Electronic Supplementary Information

Polymer membrane wearing a mineral coating for enhanced curling resistance and surface wettability

Hao-Cheng Yang, Yi-Fu Chen, Yi-Ning Jin, Chen Ye, Hanying Li and Zhi-Kang Xu*
MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Experimental Section

Materials

Polypropylene microfiltration membranes were obtained from Membrana GmbH (Germany) and Beijing Normal University (China), respectively. One was prepared by thermally induced phase separation with mean pore size of 0.2 μm and porosity of 75%, another was prepared by biaxially orientation with mean pore size of 0.2×0.02 μm and porosity of 45%. Poly(vinylidene fluoride) (PVDF) microfiltration membranes (mean pore size ~0.45 μm) were purchased from Yibo Co., Ltd. (China). The membranes were cut into rounds with a diameter of 25 mm and rinsed by acetone under oscillation overnight. Then the membrane samples were dried in a vacuum oven at 40 °C. Dopamine hydrochloride and PEI (Mw=600 Da) were procured from Sigma-Aldrich and Aladdin Co. respectively. Other reagents such as zirconium sulfate ($Zr(SO_4)_2$), tris(hydroxymethyl) aminomethane, hydrochloric acid, ethanol and acetone were obtained from Chemical Reagent Co., Ltd. (China) and used without further purification.

ZrO_2 mineralization

The deposition process was conducted as described in previous work.[16b] Firstly, the membranes were immersed into the dopamine/PEI mixed solution (Tris-buffer solution, pH=8.5, 50 mM) for 4 hr under room temperature. The concentration of dopamine and PEI were 2 mg/mL, respectively. Then the membranes were rinsed by the de-ionic water and dried in a vacuum oven.

0.17 mg $Zr(SO_4)_2·4H_2O$ was dissolved in 10 mL HCl solution. The concentration of HCl is 10 mM. The as-prepared membranes were immersed into the solution and mineralized for 6 hr under 25 °C. Then the membranes were washed by de-ionic water and dried for further characterization. We tuned the temperature, HCl concentration and reaction time respectively to investigate the effects of hydrolysis conditions on mineralization.

Characterization

The surface morphologies of membranes were characterized by field emission scanning electron microscopy (FESEM, Hitachi, S4800, Japan). The surface chemistries were revealed by attenuated total reflectance Fourier transform infrared spectrophotometer (FT-IR/ATR, Thermo, Nicolet 6700, USA) and X-ray photoelectron spectroscopy (PerkinElmer, USA). The mass fraction of ZrO_2 in the mineralized membranes were detected by a thermogravimetric analyzer (TGA, TA Instruments, TA-Q50, USA). The temperature was elevated from 50 °C to 700 °C with a heating rate of 20 °C/min under air.

The surface wettability was characterized by measuring static contact angles from a contact angle system (MAIST Vision Inspection & Measurement Co. Ltd., DropMeter A-200, China), and three data points were collected for each oil during the OCA measurement. The stress-stain curves were obtained by a tensile test instrument (RGM-4000, Shenzhen REGER Instrument Co., Ltd., China). The thermal shrinkage was evaluated by measuring the area of membranes before and after treatment under 140 °C for 1 h. Three parallel samples were employed in this experiment.

The oil-in-water emulsions were prepared as reported in our previous work. Briefly, the oils including diesel, gasoline, petroleum ether and n-hexane were mixed with water in 1/99 (v/v) respectively, and 0.02 mg sodium dodecyl sulfate was dissolved in per mL of solution as the emulsifier. The mixtures were stirring under 3000 rpm for 6 h until uniform emulsions were obtained. The permeate flux was measured by a dead-end filtration apparatus (Millipore) the trans-membrane pressure was provided and adjusted by a nitrogen tank. Before the test, the membranes were pre-compacted by the pure water under

0.3 MPa to reach a stable membrane structure and the permeate flux measurement was performed under 0.04 MPa. The permeate flux was obtained by averaging the whole flux during the first 5 min, and three points were measured for each emulsion. The rejection was detected by the UV-vis spectrophotometer (Shimadzu, UV 2450, Japan).

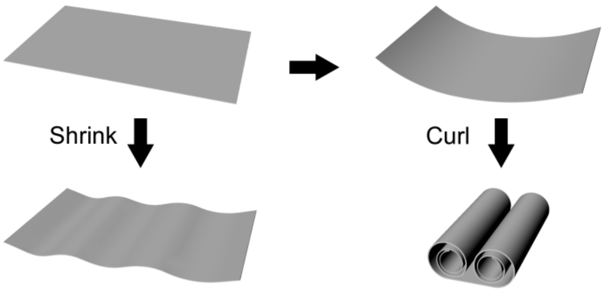

Figure S1 Schematic representation of shrinkage and curling for polymer membranes.

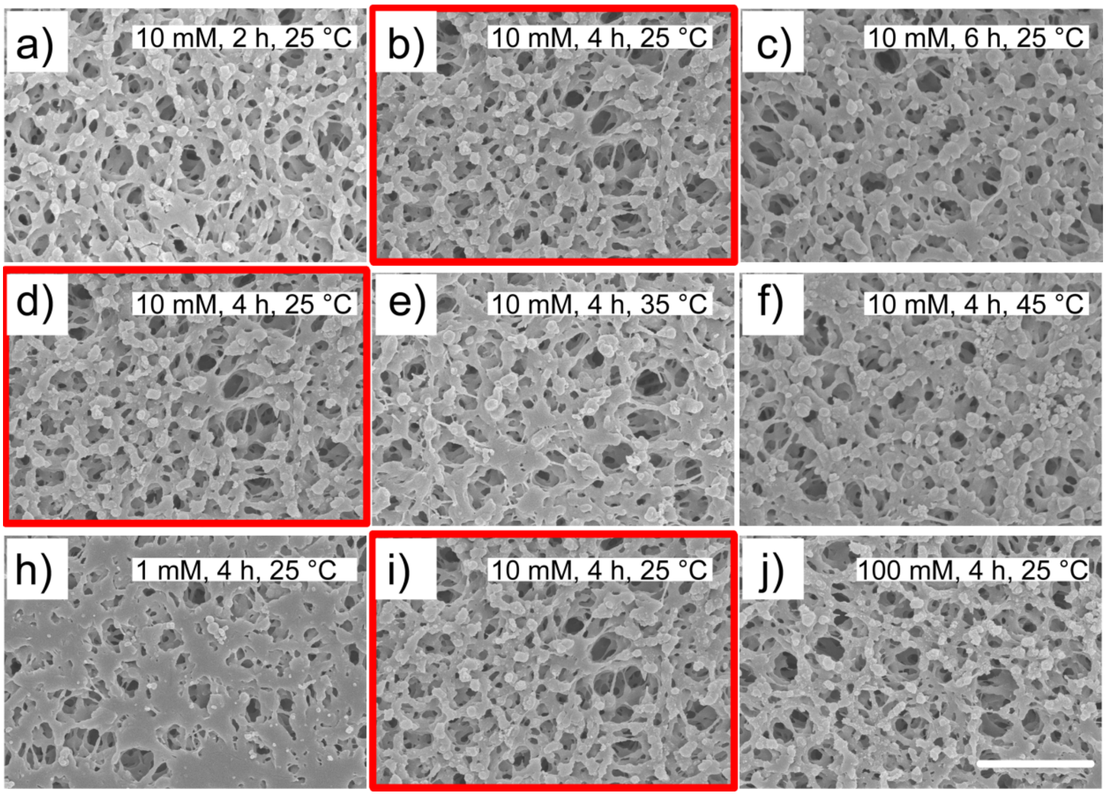

Figure S2 SEM images of ZrO_2-wrapped polypropylene membranes fabricated with different hydrolysis time, temperature and HCl concentration. The scale bar is 1 μm.

Table S1 The weight percent left of the membranes after TGA

Preparation parameters			TGA [a] (%)
Temperature (°C)	Reaction time (h)	HCl con. (mM)	
25	2	10	9.6
25	4	10	11.7
25	6	10	13.4
25	4	1	13.7
25	4	100	7.0
35	4	10	12.9
45	4	10	11.8
Nascent membrane			3.5
PDA/PEI-deposited membrane			4.9

[a] The weight percent left after heating cycle is complete.

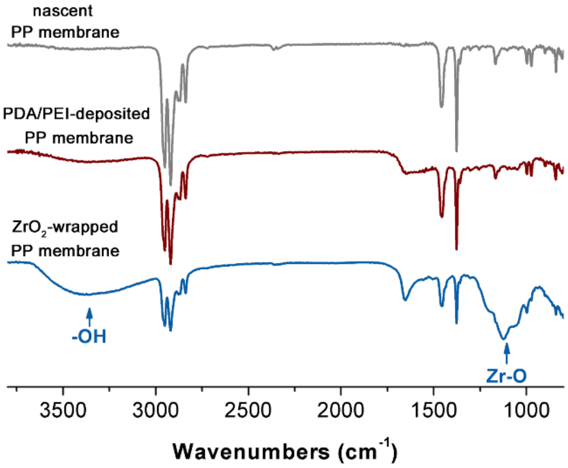

Figure S3 FT-IR/ATR spectra of the nascent, PDA/PEI-deposited and ZrO_2-wrapped polypropylene membranes.

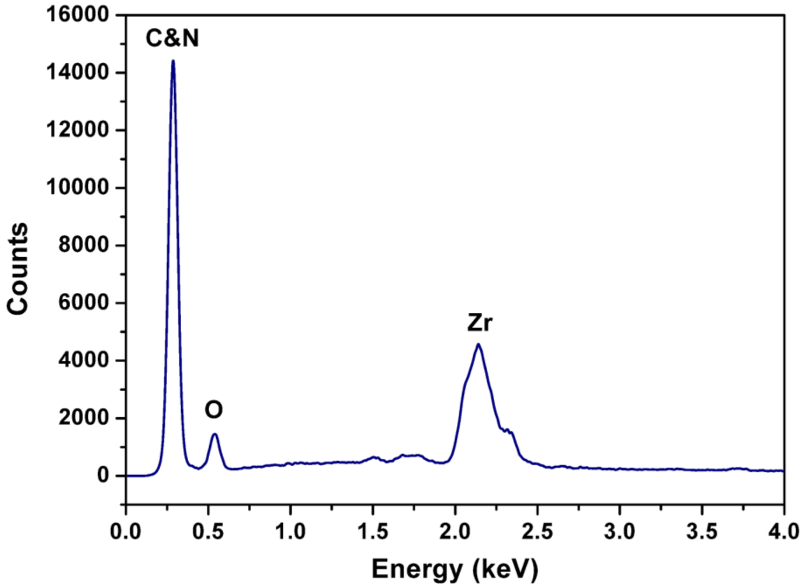

Figure S4 Typical EDX spectrum from the cross-section of a ZrO_2-wrapped membrane.

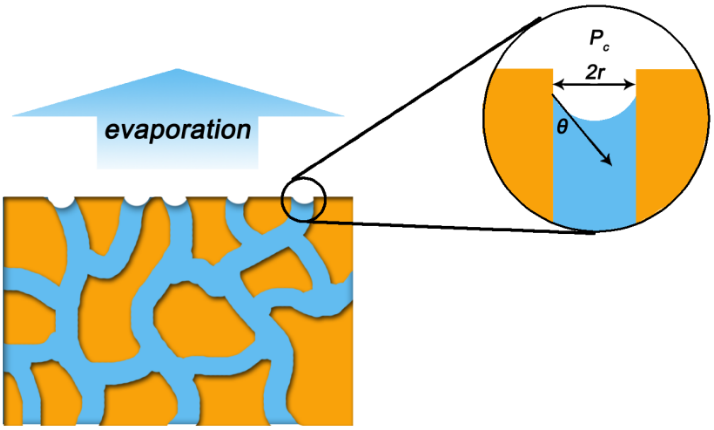

Figure S5 Schematic representation of the internal pressure in hydrophilic pores.

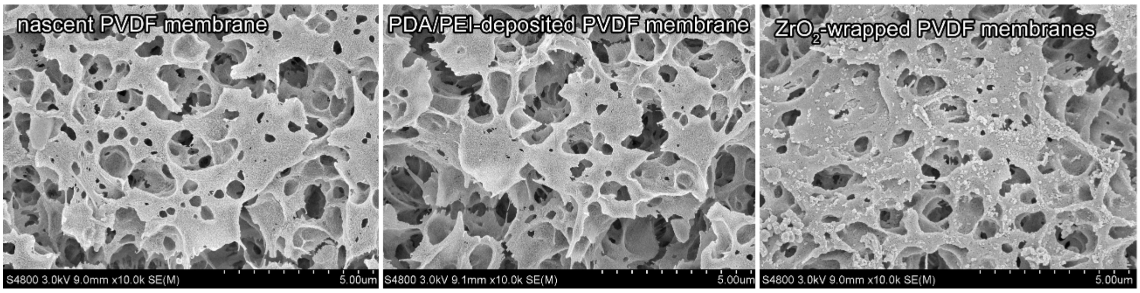

Figure S6 SEM images of the nascent, PDA/PEI-deposited and ZrO_2-wrapped PVDF membranes.

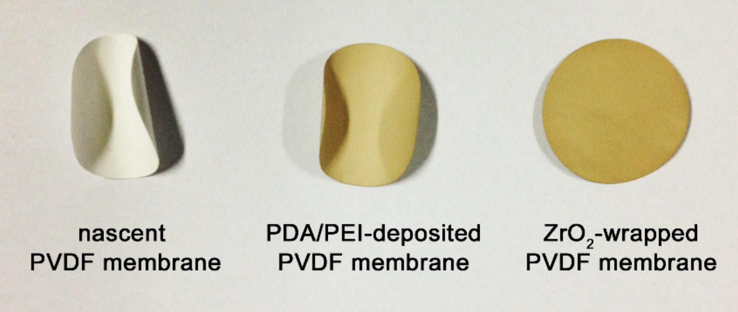

Figure S7 Digital photograph of the nascent, PDA/PEI-deposited and ZrO_2-wrapped PVDF membranes after thermal treated at 120 °C for 1 h.

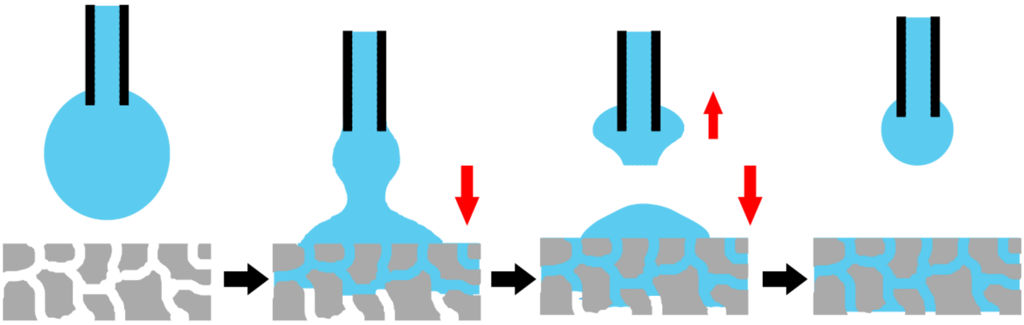

Figure S8 Schematic representation for breakup of a water drop when it contacts a hydrophilic porous substrate.

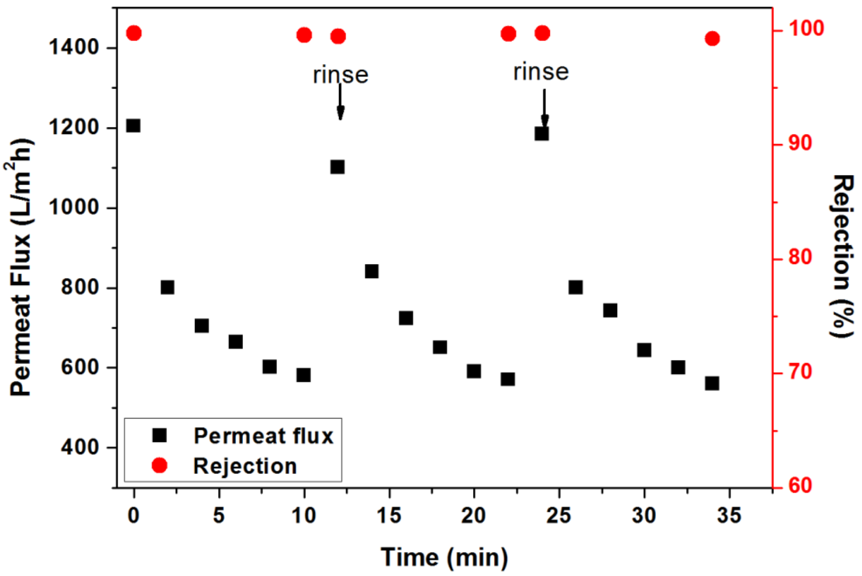

Figure 9 The flux recovery of ZrO_2-wrapped membranes during the diesel-in-water emulsion filtration.