Electronic Supplementary information (ESI)

Polymer supported ZIF-8 membranes prepared via an interfacial synthesis method

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1. Experiments

1.1 PES supporting membrane preparation

PES ultrafiltration membranes were prepared for using as supports. The polymer solution (PES X%, PEG 10%, NMP 90-x%, X=16,18,20 and 22%) was cast on a polypropylene non-woven support with a 200 μm casting knife followed by immersing in a room temperature water bath. The membranes were stored in water.

1.2 Preparation of ZIF-8 and PES supported ZIF-8 membranes by the interfacial synthesis method

A solution of zinc nitrate (1.5 g) in water (100ml) and a solution of 2-methylimidazole (1.614 g) in hexane (95.6 ml) with co-solvent methanol (1.9ml) and ethanol (2.5ml) were prepared separately. 5 ml of the zinc nitrate solution was add in a glass vial first, 5 ml of the 2-methylimidazole solution was added gently afterwards. Subsequently, a white layer at the interface started to form and to grow toward the water phase. Finally, the solution was centrifuged; the precipitate was washed by water and dried at 120 °C.

For preparation of the PES supported ZIF-8 membrane, the PES supporting membranes were immersed in the zinc nitrate solution for overnight. After removal the excess aqueous solution from the membrane using rubber wiper, the 2-methylimizazole solution as mentioned above was gently poured on the surface. The solution was drained off after certain of reaction time. Finally the membranes were post-treated at 100 ºC for overnight.

1.3 Characterizations

The ZIF-8 synthesized by the interfacial method (ZIF-8-i) and the membranes were characterized by a powder X-ray diffractometer (STOE StadiP diffractometer in high-throughput transmission mode employing Cu Kα1 radiation). The thermal stability of the ZIF-8-i was investigated by thermo-gravimetric analysis (TGA, Q 500, TA Instruments, US) under nitrogen at a heating rate 5℃/min from room temperature to 900℃.

The morphologies of ZIF-8-i and membranes were characterized by a scanning electron microscope (SEM, Philips XL-30 FEG instrument equipped with a tungsten filament. Prior to

analysis, sample was spread on carbon discs mounted to SEM aluminum pin stubs and gold sputtered.

Attenuated Total Reflection infrared (ATR-IR, Bruker, Alpha) spectrophotometer was employed to investigate the surface chemistry of the membranes.

The water contact angle of the membranes was measured using a DSA 10 Mk2 (Krüss, Germany) system.

AFM measurements were performed on a Multimode AFM equipped with a Nanoscope IV controller (Veeco/Digital Instruments, Santa Barbara, USA). Dry samples were imaged in tapping mode with a drive frequency of 200-300 kHz. Oxide-sharpened silicon-nitride tips with 1nm radius (NCHR, Nanosensors, Germany) were used. The average roughness (R_a) and the root-mean-square value (R_{ms}) were calculated by Eq.(1) and (2), respectively.

$$R_a = \frac{1}{N}\sum_{i=1}^{N}|z_i - \bar{z}| \qquad \text{equation(1)}$$

$$R_{ms} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}|z_i - \bar{z}|^2} \qquad \text{and equation(2)}$$

1.4SRNF experiments

Dead-end filtrations were carried out at room temperature A 17.5 μ mol Rose Bengal solution in water, ethanol or IPA was used as feed solvent. Membrane permeance and rejection were calculated by

$$P = \frac{W}{t \cdot A \cdot \Delta P} \quad \text{and} \quad R = \left(1 - \frac{C_p}{C_F}\right) \times 100\%$$

where

P is permeability, W weight of the permeate sample, t collecting sample time, A membrane area, R rejection, C_p the solute concentration in the permeate and C_F solute concentration in the feed.

In order to investigate the ZIF-8 membrane stability, 50 h SRNF filtration was performed by using RB in IPA as a feed on membrane ZIF-8(1h)/PES-20%.

2. Results

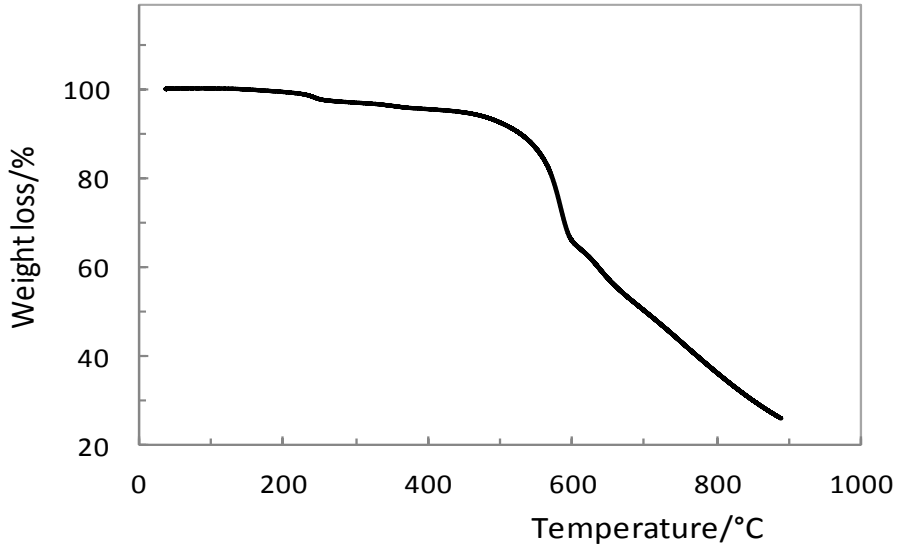

Fig.1 TGA curve of ZIF-8-i

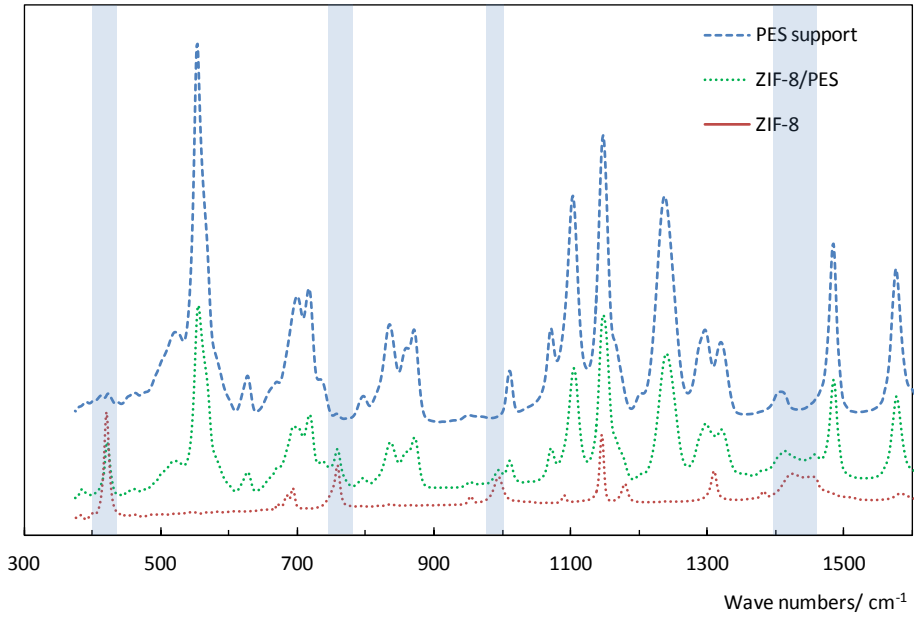

Fig.2 ATR-IR spectrums of ZIF-8, PES support and PES supported ZIF-8 membrane (ZIF-8/PES).

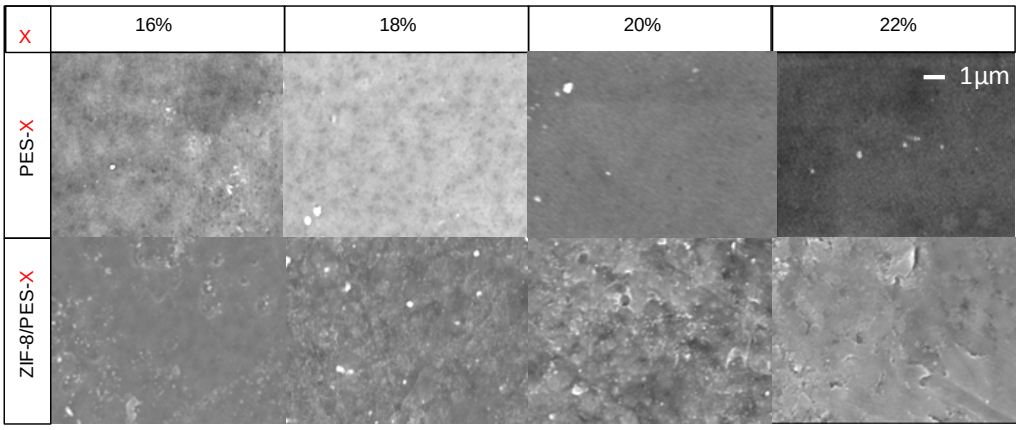

Fig.3 SEM images of membrane surfaces. PES-X, supporting membranes. ZIF-8/PES-X, PES supported ZIF-8 membranes. X indicates the polymer concentration of the support casting solution.

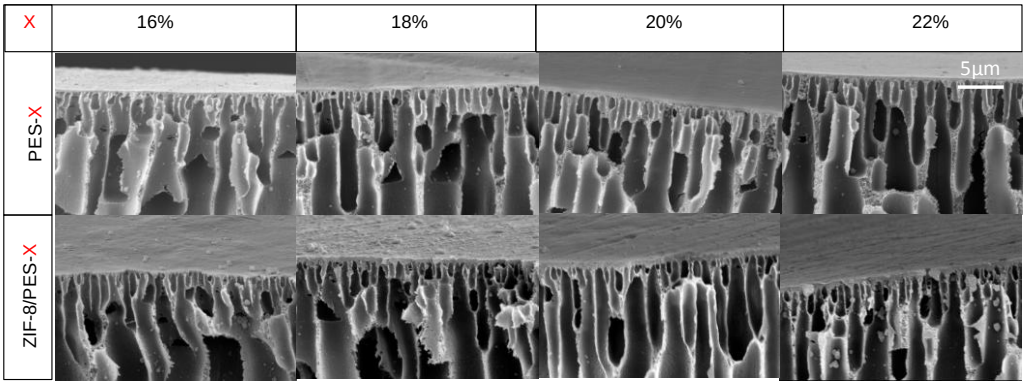

Fig.4 SEM images of membrane cross section. PES-X, supporting membranes. ZIF-8/PES-X, PES supported ZIF-8 membranes. X indicates the polymer concentration of the support casting solution.

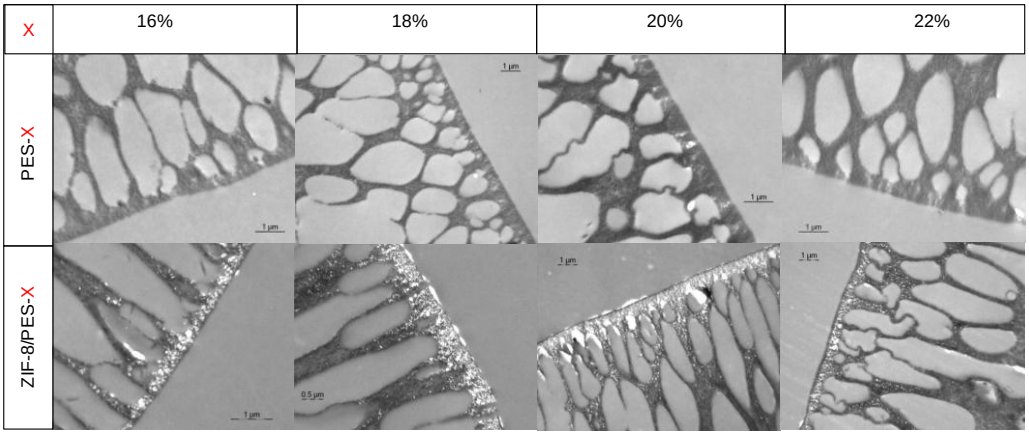

Fig.5 TEM images of membrane cross section. PES-X, supporting membranes. ZIF-8/PES-X, PES supported ZIF-8 membranes. X indicates the polymer concentration of the support casting solution.

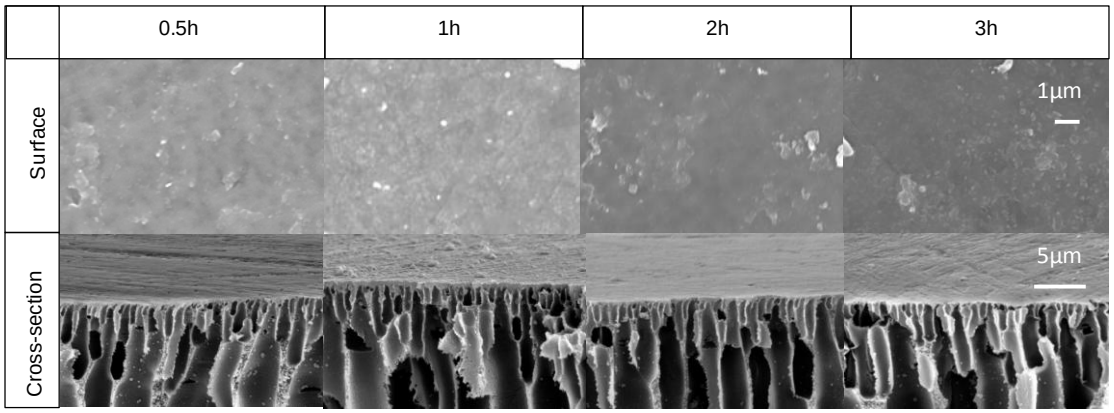

Fig.6 Effect of interfacial reaction time on the surface and cross-section morphologies of the ZIF-8/PES -18% membranes.

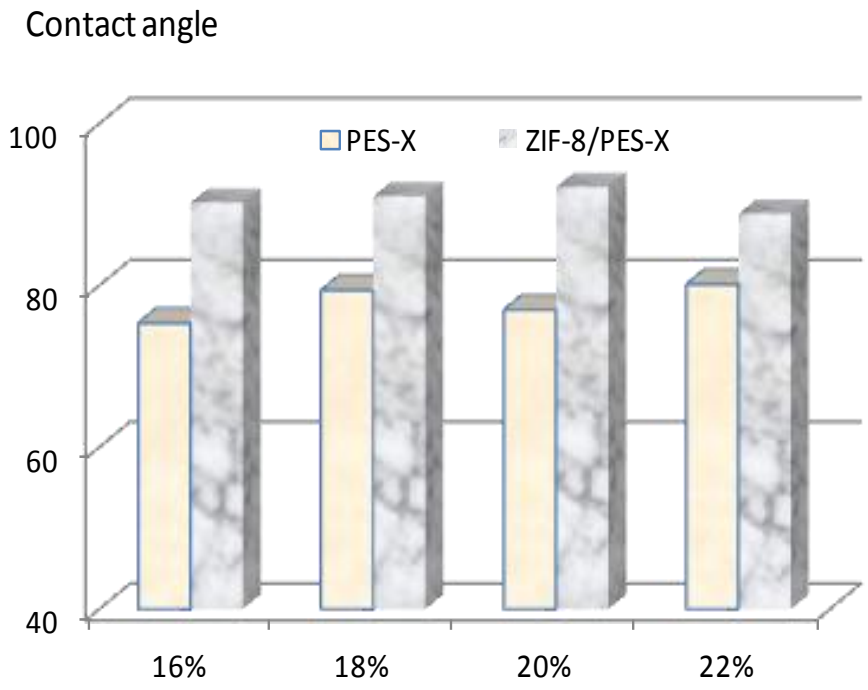

Fig.7 Water contact angle of the membranes. PES-X, supporting membranes. ZIF-8/PES-X, PES supported ZIF-8 membranes. X indicates the polymer concentration of the support casting solution.

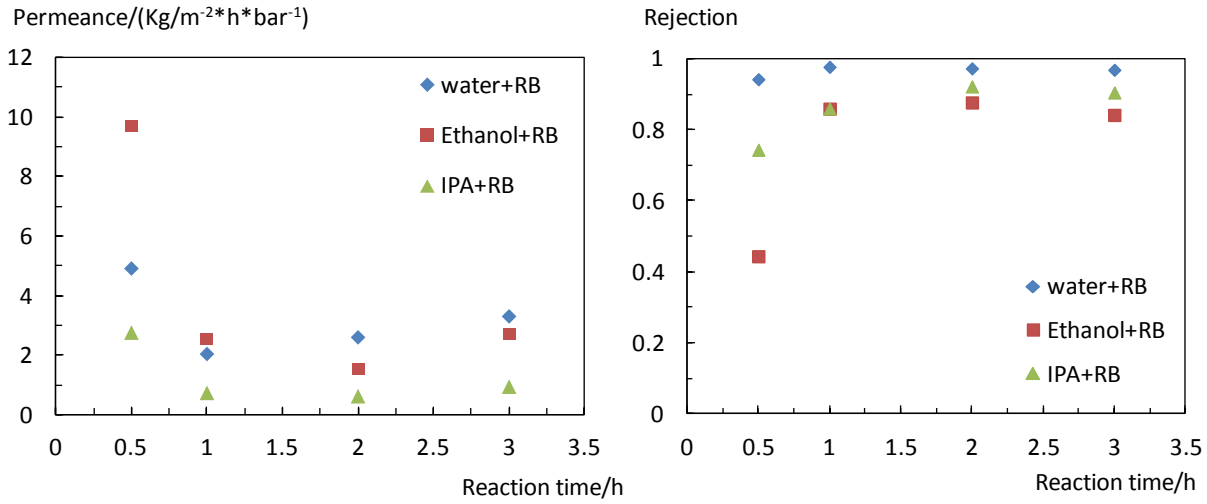

Fig.8 Effect of the interfacial reaction time on the SRNF performance of ZIF-8/PES-18% membranes.

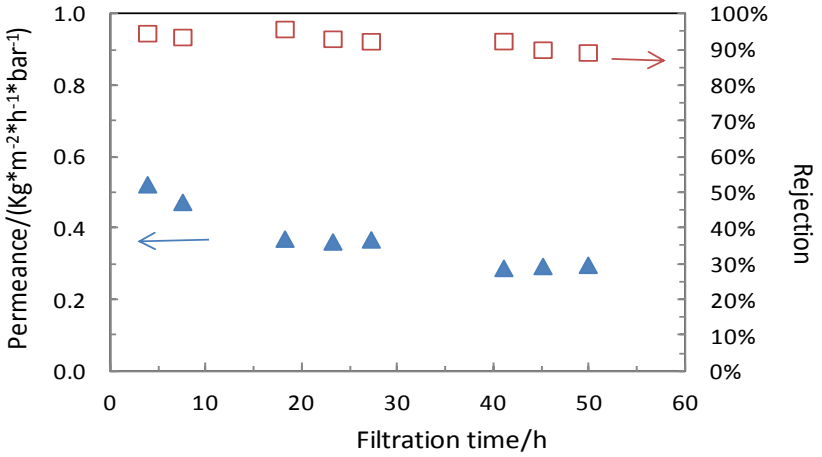

Fig. 9 The results of 50 h SRNF filtration, feed RB in IPA, membrane ZIF-8(1h)/PES-20%.

Table 1 Average (R_a) and root-mean-square surface roughness (R_{ms}) of the membranes as calculated from the AFM-analysis. PES-X, supporting membranes; ZIF-8/PES-X, PES supported ZIF-8 membranes, interfacial reaction time 1h, X indicates the polymer concentration of the support casting solution.

Surface roughness	Membranes					
(scanned area)	PES 16%	ZIF-8/PES16%	PES 18%	ZIF-8/PES18%	PES 20%	ZIF-8/PES20%
R_a (5μmX5μm)	12.0 nm	30.4 nm	11.2 nm	21.6 nm	9.74 nm	19.2 nm
R_a (1μmX1μm)	3.46 nm	7.0 nm	2.71 nm	4.34 nm	2.34 nm	5.32 nm
R_{ms} (5μmX5μm)	16.9 nm	40.5 nm	18.3 nm	29.5 nm	12.19 nm	24.0 nm
R_{ms} (1μmX1μm)	4.35 nm	9.2 nm	3.43 nm	5.48 nm	2.94 nm	6.79 nm