

Electronic Supporting Information:

“Pre-seeding”-assisted synthesis of high performance polyamide-zeolite nanocomposite membrane for water purification

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Experimental

Zeolite crystals Fabrication

The zeolite crystals were fabricated from zeolite Y microcrystals by a simple grinding method. The preparation process was as follows. First, a specific amount of microcrystal zeolite powder was loaded in the grinding machine for a milling time of 3 hours. Second, the milled powder was dispersed in an aqueous solution under ultrasonication for 30 min, and then the large zeolite particles were removed by centrifugation at 2000 rpm for 20 min. Third, the small zeolite crystals were recovered by centrifugation at 5000 rpm for 30 min, and then the recovered products were dried at 120°C for 1 day. Finally, the products were stored in a dry box for use in organic-inorganic polymer membrane preparation. The products were illustrated by the field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) and Dynamic Light Scattering (DLS) (Fig. S1). The results indicated that the size distribution of the as-prepared crystal was narrow (~250 nm) and the zeolite Y structure was not destroyed after grinding.

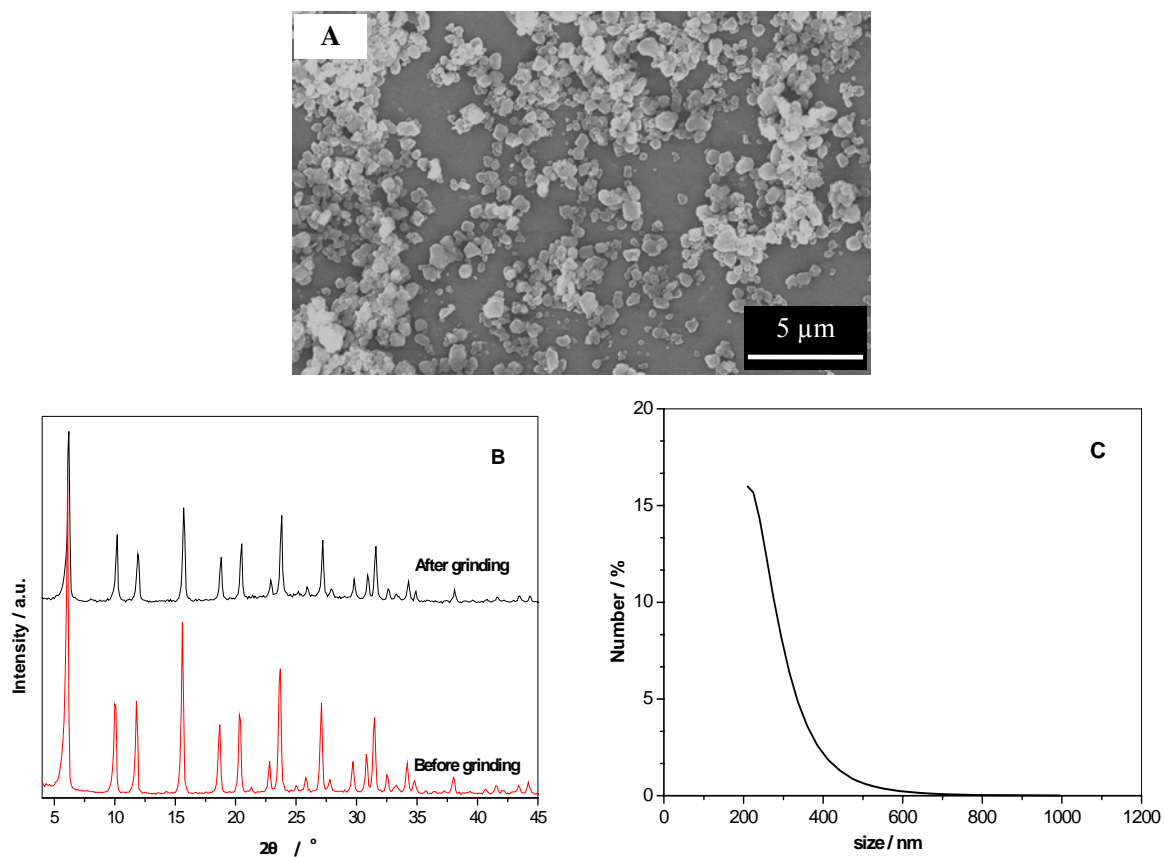


Fig. S1 FE-SEM images (A), XRD patterns (B) and DLS patterns (C) of the zeolite crystals fabricated from zeolite Y microcrystals by a simple grinding method.

Polyamide-zeolite (PZ) membrane and pure (PA) polyamide membrane Fabrication

Both PZ and PA membranes were prepared on polysulfone (PSF) ultrafiltration membranes (provided by NITTO DENKO Co., Japan) by interfacial polymerization. The PZ membranes were prepared by a novel method and the conventional method, respectively. The procedure used for the novel method was as follows (Fig. S2). First, the PSF support was placed in an aqueous solution of 2 wt% MPD and 0.15 wt% sodium lauryl sulfate for 2 min, and then the excess solution was poured off. Subsequently, the PSF support (diameter: 4.0 cm) was uniformly coated with a 0.2 ml well-dispersed solution of 0.05~0.6% (wt%) zeolite, 0.02~0.05% TMC (wt%), and 5~15% (wt%) ethanol in a hexane phase. After unforced evaporation of the excess solvent, the solution of 0.1% (wt%) TMC and hexane was immediately and mildly poured onto the support for a 40~50 second polymerization reaction, and then the excess of the solution was poured off and the membrane was dried in air for

5~10 min. Finally, the membrane was rinsed with deionized water. The well-dispersed solution of zeolite, TMC and ethanol in the hexane phase was prepared as follows. A specific amount of dry Y zeolite crystals were completely dispersed in a hexane and ethanol solution, and was subjected to ultrasonication for 30 min at room temperature. Then a specific amount of TMC was added and was under ultrasonication for 10 min at room temperature just before preassembling zeolite on the PSF support that was impregnated with MPD solution.

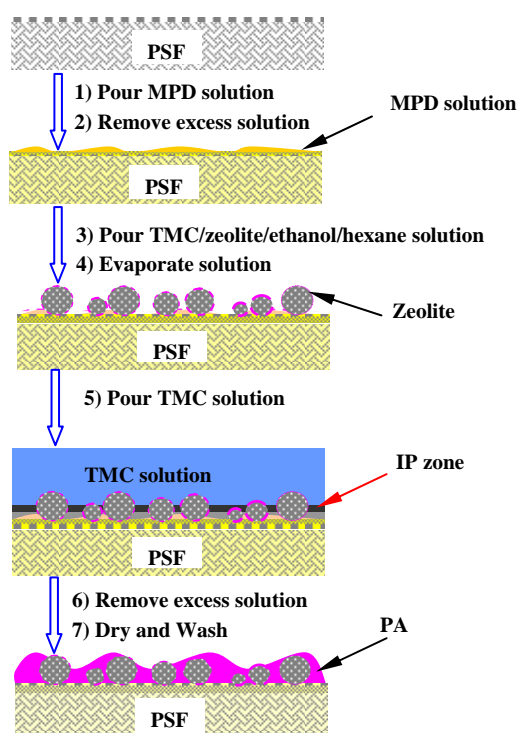


Fig. S2 Schematic representation of the fabrication of PZ membranes on the PSF supports via the novel method.

The process of the conventional method was as follows (Fig. S3). First, the MPD solution without (or with) zeolite was mildly poured on the PSF support. Second, the solution of TMC with (or without) zeolite was immediately and mildly poured on the PSF support after removal of the excess solution. Finally, the as-prepared PZ nanocomposite membranes were dried in air atmosphere, and then were sufficiently washed by the deionized water. The solution of MPD or TMC containing zeolite was prepared as follows. A specific amount of dry FAU zeolite was added into the TMC or MPD solution under ultrasonication for 20 min at

room temperature immediately prior to interfacial polymerization. The PA membrane was prepared using the same process without zeolite.

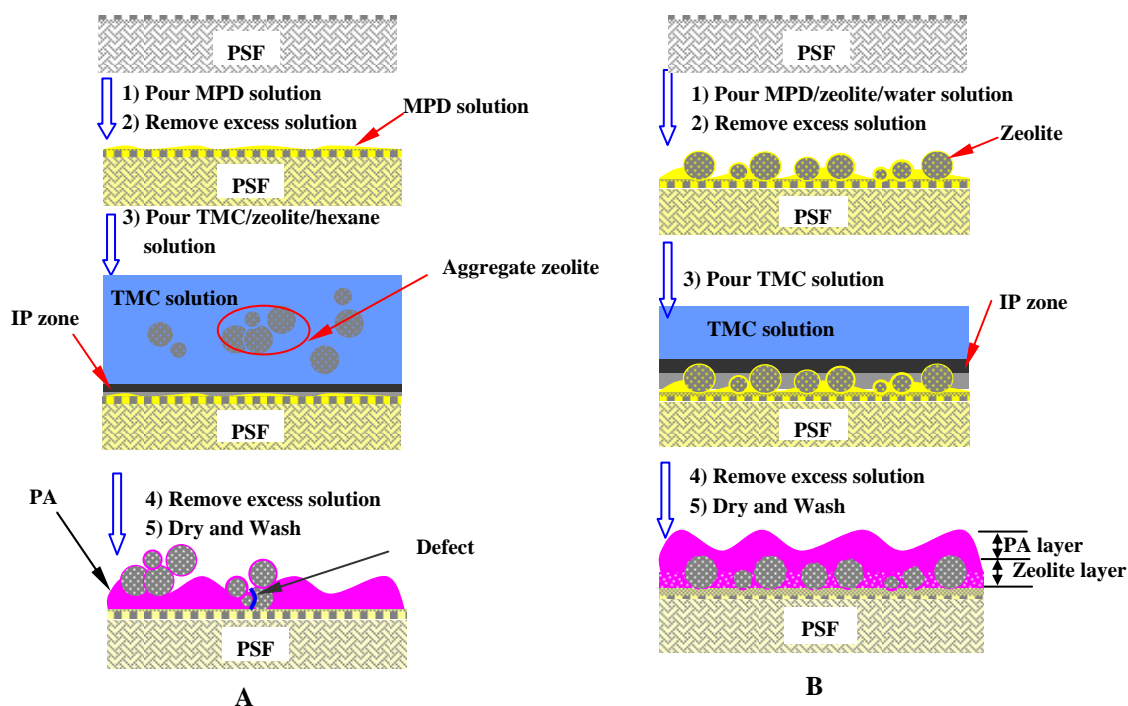


Fig. S3 Schematic representation of the PZ membranes fabricated on the PSF supports via the conventional method. A) zeolite added in the TMC-hexane solution; B) zeolite added in MPD aqueous solution.

Characterization

The FT-IR patterns were obtained using a FTIR-8300 (Shimadzu, Japan). SEM-EDX images were obtained using a JEOL S5200 (Hitachi, Japan). The XRD patterns were obtained using a Rint 2000 (Rigaku, Japan). The DLS patterns were obtained using a PLS-450 (Otsuka, Japan). The effective membrane area was 5.1 cm². Rejections and solution fluxes of probe molecules were collected through the PZ and PA membranes. All results were obtained with 2000 ppm (wt%) NaCl and 500 ppm (wt%) ethanol, IPA, s-butanol, glucose and maltose in deionized water and at an operating pressure of 1.5 MPa and a temperature of 298 K. The electric conductivity and TC rejections of inorganic salt and organic solution were characterized using a conductivity meter ES-12 (Horiba, Japan) and a TOC-VE (Shimadzu, Japan). Rejection and permeability were calculated using the following equations:

$$\text{Rejection (\%)} = \left(1 - \frac{c_p}{c_f}\right) \times 100$$

$$\text{Water permeability} = \frac{\Delta v}{t \cdot \Delta p \cdot s}$$

where c_p (mg/l) is the permeate concentration, c_f (mg/l) is the feed concentration, Δv is the permeate volume (m^3), t is the permeate time (s), Δp is the operation pressure (Pa), and s is the effective membrane area (m^2).

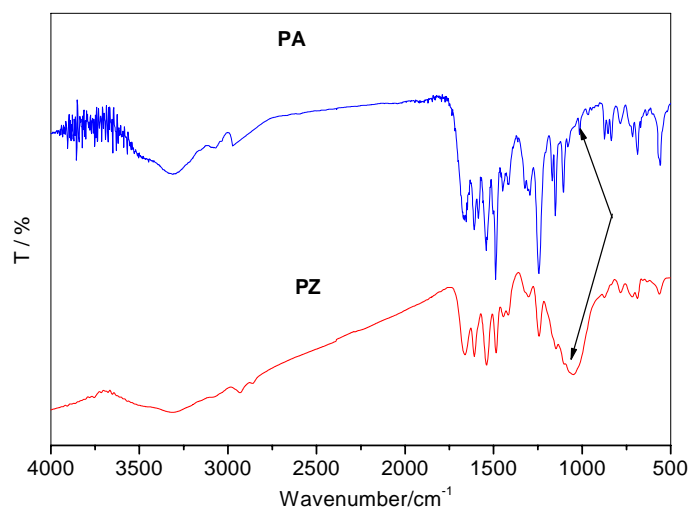


Fig. S4 FT-IR spectra of the PA and PZ (0.4 wt%) membranes after removal of the membranes from the PSF supports.

The band at 1660 cm^{-1} is characteristic of C=O stretch, the 1547 cm^{-1} band is due to C-N stretch, the 1609 cm^{-1} band is due to polyamide aromatic ring breathing, and the 786 cm^{-1} band can be ascribed to amide. The narrow peaks between 1200 and 1000 cm^{-1} correspond to the C-O stretching vibrations in pure PA membrane. By contrast, multiple wide peaks appear between 1200 and 1000 cm^{-1} in the PZ membrane. The intensity of these peaks greatly increased as zeolite was loaded into the membrane, which indicated the assembled-zeolite was incorporated within the polyamide membrane and removed from the PSF support with polyamide membrane during preparation of FT-IR sample. This was due to the presence of Si-O groups of zeolite (L.J. Bellamy, *The Infrared Spectra of Complex Molecules*, Chapman

and Hall Ltd., London, 1975.), which appeared almost at the same frequency of C-O stretching.

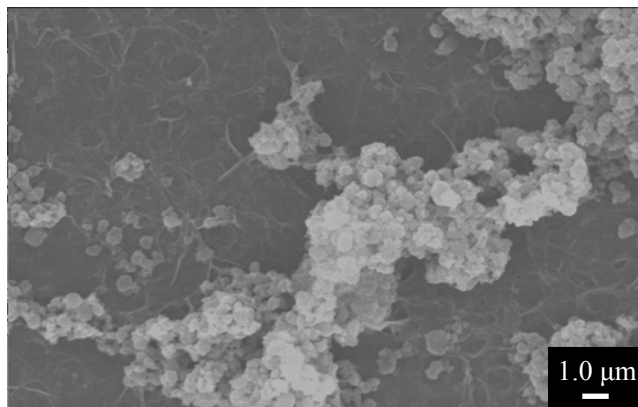


Fig. S5 FE-SEM images of the PZ nanocomposite membrane fabricated by adding zeolites in the TMC-hexane solution. Many aggregate zeolite crystals can be seen on the membrane surface, which possibly lead to the resultant membrane with large defects.

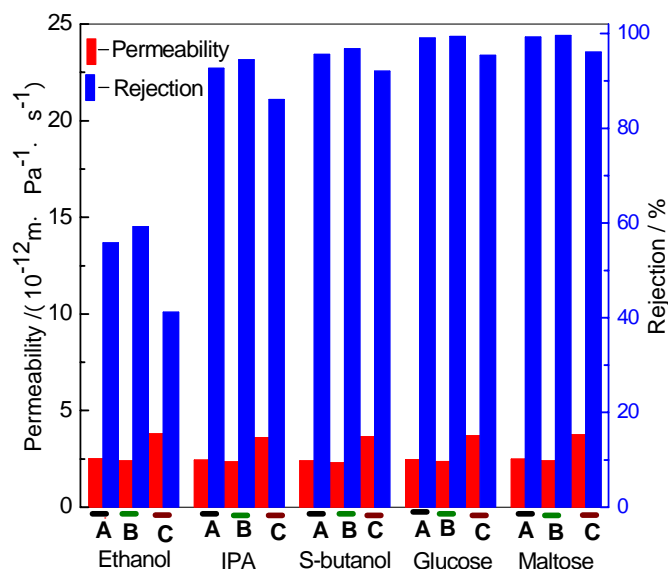


Fig. S6 Permeability properties of the pure PA membrane (A) and PZ membranes prepared by conventional method (B, C) for a series of neutral organic solutions of different molecular sizes at a temperature of 298 K and pressure of 1.5 MPa. Membrane B was prepared by adding zeolite in MPD aqueous solution; Membrane C was prepared by adding zeolite in TMC/hexane solution.

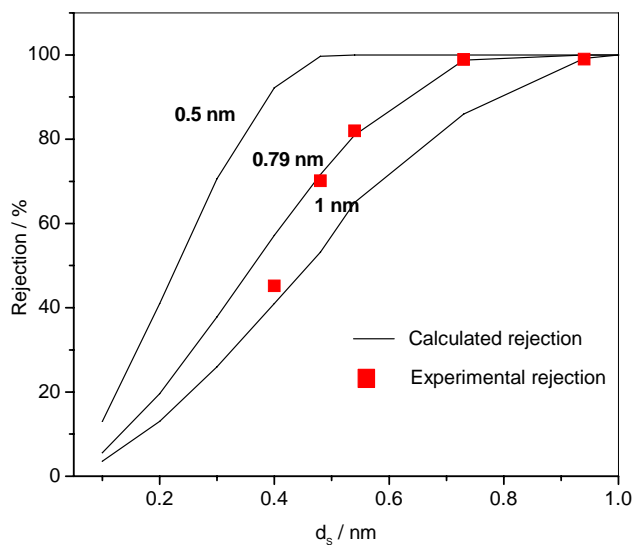


Fig. S7 Calculated and experimental rejections for the PZ (0.4 wt%) nanocomposite membrane with the neutral molecules of different sizes.

The solid curve represents the calculated rejections of the neutral organic solutes for a membrane with a uniform pore size (i.e., diameter) (d_p) of 0.5 nm, 0.79 nm and 1 nm using the Ferry equation (Eqn S1), respectively, which has been used to correlate the rejection of spherical solutes for membranes with uniform pore size distributions (P. Aimar, M. Meireles, V. Sanchez, *J. Membr. Sci.* **1990**, 54, 321.). Herein, the “pore” size of the PZ membrane was approximately calculated by the method. From the observed percent rejections of the neutral organic molecules and their estimated diameters, the effective “pore” size of the PZ membrane was calculated to be ca. 0.79 nm by fitting the experimental rejection data to an “ d_p ” value of 0.79 nm for the effective “pore” diameter.

$$\text{Eqn} \quad R (\%) = \left[1 - \left(1 - \frac{d_s}{d_p} \right)^2 \right]^2 \times 100 \quad (\text{S1})$$

where R is the percent rejection, d_s is the solute diameter, and d_p is the pore size (diameter) of the membrane (assuming a uniform pore size).