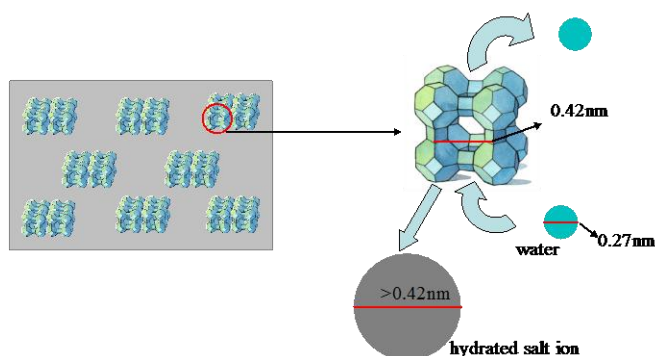


Supporting Information



Scheme 1 Schematic of ion sieving TFN membrane for desalination.

Materials

Polysulfone (PSF) ultrafiltration (UF) membrane (MWCO: 20,000) was used as the support and was purchased from the Center of Water Treatment Technology, Hangzhou, China. NaA-type zeolites were synthesized in this lab. Tetraethyl orthosilicate (TEOS, 98%), tetramethylammonium hydroxide (TMAOH, 25wt% in water), m-phenylenediamine (MPD, >99%), and trimesoyl chloride (TMC, 98%) were from Sigma-Aldrich, USA. Ethanol and hexane were purchased locally. Deionized water was used in all experiments.

Characterization.

The transmission FT-IR spectra of NaA particles were measured with a Tenson27 spectrophotometer (Bruker Germany) with a resolution of 4 cm^{-1} . The grazing angle FT-IR spectra were recorded with a resolution of 4 cm^{-1} , an incidence angle of 80° , and 256 accumulating scans.

The crystalline structures of the zeolites were characterized at room temperature using a Brucker's D-8 advanced wide-angle X-ray diffractometer. The X-ray source was Ni-filtered Cu K α radiation (40 kV, 30mA). The patterns were recorded in the reflection mode at an angle 2θ over a range of 5–60° at a scan rate of 8° /min.

Surface and cross-section morphologies of membranes were examined by SEM (SIRION-100, FEI, USA) at an accelerating voltage of 5 kV.

The cross-section of the membrane was also examined by TEM (JEM-1230, JEOL, Japan) at an accelerating voltage of 100 kV. Ultrathin film samples for TEM were prepared by cutting from the epoxy block with the embedded small pieces of the membrane samples using an ultramicrotome (ULTRACUTE, Reichert-Jung, Austria), and placed on Formvar-coated copper grids.

The XPS spectra were recorded on a Kratos Axis Ultra DLD (Shimadzu-KRATOS, Japan) Infinity Spectrometer. The spectra were measured at a spinning speed of around 4.0 kHz using RF fields of 32 kHz, a contact time of 5 ms, and a recycle delay of 5 s.

NaA zeolite synthesis

The mean particle size of the calcined zeolite nanocrystals is about 70~80 nm. Zeolite nanoparticles (NaA-type) were synthesized by applying a solution with molar composition of 0.3Na₂O:4.5SiO₂:0.6Al₂O₃:9.0(TMA)₂O:400H₂O in a sealed polypropylene bottle. This mixture was stirred for 24 hours and then heated at 40°C under vapor reflux for 10 days. After the reaction mixture was cooled, zeolites were separated from solution by a repeat cycle of one hour centrifugation at 12,000 rpm until pH<8. Then zeolites were added to a 2 wt% polyvinyl alcohol (PVA) solution, and the mixed solution formed a film, and the PVA polymer network was

designed as a temporary barrier to prevent nanoparticle aggregation during the calcination process. The pore-opened zeolite nanoparticles were obtained after the PVA/zeolite hybrid membrane was calcined.

Polyamide and polyamide/zeolite nanocomposite membrane preparation

Polysulfone (PSF) UF membrane was taped on a glass plate, immersed into an aqueous solution of 2% (w/v) m-phenylenediamine (MPD, >99%,) for approximately 20 min, and then was removed. The excess MPD solution on support membrane surface was removed. The MPD saturated UF membrane was then immersed in a solution of 0.2% (w/v) trimesoyl chloride (TMC, 98%) in hexane. After 1 min of reaction, the TMC solution was poured off and the resulting membrane was rinsed with deionized water. Nanocomposite membranes were prepared by scattering 0.006–0.2% (w/v) of the NaA zeolite nanoparticles into the aqueous phase or the organic phase. To improve the dispersion of zeolite nanoparticles, the nanoparticle loaded organic or aqueous phase was ultrasonicated for 20min at room temperature immediately prior to interfacial polymerization.

Reverse osmosis process

The nanocomposite membranes were tested with 2000 ppm NaCl solution at 25°C. Effective permeation area of each membrane was about 44cm². The membranes were pre-compressed for 30min and evaluated under the pressure of 1.6 MPa. The concentration of permeate was measured using conductivity meter. The water flux and solute rejection for all membranes were calculated according to equations (1) and (2):

$$J = \frac{V}{S \times \Delta t} \quad (1)$$

$$R = \frac{C_f - C_p}{C_f} * 100\% \quad (2)$$

Where V is the volume of permeate collected during the operation time Δt , S is the membrane area, C_p and C_f are the solute concentration in the permeate and in the bulk feed solution, respectively.

Results and discussion

SEM, XRD spectra of zeolite nanocrystals

The calcined zeolite nanocrystals were examined by SEM (Figure. 1) and the mean particle size is about 70~80 nm. The XRD pattern of calcined zeolite nanocrystals (Figure. 2) confirms that the zeolite is the A-type.

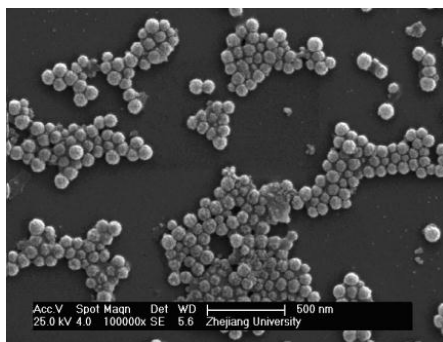


Figure 1 SEM images of synthesized NaA zeolites calcined.

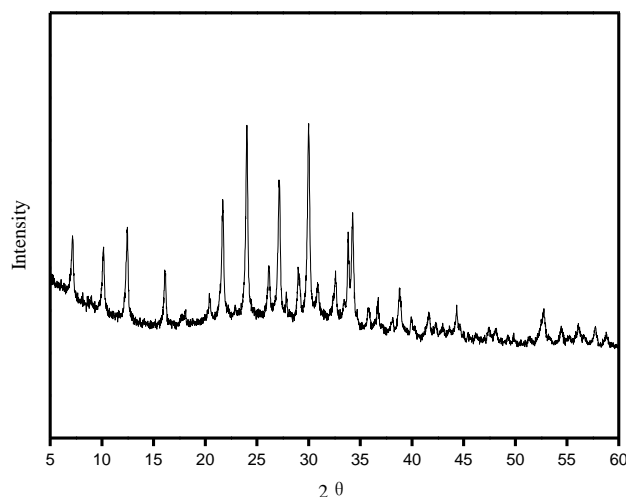


Figure 2 XRD spectra of the synthesized zeolites

Membrane surface morphology

When zeolites were added into the aqueous phase (Figure. 3b), the membrane surface possessed a more nodule structure and was smoother than the bare polyamide membrane. When zeolites were added in the organic phase, the membrane exhibited more “leaf-like” folds on its surface and became rougher (Figure. 3c). It is possible that when nanocrystals scattered in the organic phase, the amine diffusion was promoted, resulting in a higher membrane formation rate and thus a rougher membrane surface.

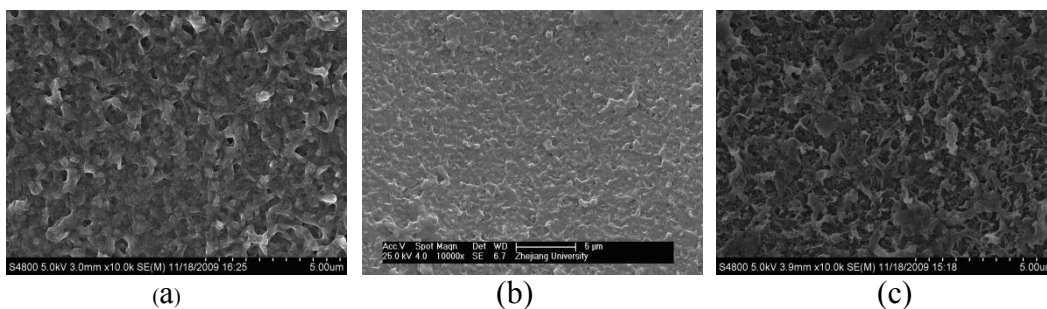


Figure 3 SEM images of (a) bare polyamide membrane, (b) TFN membrane with 0.1 wt% zeolites added in the aqueous phase, (c) TFN membrane with 0.1 wt% zeolites added in the organic phase.