

## SUPPORTING INFORMATION

*for*

### **AEL Zeolite Nanosheet-Poly(amide) Nanocomposite Membranes on $\alpha$ -Alumina Hollow Fibers with Enhanced Pervaporation Properties**

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## Experimental Methods

### *Preparation of $\alpha$ -alumina hollow fibers*

The  $\alpha$ -alumina hollow fibers were prepared as reported in our recent work,<sup>32</sup> with the sintering temperature reduced to 1573 K. Similar to our previous works,<sup>32,33</sup> the composition (wt%) of the spinning dope was 38.0 NMP: 6.8 PES: 54.7 Al<sub>2</sub>O<sub>3</sub>: 0.5 PVP and the spinning of the hollow fibers was carried out with an in-house apparatus constructed at Georgia Tech. The dope and the bore fluid flow rates were 120 and 80 mL/h respectively, while deionized (DI) water and tap water were used as the bore fluid and external coagulant fluid respectively. The dope and the water bath were at room temperature and the air gap was 3 cm. The fibers fell freely into the water bath and were collected and soaked in DI water for 3 days (water was changed daily) to exchange the residual solvent, after which they were thoroughly dried. The raw/“green” fibers were then sintered at 873 K for 2 h, followed by ramping to 1573 K for 6 h, with the ramp rate being 5 K/min in both steps. The finished fibers had an OD of 800  $\mu$ m and wall thickness of 150  $\mu$ m.

### *Synthesis of AEL nanosheets*

AEL zeolite nanosheets were synthesized as reported earlier<sup>31</sup> using a surfactant-like amphiphilic tertiary diamine as the structure-directing agent (SDA). For SDA synthesis, 0.01 moles of 1-bromodocosane (TCI America) and 0.1 moles of 1,6-diaminohexane (Sigma-Aldrich) were added to 100 mL of acetonitrile in a 250 mL round-bottom flask. The mixture was stirred at 308 K overnight and the product was precipitated by adding DI water, which was subsequently filtered and washed with DI water to remove the unreacted diamine. The solid product was dried overnight at room temperature in a fume hood. 2.76 g of this product was added to 12.62 g of 37 wt% formaldehyde solution in water (EMD Millipore) and 3.85 g of 85 wt% formic acid (Sigma-Aldrich) in a 100 mL round-bottom flask fitted with a condenser. The mixture was stirred at 373 K overnight, then cooled down, and 10 mL of 7 M aq. NaOH was added to neutralize the excess formic acid. The liquid mixture was transferred to a separating funnel and the product extracted using 100 mL of diethyl ether. The organic phase (product + ether) was separated and dried over MgSO<sub>4</sub> (Sigma-Aldrich). The diethyl ether was removed by rotary evaporation to yield the SDA.

To synthesize the AEL nanosheets, 0.25 g of pseudoboehmite (Catapal Alumina, 75 wt%) was added to 16.27 g of DI water in a 30 mL poly(propylene) bottle with a cap. 0.42 g of 85 wt%

phosphoric acid (Sigma-Aldrich) was then added dropwise to the mixture while stirring at 1000 rpm. The mixture was then aged at room temperature while stirring for 8 h followed by the addition of 0.425 g of the SDA. The resulting gel with a composition of 1 Al<sub>2</sub>O<sub>3</sub> : 1 P<sub>2</sub>O<sub>5</sub> : 500 H<sub>2</sub>O : 0.5 SDA was aged at room temperature for 2 h followed by hydrothermal treatment at 453 K in a Teflon-lined autoclave tumbling at 60 rpm for 24 h in an oven. The AEL nanosheets were collected by centrifuging and washing with DI water 3 times and dried in an oven at 348 K overnight.

#### *Exfoliation of AEL nanosheets*

The exfoliation of the multilamellar AEL nanosheets was carried out in a manner similar to that of multilamellar MFI nanosheets.<sup>26</sup> First, 3.84 g of poly(styrene) (Scientific Polymer Products, 45000 MW) was mixed with 0.16 g of as-made AEL nanosheets and added to a twin-screw extruder (HAAKE Minilab). The screw speed was set to 300 rpm and the poly(styrene) – AEL nanosheet mixture was blended sequentially at 393 K for 20 mins, 443 K for 25 mins, 423 K for 30 mins and 493 K for 20 mins. The resulting nanocomposite was then extruded at 423 K. To obtain a suspension of the exfoliated AEL nanosheets that could be used for coating substrates, 0.4 g of the extruded nanocomposite was added to 32 g of toluene in a 50 mL centrifuge tube. The nanocomposite was dissolved by sonication for 1 hour with occasional vortexing to disperse the zeolite nanosheets. The suspension was then centrifuged at 15000 RCF for 20 mins to settle the large, unexfoliated particles. The toluene suspension, except the bottom 10 mL, was then pipetted out and filtered through a 1 µm syringe filter to further purify the suspension and used for coating the alumina hollow fibers.

#### *AEL nanosheet coatings on alumina hollow fibers*

AEL nanosheets were coated on the outer surface of alumina hollow fibers using a setup similar to that used for coating MFI nanosheets in our previous work.<sup>32</sup> One end of a ~9 cm long fiber was sealed with epoxy (3m – DP 100 Translucent) to prevent infiltration of the nanosheet suspension, while the other end was connected to one end of a PTFE tubing (1/16") using the same epoxy. The other end of the PTFE tubing was connected to a vacuum pump with Swagelok fittings. This assembly, with the alumina hollow fiber sticking out of the PTFE tubing, was immersed into the exfoliated AEL nanosheet suspension in toluene and vacuum was applied in order to ‘filter’ the solvent through the macropores of the alumina hollow fiber and deposit the AEL nanosheets on the outer surface. The solvent passing through the fiber was collected in a trap and coating was

completed when 20 mL of solvent was collected. The coated fibers were then detached from the PTFE tubing and calcined at 823 K for 6 h with a ramp rate of 2 K/min.

#### *Interfacial polymerization (IP)*

The PA layer was formed on the AEL nanosheet coated fibers by the IP of *m*-phenylenediamine (MPD) (Sigma-Aldrich) with trimesoyl chloride (TMC) (Sigma-Aldrich). The hollow fiber that was calcined after the AEL nanosheet coating was reattached to the PTFE tubing using epoxy, with one end of the fiber sealed. It was then vertically dipped into a 2 wt% aqueous MPD solution for 5 mins, after which it allowed to dry in ambient conditions for 20 mins. Next, the MPD-soaked fiber was dipped into the TMC solution in hexane (0.3 wt%) for 10 min. The fiber was again dried in ambient conditions for 1 min before being cured in an oven preheated at 343 K for 5 mins. After 3 hours in ambient conditions, the fibers were washed with 5 mL of methanol and dried overnight in ambient air. These membranes were designated as AEL-TFN. Control samples, with no AEL nanosheet coating (TFC), were prepared in the same manner, except that bare alumina hollow fibers were used for the IP.

#### *Characterization*

X-ray diffraction (XRD) patterns were collected on a PANalytical X'Pert Pro MPD diffractometer with CuK $\alpha$  radiation (45 kV, 40 mA). It was difficult to obtain XRD patterns of the AEL nanosheet coating on hollow fibers in the Bragg-Brentano mode due to their curvature. Thus, AEL nanosheets were also deposited on a flat alumina disk and these were used to measure the XRD pattern as reported in our previous work.<sup>32</sup> SEM images were obtained on a Hitachi SU-8010 electron microscope operating at 3 kV and 10  $\mu$ A and the samples were first sputter coated with gold for 45 s. EDS mapping was done on a Hitachi SU-8230 electron microscope operating at 5 kV and 20  $\mu$ A. TEM images were obtained on a FEI Tecnai G<sup>2</sup> F30 operating at 300 kV. X-ray photoelectron spectroscopy analysis was conducted on a Thermo K-alpha spectrometer equipped with a Al K $\alpha$  source and the elemental composition was used to calculate the degree of cross-linking as reported previously.<sup>43</sup> An Agilent 5500 Atomic force microscopy (AFM) (Agilent Technologies, Inc., Santa Clara, CA, USA) was used to analyze the membrane surface roughness. An area of 2 $\times$ 2  $\mu$ m<sup>2</sup> was analyzed at a scan rate of 256 lines/s. At least three different positions were measured, and the average surface roughness values were reported.

### *Pervaporative desalination measurements*

The membranes were mounted into home-made modules reported in our previous works<sup>32,34,35</sup> for testing using pervaporative desalination at 298 K. First, 65 mL of aqueous NaCl solution (2 g/L or 36 g/L) was poured into the shell side cavity of the module and the module was sealed. The sealing of the module ensures that the pressure on shell side is equal to the saturation pressure of the solution. Vacuum (< 50 mTorr pressure) was applied to the bore side to create the driving force for pervaporation. The vapor permeating through the membrane was collected in a trap cooled using liquid nitrogen. The experiment was run for 4 h, where the first 3 h was used to reach a steady state flux, which was determined based on consistent values of flux obtained for 2 consecutive time points (within 5% of each other). The water flux was calculated based on the mass of permeate collected in the cold traps as shown in the following equation:

$$J = \frac{m}{A\Delta t} \quad (1)$$

Here  $J$  is the flux in  $\text{kg}\cdot\text{m}^2\cdot\text{h}^{-1}$ ,  $A$  is the area of the membrane ( $1\text{ cm}^2$ ),  $m$  is the mass of the permeate collected during an operation period of  $\Delta t$ . The water permeance was calculated using the flux ( $J$ ) obtained from Eq 1, by normalizing it based on the pressure driving force as follows:

$$\text{Permeance} = \frac{J}{a_w P_{sat,w} - P_p} \quad (2)$$

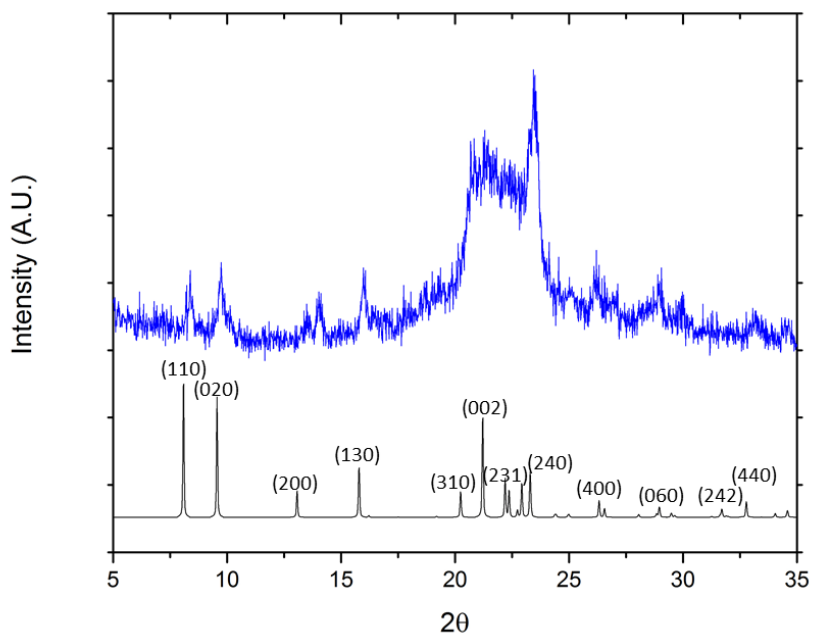
Here  $a_w$  is the water activity of the salt solution which was calculated based on the correlation outlined by Miyawaki et al.<sup>36</sup>  $P_{sat,w}$  is the saturation pressure of pure water at 298 K and  $P_p$  is the permeate side pressure (negligible here due to the application of ultra-high vacuum  $< 7 \times 10^{-3}$  kPa). The salt rejection is calculated based on the permeate composition using the following equation:

$$\text{Rejection (\%)} = \frac{C_f - C_p}{C_f} \times 100 \quad (3)$$

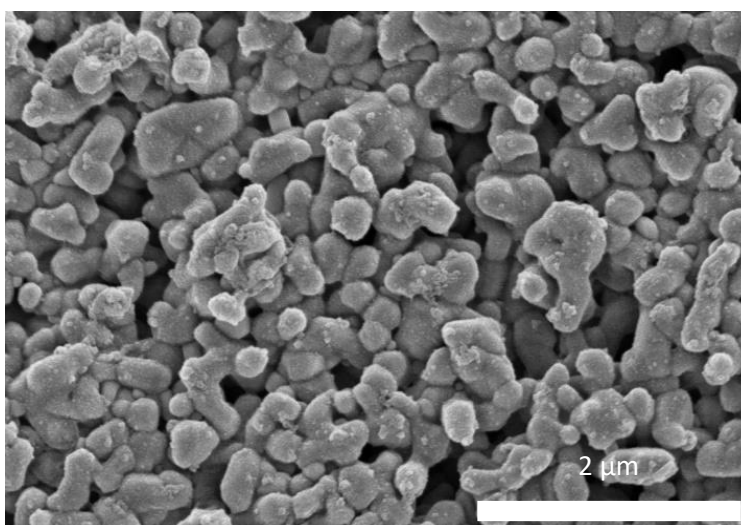
Here  $C_f$  and  $C_p$  (g/L) are the salt concentrations of the feed and permeate (condensed in the trap) respectively. They were calculated from the conductivity of the solution measured using a conductivity meter (Hanna Instruments). For the long-term stability experiment, pervaporation was carried out using the 2 g/L NaCl solution for 150 h. However, based on the flux of the membrane and the amount of salt solution needed to keep the membrane submerged at all times, the experiment had to be stopped for a short duration every 36 h to open the membrane module,

pipette out the remaining solution and replenish it with fresh salt solution. The experiment was then resumed with sample collection being done every few hours to measure the flux and rejection.

### Supporting Figures

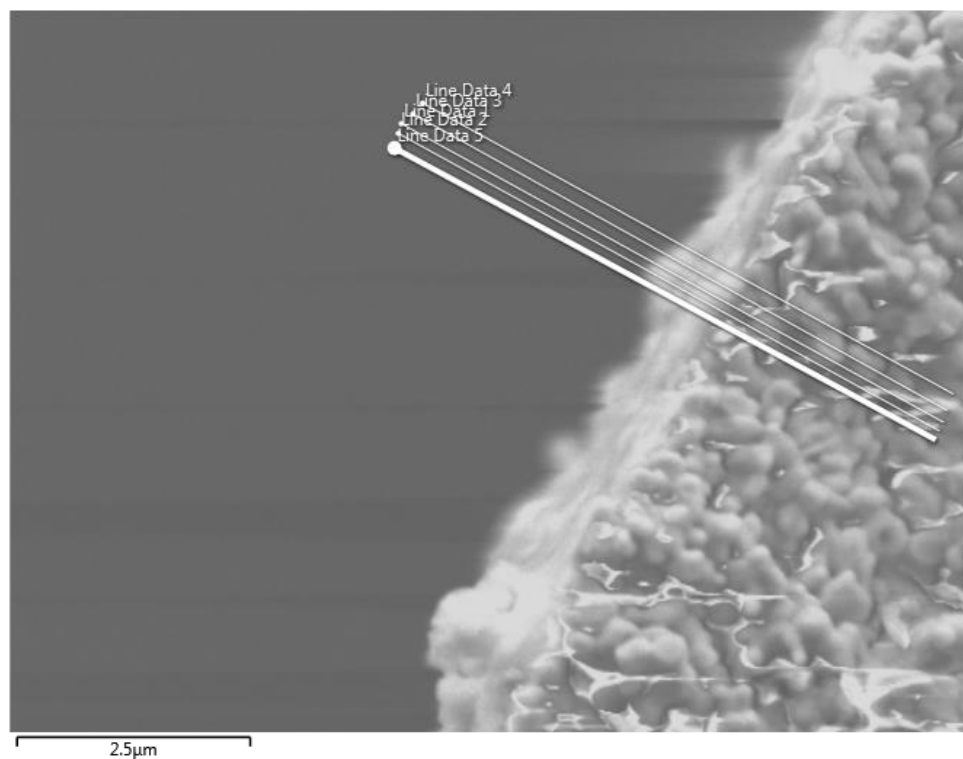


**Figure S1.** XRD pattern of the as-made AEL nanosheets (blue) compared with that of conventional AEL (black).

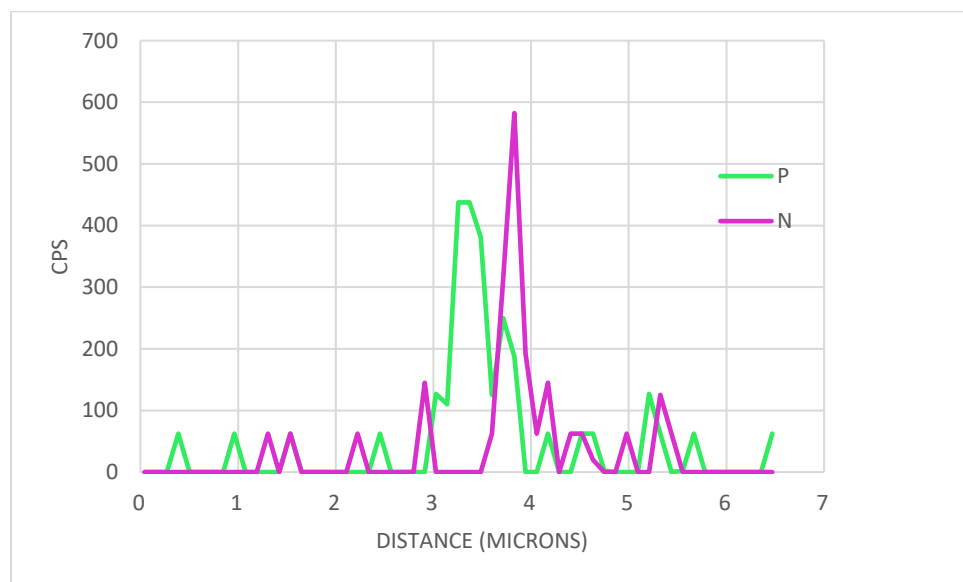


**Figure S2.** Example SEM image of the alumina hollow fiber surface after interfacial polymerization without the AEL zeolite nanosheet coating.

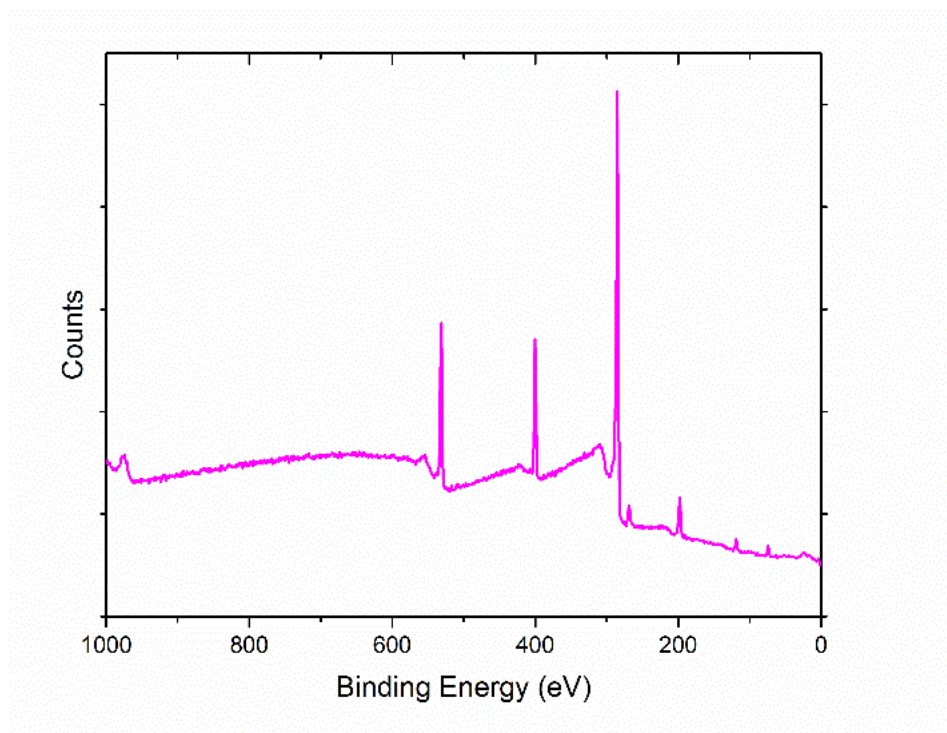
a)



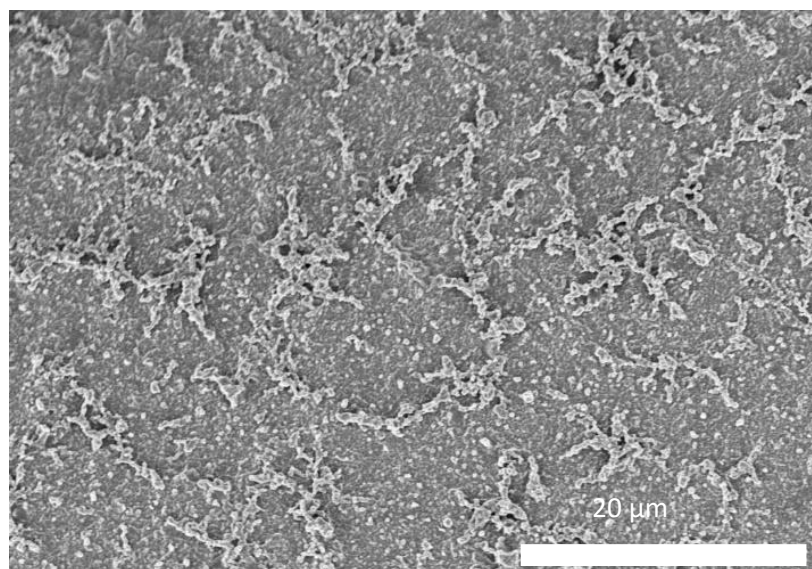
b)



**Figure S3.** a) SEM image corresponding to the EDS elemental mapping shown in **Fig. 3c**. EDS signals along each of the five lines were obtained as profile traces. b) Average profiles of P and N composition as a function of distance along the out-of-plane axis, obtained by averaging the five profiles obtained along the lines shown in **Fig. S3a**.

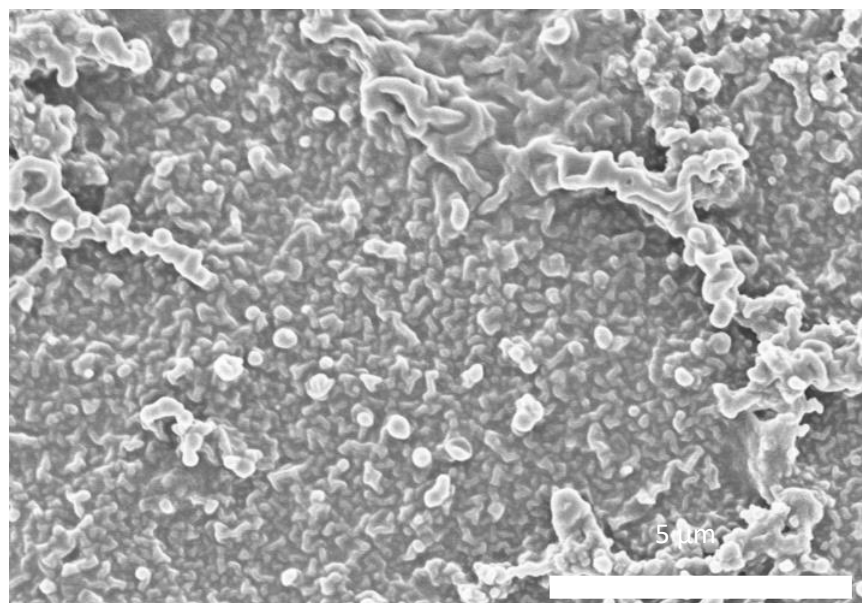


**Figure S4.** XPS spectrum of the sample formed with the interfacial polymerization carried out on a bare alumina hollow fiber.

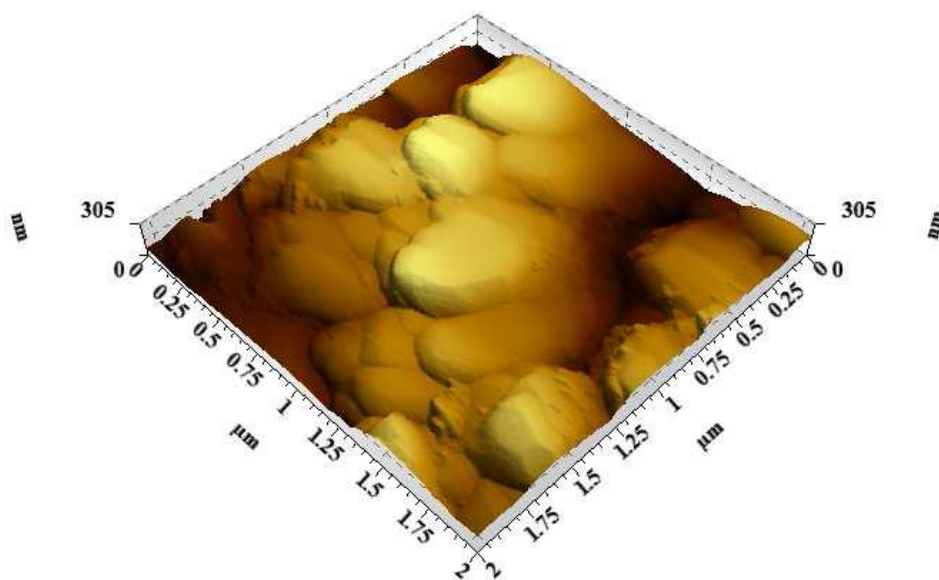


**Figure S5.** SEM image of the surface of AEL nanosheet/PA composite membrane.

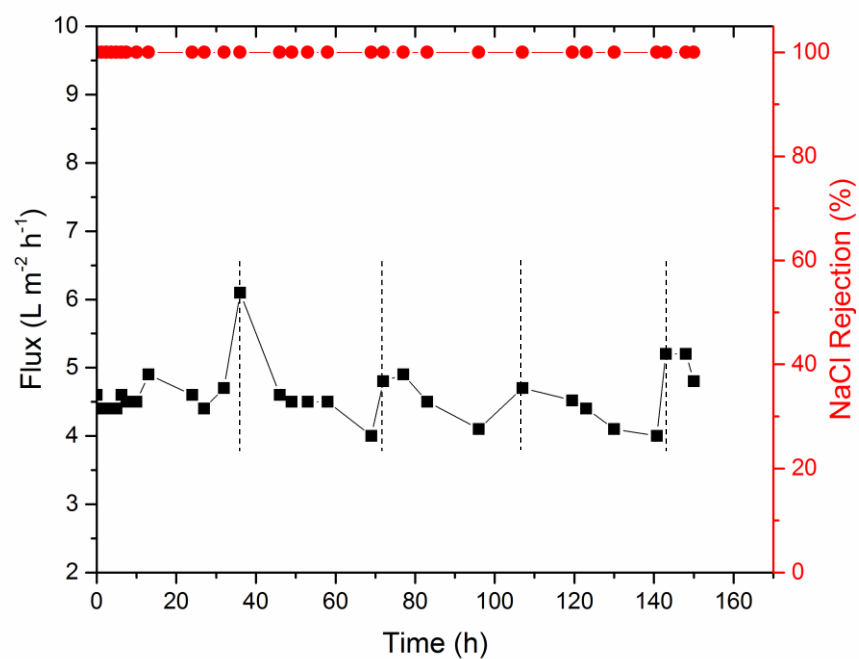




**Figure S6.** SEM image of the surface of AEL nanosheet/PA composite membrane.



**Figure S7.** AFM image of the surface of the AEL nanosheet/PA composite membrane



**Figure S8.** On-stream stability of the AEL nanosheet/PA composite membrane tested via pervaporative desalination of 2 g/L NaCl solution at 298 K. The vertical dashed lines indicate the points where the experiment was briefly paused to replenish the salt solution in the testing module.

## Supporting Tables

**Table S1.** Comparison of the AEL nanosheet/PA nanocomposite membrane with other membranes reported in the literature.

Membrane	Intermediate layer	Support	Aqueous Feed	Method & conditions	Water permeance (L.m <sup>-2</sup> h <sup>-1</sup> bar <sup>-1</sup> )	Salt Rejection (%)
PIP + TMC PA <sup>16</sup>	PDA wrapped SWCNT	PES MF	1 g/L Na <sub>2</sub> SO <sub>4</sub>	NF, 6 bar, 298 K	32	95.9
PIP + TMC PA <sup>17</sup>	MWCNT	PES MF	1 g/L Na <sub>2</sub> SO <sub>4</sub>	NF, 6 bar, 298 K	17.6	95
PIP+TMC PA <sup>18</sup>	CNC	PES MF	1 g/L Na <sub>2</sub> SO <sub>4</sub>	NF, 6 bar, 298 K	34	97
PIP+TMC PA <sup>19</sup>	COF	PES	1 g/L Na <sub>2</sub> SO <sub>4</sub>	NF, 4 bar, 298 K	31.3	95
PIP + TMC PA <sup>20</sup>	Tannic acid/Fe <sup>+3</sup> scaffold	PSF	1 g/L Na <sub>2</sub> SO <sub>4</sub>	NF, 3.5 bar, 298 K	19.6	95
PEI + TMC PA <sup>23</sup>	TiO <sub>2</sub>	$\alpha$ -alumina hollow fibers	2 g/L MgCl <sub>2</sub>	NF, 4 bar, 298 K	26.4	95.5
PIP + TMC PA <sup>44</sup>	GO	PAN	35 g/L NaCl	PV, 343 K	86.8	99.99
GO <sup>45</sup>	-	PAN	36 g/L NaCl	PV, 363 K	94	99.8
MFI zeolite nanosheets <sup>46</sup>	-		31 g/L NaCl	PV. 353 K	22	>99.5
Poly(vinyl alcohol cross-linked with glutaraldehyde <sup>47</sup>	PAN nanofibers	Nonwoven PET	36 g/L NaCl	PV, 298 K	234.5	99.8
MXene <sup>48</sup>	-	PAN	36 g/L NaCl	PV, 338 K	345.4	99.5
MPD + TMC PA (This work)	Exfoliated AEL nanosheets	$\alpha$ -alumina hollow fibers	2 g/L NaCl	PV, 298 K	135	>99.99
MPD + TMC PA (This work)	Exfoliated AEL nanosheets	$\alpha$ -alumina hollow fibers	36 g/L NaCl	PV, 298 K	96	>99.99

PES MF – Poly(ethersulfone) microfiltration support; NF – Nanofiltration; PV - Pervaporation