, each membrane was first pre-compacted at 150 kPa for about 60 min, and then the pure water flux was measured at a trans-membrane pressure drop 100 kPa. Pure water flux was measured constantly by collecting the permeate on a digital balance (PA2102C, Ohaus) interfaced with a computer. The data from the balance was logged to a computer using a program written in LabVIEW. Polyethylene glycol (PEG) with a molecular weight of 10, 20, 35, 100, 200 and 300 kDa (analytical grade, Sigma-Aldrich) was dissolved in deionized water to prepare 1 g L⁻¹ aqueous solutions for the estimation of MWCO and solute rejection. Rejection measurements were performed at a pressure of 100 kPa. 20 ml of permeate was collected. The permeate and feed solution were both diluted by 10 times and then the concentration of each solution was measured via a total organic carbon analyser (TOC-LCSH, Shimadzu, Japan). The PEG rejection was calculated from the measured feed (C_f) and permeate (C_p) concentrations by

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$$

All results represent average values for at least three repeated experiments with less than $\pm 5\%$ deviation. The pore size of the membrane was defined as the hydrodynamic diameter of PEG. The hydrodynamic radius of PEG can be calculated from the MWCO of the membrane by the following equation:²

Solute Radius $(nm) = 0.0262\sqrt{MW} - .03$

where MW is the lowest molecular weight of the PEG molecule which has a rejection of 90% in the ultrafiltration measurements.

Gas permeation experiments

The gas permeation test is carried out as previously reported.³ The composite membranes were attached to a stainless steel stand with pore size ~ 200 nm, which was fixed in a sample

holder with Torr Seal epoxy resin (Varian). The film was dried at 100 °C for 2 h to remove H₂O. Gas permeation tests were performed at 20 °C for pure H₂, CO₂ and N₂. Between each measurement, the system was evacuated for 30 min prior to introduction of the next gas. The pressure increase of the permeate stream was measured and the permeance P_i of each gas calculated by:

$$P_i = \frac{N_i}{\Delta P_i A}$$

where N_i is the permeating flow rate of component *i* (mol/s); ΔP_i is the transmembrane pressure difference of component *i* (Pa), and A is the membrane area (m²). The ideal selectivity S_{ij} is defined as the ratio of the two permeances P_i and P_j .

Characterization

Fourier Transform Infrared (FTIR) spectra of the membranes were recorded using an attenuated total reflectance (ATR) FTIR (Perkin Elmer, USA) in the range of 500-4000 cm⁻¹ at an average of 32 scans with a resolution of 4 cm⁻¹. Thermogravimetric analyses (TGA) were carried out on a SETARAM (TGA 92) device from 30 to 800 °C at a heating rate of 10 °C min⁻¹ under air flow. Scanning electron microscopy (SEM) (FEI Nova NanoSEM 450) with a X-ray detector (Bruker Nano GmbH, Germany) was used for imaging the surface and cross-sectional morphologies of membranes. Energy-dispersive X-ray sepectroscopy (EDS) line-scan analysis of the membrane samples was conducted using EDX equipped in Nova NanoSEM 450 (Quantax 400 X-ray analysis system, Bruker, USA). The membranes were fractured in liquid nitrogen, fixed on stubs with double-sided carbon tape and then sputter coated with roughly 2 nm iridium (Ir) layer to ensure good electrical conductivity. The images were recorded at an accelerating voltage of 5 kV with different magnifications. Transmission electron microscopy (TEM) micrographs were obtained using a JEOL JEM-2100F instrument operating at 200 kV. Selected-area electron diffraction (SAED) patterns were taken using the same instrument. The ZIF-8 samples were dispersed on a coppersupported carbon grid for TEM observation. Powder X-ray diffraction (XRD) patterns were measured using a Miniflex 600 diffractometer (Rigaku, Japan) with Cu Ka radiation (15 mA and 40 kV) at a scan rate of 2° min⁻¹ with a step size of 0.02°. The XRD studies were carried out at room temperature. Nitrogen (N₂) adsorption-desorption isotherms were measured using physisorption analyzer (Micromeritics ASAP 2020, USA) at liquid nitrogen temperature (77 K). All the samples were degassed at 100 °C for 12 h prior to analysis.



Figure S2 TGA curves (under air flow) of (1) untreated BPPO support, (2) MBPPO-16, (3) ZIF-8-BPPO, (4) ZIF-8-MBPPO-16, and (5) synthesized ZIF-8 powder.

TGA measurements of the untreated BPPO support show a two-step degradation pattern (Figure S2 (1)) primarily due to the weight loss commencing at ~ 240 °C associated with the degradation of bromomethyl side groups ($-CH_2Br$) followed by the decomposition of the aromatic main chains at ~ 468 °C. In contrast, MBPPO (Figure S2 (2)) shows a slight mass loss (about 4 wt%) at lower temperatures due to the loss of absorbed water. The loading amounts of ZIF-8 can be roughly estimated from the zinc oxide (ZnO) residue at 800°C in TG curves. The results show the ZIF-8 loading amounts increase from 1.9 % for ZIF-8-BPPO to 13.8 % for ZIF-8-MBPPO-16. These results clearly show the importance of EDA modification in the growth of ZIF-8 on the supporting membranes.



Figure S3 Pure water flux and pore size of BPPO membranes as a function of exposure time to EDA vapour (i.e., ethylenediamination time).

Pure water flux and PEG rejection of the membranes were analysed to evaluate the influence of the chemical modification on the membrane permeability in correlation with the change of membranes surface microstructure after EDA-vapour modification. There was a pronounced drop in pore size from 17.5 nm for BPPO to 11.5 nm for the membrane following 16 hours EDA-vapour treatment (MBPPO-16). It is worth noting that the values of the pure water flux and the pore size show that all the membranes fall in the ultrafiltration range. Membranes with such porosity are desirable as support for ZIF membranes since they provide a platform for the growth of ZIFs with no resistance or interruption to gas permeation.



Figure S4 EDS line scan across ZIF-8-MBPPO-16 cross-section for the zinc atoms.





Figure S5 SEM images of the (a) surface and (b) cross section of the BPPO support, (c) surface of the ZIF-8-BPPO, (d) surface of the ZIF-8-MBPPO-4, (e) surface of the ZIF-8-MBPPO-10, (f) surface and (g, h) cross-section of the ZIF-8-MBPPO-16.

All the membranes exhibit a typical asymmetrical ultrafiltration structure with a dense top (skin) layer, a porous sublayer and finger-like macrovoids at the bottom (Figure S5). As compared with the untreated BPPO support, no significant changes in modified BPPO and ZIF-8 membranes are observed from the cross-section morphologies. These indicate that the main membrane-structure was not altered after the EDA-vapour modification and ZIF-8 crystallization steps. Additionally, these images reveal that the shorter EDA exposure resulted in ZIF-8 membranes with larger defects and pinholes.



Figure S6 FTIR ATR spectra of (1) untreated BPPO support, BPPO modified with EDAvapour for (2) 4 h (MBPPO-4), (3) 10 h (MBPPO-10), (4) 16 h (MBPPO-16), (5) ZIF-8-MBPPO-16, (6) synthesized ZIF-8 powder.

Figure S5 shows the ATR-FTIR spectra of BPPO, MBPPO-4, MBPPO-10, MBPPO-16, ZIF-8-MBPPO-16, and ZIF-8 crystals. The ZIF-8 crystals show characteristic infrared bands at around 1588 (C=N stretch), 1144, and 995 cm⁻¹ (C–N stretch), in good agreement with published values.⁴ In the case of BPPO, MBPPO-16, and ZIF-8-MBPPO-16, characteristic peaks of PPO units are observed at 1602, 1458, 1303 and 1188 cm⁻¹ in all the three curves.⁵ ZIF-8-MBPPO-16 distinctively shows the presence of additional peaks assigned to ZIF-8, which confirms the presence of ZIF crystals on the polymer support. In addition, the BPPO showed IR bands at around 586 cm⁻¹ and 633 cm⁻¹ (Fig. S6 (1)), which are attributed to the benzyl bromide (–CH₂Br) groups (C–Br stretching). With increasing EDA exposure time, the peak intensity of these bands decreased (Fig. S6 (2) and (3)) and almost disappeared after 16 hours in the case of MBPPO-16 (Fig. S6 (4)). This indicates that a reaction between the BPPO and EDA occurred and that most of the C-Br groups have been consumed during EDA vapour phase modification.

ZIF-8 nanosized seeds

For ZIF-8, the nucleation rate controls the crystallization process,⁶ which is crucial to the particle sizes. Due to the generation of localized extremely high temperatures and pressures, the fast in situ seeding method,⁷ employed in this study, results in a high nucleation rate and subsequently in small-sized crystals. The introduction of ammonium hydroxide, in addition, can deprotonate organic ligands and thereby accelerate ligand exchange reactions, resulting in an even higher nucleation rate and consequently in a smaller final crystal size. As shown in Fig. S7a, the XRD pattern of the particles collected after 1h seeding is exactly same as the simulated SOD-type ZIF-8 structure, which confirms the formation of pure crystalline ZIF-8 phase. The average crystal size was ~ 20 nm estimated from the full width at half maximum of the (011) peak using the Scherrer's equation. The formation and size of the ZIF-8 crystals were further confirmed by TEM, as shown in Fig. S7b. The diffraction rings of the different planes, shown in inset of Fig. S7b, are in good agreement with the XRD peaks of ZIF-8. Spherical particles of ~20 nm observed in the TEM image was also consistent with crystallite size obtained from XRD patterns. It should be noted that the small ZIF-8 nanocrystals are easily damaged in the high energy of the electron beam of a TEM.⁸ Type I nitrogen sorption isotherms (Fig. S7c) were observed representing the microporous nature of the as-synthesized ZIF-8 crystals. The second step (at P/Po > 0.8) observed in the isotherm with an obvious adsorption-desorption hysteresis loop is attributed to interparticle mesopores. The micropore volume of the ZIF-8 nanocrystals is 0.74 cm³/g, and the BET and Langmuir surface areas are 1146 and 1715 m²/g, respectively.







Figure S7. XRD pattern (a), TEM image and SAED pattern (inset) (b) and nitrogen sorption isotherm (c) of as-synthesized ZIF-8 nanocrystals.

Table S1 Single gas permeances and ideal selectivities for the composite membranes at 25 ^oC and 1 bar.

	Permeance $(10^{-7} \text{ mol.m}^{-2}.\text{s}^{-1}.\text{Pa}^{-1})$	Ic	leal selectivity
Sample	H ₂	H_2/N_2	H_2/CO_2
BPPO	80.8	1.6	2.1
MBPPO	40.0	2.0	2.9
ZIF-8@BPPO	75.5	1.8	2.2
ZIF-8@MBPPO-4	32.7	2.2	3.0
ZIF-8@MBPPO-10	31.2	2.5	3.4
ZIF-8@MBPPO-16	20.5	9.7	12.8

Table S2 Comparison of gas permeation properties (H_2 permeance, H_2/N_2 and H_2/CO_2 selectivity) of ZIF-8 membranes on inorganic and polymeric supports reported in recent literature.

				Р	ermean	ce	Selec	tivity	
				(10 ⁻⁷ mol/m ² .s.Pa)					
Support	Synthesis Method	Inickness	Т	H ₂	N ₂	CO ₂	H_2/N_2	H ₂	Ref.
		(µm)	[°C]					/CO ₂	
Polymeric support									
BPPO	Simultaneous Surface	~0.2	Room	20.5	2.1	1.6	9.7	12.8	This
	chemistry and pore								work
	structure modification								
PVDF	Chemical	~30	Room	24.4	1.7	2	14.3	12.1	9

	modification								
Nylon	Contra-diffusion	16	25	19.7	4.6	NR*	4.3	NR	3
Nylon	Contra-diffusion	2.5	25	11.3	2.5	NR	4.6	NR	10
Torlon	Interfacial microfluidic membrane processing (IMMP)	~9	25	8.5	NR	NR	NR	NR	11
PES	Secondary growth	7.2	60	4	0.4	NR	9.9**	NR	4a
PSf	In situ followed by layer-by-layer	10	25	3.98	NR	1.06	NR	3.8	4b
PAN	Surface chemical modification	NR	20	3.05	NR	0.44	NR	6.85**	12
PSf	In situ	35	35	2	0.16	NR	12.4**	NR	13
Inorganic su	pport	I		1	1	1	1	1	
Alumina/P TFE	Seeded growth	2	25	76.8	8.1	NR	9.4	NR	14
Alumina hollow fiber	Hot support seeding	20	25	7.3	0.79	1.35	9.2	5.4	15
Alumina hollow fiber	Repeated growth	6	25	5.2	2.1	0.16	2.5	32.2	16
Alumina tube	APTES and cycling precursors	2	Room	4.3	0.35	1.2	11.1	3.6	17
Alumina	Surface chemical modification	12	25	1.7	0.15	0.44	11.4	3.8	18
γ-Al ₂ O ₃	Surface chemical modification	20	Room	1.4	0.14	0.33	10	4.2	19
AAO	Fast in situ seeding and secondary growth	0.5	25	1.34	0.32	0.21	4.19	6.38	7
Al ₂ O ₃ tube	Repeated synthesis	25	100	1.2	NR	0.05 8	NR	20.7	20

Titania	Direct synthesis	30	25	0.6	0.05	0.13	11.5	4.5	21
					2				
Alumina	Layer-by-layer	~1.5	35	0.19	0.01	0.04	11	5	22
					9	1			

*NR: Not reported; **Mixture separation factor.

 $1 GPU = 3.348 \times 10^{-10} mol m^{-2} s^{-1} Pa^{-1}$

Reproducibility of membranes

To examine the reproducibility of ZIF-8-MBPPO-16 composite membranes, two additional membranes (denoted by membranes 2 and 3) were obtained in the same conditions, and their gas separation performance was tested. Their corresponding single gas permeation data is presented in Table S3. All three membranes have similar permeances and selectivities, indicating that the good reproducibility of the membranes was achieved using our synthesis method.

Table S3 Single gas permeances and ideal selectivities of three ZIF-8-MBPPO-16 membrane samples tested at 25 °C and 1 bar.

Sample	Permeance (10 ⁻⁷ mol.m ⁻² .s ⁻¹ .Pa ⁻¹)	Ideal selectivit	y
	H ₂	H_2/N_2	H_2/CO_2
Membrane 1	20.5	9.7	12.8
Membrane 2	20.0	9.8	13
Membrane 3	20.3	9.7	12.5

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