Electronic Supplementary Information for

**Zeolite-imidazolate framework (ZIF-8) membrane synthesis on mixed-matrix substrate**

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Experimental details:

**Materials:** Polyetherimide (Ultem® 1000) was purchased from Sabic, Polydimethylsiloxane (Dehesive 940) was purchased from Wacker, Polyester nonwoven support (PE 05TH-100) was purchased from HIROSE and g-Butyrolactone (GBL) was purchased from DAEJUNG Chemicals & Metals CO. LTD. Zinc oxide nanopowder (ZnO), zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6 H$_2$O), sodium hydroxide (NaOH) and 2-methylimidazole were supplied by Sigma-Aldrich. Methanol was supplied by Fluka Analytical, iso-octane by Fisher Scientific and N-dimethylacetamide (DMAc) by Acros Organics. All chemicals were used as purchased directly without further purification.

**Synthesis of ZIF-8 membrane**

**Synthesis of porous support:** The porous PEI+ZnO supports were fabricated by non-solvent induced phase separation. A solution consisting of ZnO nanopowder (20 g), GBL (55 g) and DMAc (101 g) was sonicated for 30 min. Subsequently PEI (34 g) was added to this dispersion and stirred at 75 ºC for 10 hours to dissolve. After cooling down to room temperature the solution was casted on a polyester support using a casting machine with water at room temperature as coagulation bath by phase inversion method. Prior to ZIF-8 seeding step, membranes were polished with 1500 grit SiC sandpaper and washed under running water. After polishing, they were sonicated for 30 s in deionized water.

**Synthesis of ZIF-8 crystals:** The recipe of ZIF-8 crystals synthesis was taken from Pan et al. work.\(^1\) Zn(NO$_3$)$_2$.6 H$_2$O (1.17 g) and 2-methylimidazole (22.7 g) were dissolved in 88 mL deionized water. The solution was stirred at room temperature for 12 hours. The crystals were obtained by centrifugation (10,000 RPM for 10 min) and washed 3 times with DI water and 3 times with methanol. Then the obtained white powder was dried at 45 ºC in oven and kept for next step.

**Seeding procedure:** Seeding step combines two methods: rubbing and dip-coating. From ZIF-8 powder and DI water a ZIF-8 paste at a mass ration 1:10 was prepared. The surface of supports was wiped with ZIF-8 paste along axis direction 3 times with a foam brush and left dried for 2 hours at room temperature. Then the supports were dip-coated in 1.0 wt.% seed suspension for 5 s. After dip-coating step, membranes were dried at room temperature for 12 hours.

**Secondary growth:** Two solutions were prepared separately: Zn(NO$_3$)$_2$.6 H$_2$O (0.22 g) was dissolved in 15 mL of water and 2-methylimidazole (4.54 g) was dissolved in 65 mL water. The pH value of the used water was changed to the value pH=9.5 by addition of NaOH. Then the first solution was rapidly added to the second one. The seeded membranes were placed vertically to a glass beaker in order to avoid sedimentation of crystals and left for ZIF-8 layer growth for 36 hours at 45 ºC in oven.

**Careful drying and PDMS coating:** After secondary growth the membranes were washed sequentially with methanol (50 wt.%), pure methanol, mixture of methanol and iso-octane (1:1), pure iso-octane and finally dip-coated for 20 s in PDMS (2 wt.%) solution. This process ensured slow exchange of solvents inside the ZIF-8 pores. Thus the formation of undesired cracks in ZIF-8 layer caused by drying was minimized. The PDMS layer should fill possible pinholes, also to add to the final membrane more flexibility and resistance of handling damages.
Permeation test

Single gas permeation tests were performed using the apparatus with constant feed pressure at room temperature. The volume of the permeating gas and the time needed to permeate this volume was measured by soap film flowmeter (10 mL) and stopwatch. From known area of membrane $A$, transmembrane partial pressure difference $\Delta p_i$, volume of permeating gas $V_i$ and time $t$ the permeance was calculated:

$$J_i = \frac{V_i}{A \Delta p_i t}$$

Each experimental value of volume and time for a particular gas was measured after reaching steady-state which is characterized by constant time value needed for certain volume of permeating gas. A measure of the ability of a membrane to separate two gases, $i$ and $j$, is the ratio of their permeances, $\alpha_{ij}$, called the membrane selectivity

$$\alpha_{ij} = \frac{J_i}{J_j}$$

Characterization

Scanning electron microscopy (SEM) images of the surfaces and cross-sections of membranes were carried out with FEI Quanta 200FEG SEM. Samples were first coated with either iridium or gold by sputtering under vacuum. Fig. S1 shows SEM images of the cross section of a PEI/ZnO hybrid membrane with 40 wt % loading of ZnO. The ZnO nanoparticles are well dispersed and no significant agglomeration can be seen.
**Fig. S1.** SEM images of cross section of PEI/ZnO mixed matrix membrane with 40 wt % ZnO loading

X-ray diffraction (XRD) patterns were carried out with a diffractometer Bruker D8 Advance, Cu radiation (40kV, 40 mA scan range 5 to 30 degree). Fig. S2 shows diffractogram of prepared ZIF-8 powder, ZIF-8
membrane and PE/PEI/ZnO support. ZIF-8 characteristic XRD pattern was obtained and the positions of peaks are in agreement with previously reported XRD analysis of ZIF-8.²

Fig. S2 X-ray diffractogram of ZIF-8 powder (blue), ZIF-8 membrane (red) and mixed-matrix support (green).

References