

Supplementary Information for
Surface-Modified polyimide on novel porous ceramic membranes for
pervaporation desalination

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Text S1. Materials and chemicals.

Pyromellitic dianhydride (abbreviated as PMDA, CAS:89-32-7) and 4,4-Diaminodiphenyl ether (abbreviated as ODA, CAS:101-80-4), (All AR, purchased from Shanghai Aladdin Biochemical Technology Co.). N,N-dimethylformamide (abbreviated as DMF, AR, CAS:68-12-2, purchased from Chengdu Cologne Chemical Co., Ltd.). Anhydrous ethanol (AR, CAS:64-17-5, purchased from Chengdu Lixinhe Chemical Co.). Coal fly ash (abbreviated as CFA, industrial solid state waste, was obtained from Ningbo power plant, Zhejiang Province, China.). Other chemicals like Molybdenum trioxide (MoO_3 , AR, >99%, CAS:1313-27-5), Sodium metasilicate nonahydrate ($\text{NaSiO}_3 \cdot 9\text{H}_2\text{O}$, AR, >99%, CAS: 13517-24-3), Aluminium hydroxide ($\text{Al}(\text{OH})_3$, AR, >99%, CAS: 21645-51-2), Sodium chloride (NaCl , AR, $\geq 99\%$, CAS: 7647-14-5), Magnesium chloride (MgCl_2 , AR, $\geq 99\%$, CAS:7786-30-3), Sodium sulfate anhydrous (Na_2SO_4 , AR, $\geq 99\%$, CAS:7757-82-6) and Magnesium sulfate (MgSO_4 , AR, $\geq 99\%$, CAS:7487-88-9) were obtained from Chengdu Jinshan Chemical Reagent Co., Ltd., China.

Text S2. Material characterization.

The morphology of composite membranes were analyzed using field emission scanning electron microscopy (SEM, Sigma 360, ZEISS, Germany). The surface functional groups of PAA and PI were characterized using attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR, Nicolet IS20, Thermo Fisher, USA) in the 4000-800 cm^{-1} range. To assess the hydrophilicity of the composite membranes, the water contact angle of the membranes was measured using a KRÜSS DSA 25S instrument (KRÜSS, Germany) at a temperature of $25\pm 1^\circ\text{C}$ and a relative humidity of 51.2%. The electrical properties of the membrane surface were measured using a solid surface zeta potential tester (Surpass3, Anton Paar). The crystalline shape of the porous ceramic membranes was tested and analyzed using an X-ray diffractometer (XRD, Rigaku Smartlab, Japan). The surface pore size of the composite membranes was analyzed using a fully automated specific surface and porosity analyzer (BET, Micromeritics ASAP 2460, USA) (Nitrogen adsorption temperature: 77.3 K, Degassing temperature: 200°C , Degassing time: 6 h. $U_{\text{rel}}(k=2)=4.0\%$). The surface roughness of the membranes was analyzed using an atomic force microscope (AFM, Dimension Icon, Bruker, Germany).

Text S3. Preparation of the porous ceramic membrane.

As shown in **Figure S1**, Fly ash (referred to as CFA), $\text{Al}(\text{OH})_3$, MoO_3 , $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ and Zirconia spheres were weighed and mixed in a certain proportion in a corundum ball milling jar. At the same time, a quantitative amount of anhydrous ethanol was added,

As shown in **Figure S1**, fly ash (10 g), $\text{Al}(\text{OH})_3$ (16.54 g), MoO_3 (5.31 g), $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ (10.62 g), and zirconia balls were weighed in a specific ratio and mixed in a corundum ball milling jar. At the same time, 60 ml of anhydrous ethanol was added, and the mixture was ball-milled in a planetary ball mill for 12 h. After ball-milling, the mixture was dried in an oven at 80°C for 8 h until the mixture was completely dry, and then it was ground, sieved with a 200-mesh sieve, and the resulting fine powder was put into a cylindrical mold with a diameter of 38mm for pressing, and pressed into ceramic billets with a manual tablet press (6 MPa).

The pressed ceramic blanks were fired in a muffle furnace, heated at $5^\circ\text{C}/\text{min}^{-1}$ from room temperature to 200°C and held for 60 min, then heated at $3^\circ\text{C}/\text{min}^{-1}$ from 200°C to 1175°C and held for 120 min at 1175°C . The porous ceramic membranes were sintered, cooled, rinsed, and immersed in deionized water for 12 h to remove impurities, and finally dried in an oven at 80°C for 8 h for subsequent experiments.

Text S4. Preparation of PAA.

4,4-Diaminodiphenyl ether was dissolved in N,N-dimethylformamide solution (magnetic stirring 500 r/min for 15 min). Subsequently, Pyromellitic dianhydride was added in small quantities over a period of 2 h. The dianhydride was added to the solution in small amounts. With the continuous addition of benzene tetracarboxylic acid dianhydride, the viscosity of the system continued to increase, the solution gradually turned from colorless to light yellow, and continued stirring for 4 h, resulting in a light yellow transparent viscous liquid Polyacrylamide (abbreviate PAA) solution. The 8wt%, 10wt% and 12wt% PAA solutions were prepared according to the above method for subsequent experiments.

Text S5. Preparation of the PI/ceramic membrane.

As shown in **Figure S 2**, using a KW-4A dual-speed tabletop coating machine, first attach the porous ceramic membrane to the bottom using a vacuum pump. Then, while during low-speed operation (500 RPM, 10 seconds), quickly add 2 ml of pre-prepared PAA solution to the center of the porous ceramic membrane, then cover with a protective cover and wait for high-speed operation (2000 RPM, 15 seconds) to complete. Finally, the uniformly coated composite film is placed in a 60°C oven for pre-drying and curing in preparation for subsequent thermoimidization.

The thermoimidization was carried out at a temperature gradient of 70°C, 160°C, and 250°C for 1 h with a heating rate of 2°C/min⁻¹ [36-38]. After natural cooling of the muffle furnace, polyimide-modified ceramic composite films were obtained (**Figure S 3b**). 8wt%, 10wt% and 12wt% of PAA were thermally imidized to produce composite membrane named as PI-X/ceramic membrane (X=8,10,12).

Text S6. Desalination experiment.

The PI/Ceramic membrane was placed in the middle of the membrane module to ensure that it did not leak, and a hose was used to connect the membrane module, the gas collection cylinder (note that the glass catheter in the cylinder is long in and short out), and the safety device to ensure that it did not leak, and the other end of the hose was connected to the vacuum pump. When the temperature of the water bath reaches 60°C and the temperature of the water in the special cooling tank is low enough, turn on the vacuum pump to make the device form a vacuum state, and the pressure reaches 0.1 MPa, put the membrane module with the composite membrane installed into the water bath on the left side, and put the gas collection bottle into the special cooling tank on the right side, and the device installation is completed.



Figure S1. Illustration of the preparing method of the porous ceramic membrane.

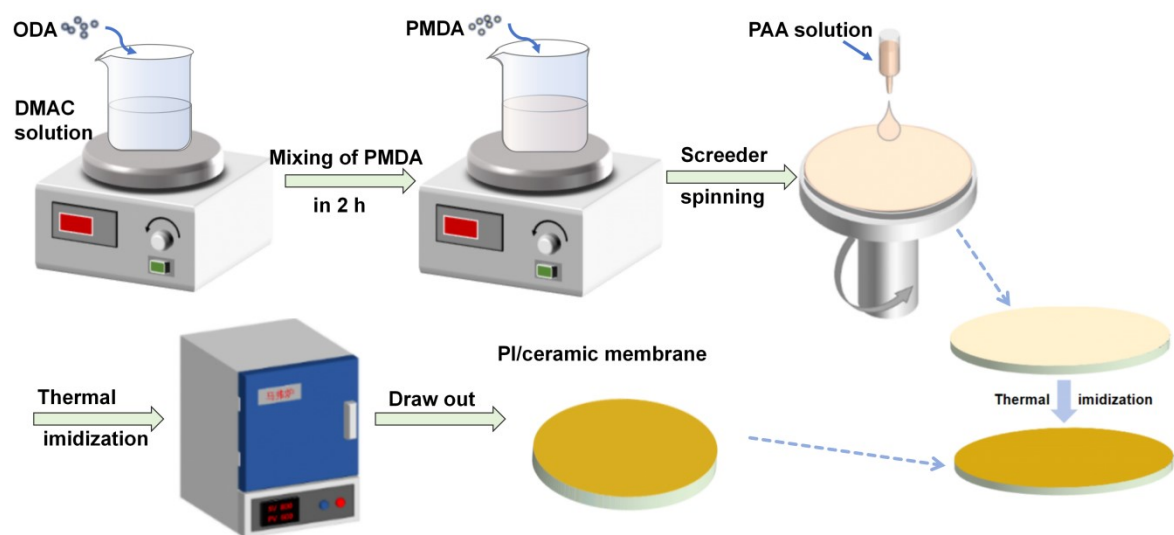


Figure S2. Illustration of the preparing method of the PI/ceramic membrane.

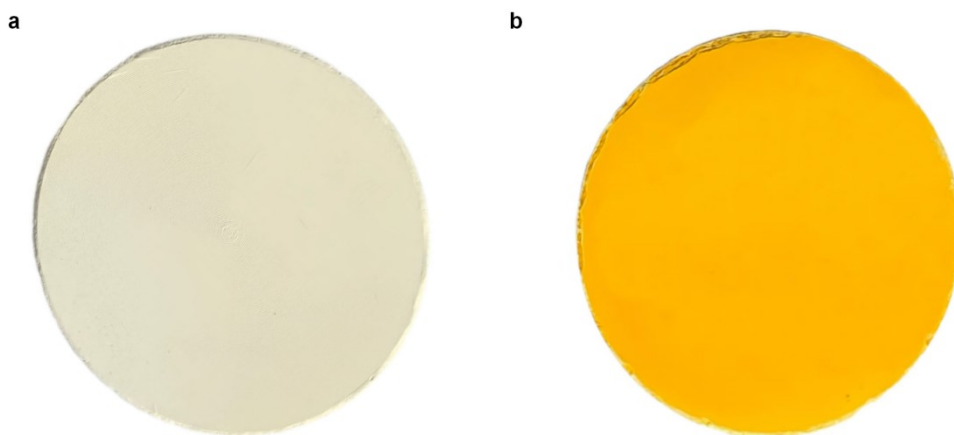


Figure S3. Membrane morphology of porous ceramic membrane (a) and PI/ceramic membrane (b).

Table S1. Surface roughness parameters of porous ceramic membrane and PI/ceramic membrane.

Membrane	Roughness	
	Ra(nm)	RMS(nm)
Porous ceramic membrane	322	220
PI/Ceramic membrane	30.3	22.8

Table S2. Comparison of the performance with similar researches about PV desalination

Membrane	Temperature (°C)	salt concentrat	water flux (L/(m ² ·h))	Salt rejection (%)	references
PDMS membrane	85	7	36	99.80	[1]
PEI/GO membrane	65	20	8.40	> 99.90	[2]
Polyester tubular	25	3.5	7.9	99.80	[3]
PVA/MA/silica <u>hybrid</u> membrane	22	0.2	6.93	> 99.50	[4]
GO/PI MMMs membrane	75	10	10.70	99.80	[5]
PVA-CNT membrane	25	3.5	6.1	99.95	[6]
PVA membrane	70.85	3.0	7.4	99.90	[7]
PI-10/Ceramic membrane	60	3.5	9.36	> 99.90	This study
PI-10/Ceramic membrane	90	3.5	10.88	> 99.90	This study

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