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Electronic Supplementary Information (ESI):

Epitaxial growth: Rapid synthesis of highly permeable selectivity T zeolite membrane

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1. Experimental details

Materials

Macroporous Al_2O_3 tubes with outer diameter of 12 mm, inner diameter of 8 mm, an average pore size of 3~4 μm, and homemade ceramic hollow fibber tubes with outer diameter of 1.6 mm were used as supports (Fig. S1). The macroporous Al_2O_3 supports were purchased from Foshan Ceramics Research Institute (FCRI) of China. The homemade ceramic hollow fibber supports were provided by Prof. Zhengbao Wang, Zhejiang University. Colloidal silica Ludox AS-40 (40 wt.% in water, Aldrich), potassium hydroxide (>85 wt.%, Sinopharm Chemical Reagent Co.,Ltd), sodium hydroxide (>96 wt.%, Tianjin Kermel Chemical Reagent CO., Ltd), sodium aluminate (Al_2O_3 : 41 wt.%, Na_2O: 24.92 wt.%, Sinopharm Chemical Reagent Co.,Ltd) and tetramethylammonium hydroxide solution (25wt.% in water, Zhejiang Ken Te Chemical Co., Ltd) were utilized as silica, potassium, hydroxide, aluminum and template, respectively. All chemicals were used without further purification.

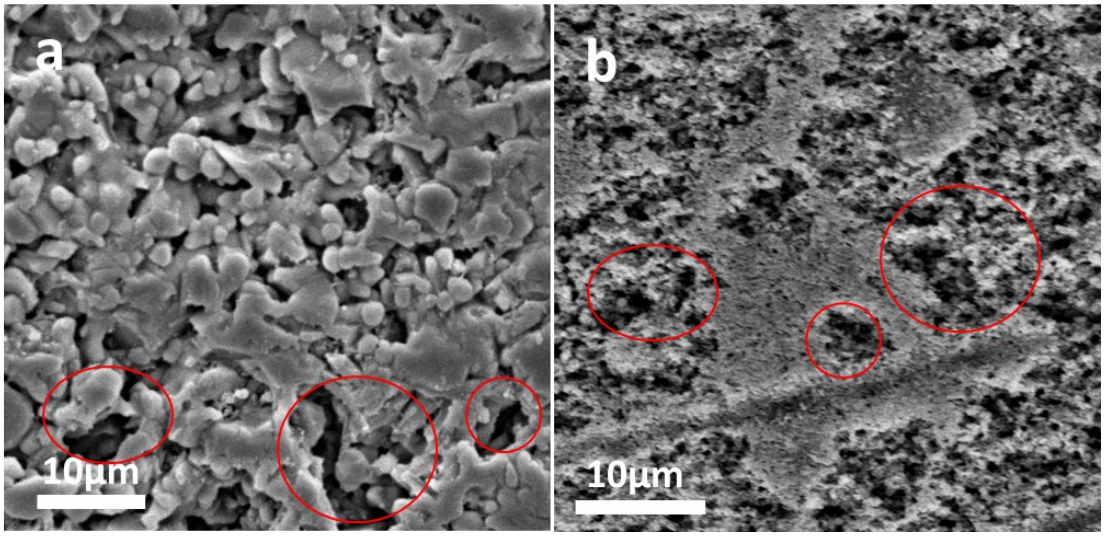

Fig. S1 Top SEM images of the a) Al_2O_3 tube and b) ceramic hollow fibber supports (large hole on the surface as red circles).

2. Synthesis and Characterizations.

Zeolite T seeds

The 600 nm and 2 μm zeolite T particles (SEM images given in Fig.S2) were prepared as follows: potassium hydroxide, sodium hydroxide and sodium aluminate were dissolved in deionized water. The template was then added into the base solution,

followed by dropwise adding colloidal silica. The resulted gel with molar composition of 18.2 SiO_2 : 1 Al_2O_3 : 4.2 Na_2O : 1.5 K_2O : x TMAOH : 212.7 H_2O (where x=0.82 or 1.5 for 2 μm and 600 nm seeds, respectively) was strongly stirred overnight in water bath at 298 K. The resulted gel was sealed into a Teflon-lied stainless steel autoclave and heated (static) at 373 K for 48 h. The crystals were collected from the bottom of the autoclave, then washed by deionized water until pH=7. Finally, the crystals were calcined in air at 823 K for 6 h.

Varying-temperature hot-dip coating (VTHDC) process

A varying-temperature hot-dip coating (VTHDC) technique [1] was used for seeding. First, the supports with two ends sealed by Teflon cap were preheated at 393 K in oven for 3h, then dipping into the water suspension containing 1 wt. % 2 μm zeolite T seeds for 20 s was followed by drying at room temperature, and heating in oven at 448 K for 3 h. Subsequently, the outer surfaces of the dried supports were wiped by cotton to remove the superfluous and loose zeolite T crystals. The wiped support was preheated at 373 K in oven for 2.0 h, and then dipped into the water suspension containing 0.6 wt. % 600 nm zeolite T crystals for 20 s, followed by drying in oven at 373 K for 2 h.

Varying-pressure vacuum seeding (VPVS) Process

The process of varying-pressure vacuum seeding (VPVS) is as follows: the ceramic hollow fibber support with one side sealed by AB glue (modified acrylate achesive, Geleihow CO. Ltd) was dipped into 1 wt. % 2 μm zeolite T water suspension for 10 s under vacuum pressure 0.02 MPa connecting with the unsealed side of the tube. After the first vacuum coating, the seeded support was dried in oven at 448 K for 3 h. Then, the dried support was rubbed gently by cotton. In order to obtain a dense, continuous and uniform seed layer, the rubbed support was dipped again into 0.6 wt. % 600 nm zeolite T water solution for 5 s under vacuum pressure 0.15 MPa, followed by drying in oven at 373 K for 2 h.

Membrane Syntheses

The milk-like synthesis sol was obtained by mixing aluminate sol with silica sol. The aluminate sol was prepared by dissolving potassium hydroxide and sodium hydroxide in deionized water, then adding sodium aluminate into the solution until the sol got clear. Subsequently, the silica sol was added dropwise with strong stirring. The resultant synthesis sol had a mole composition of 1 SiO_2: 0.05 Al_2O_3 : 0.26 Na_2O: 0.09 K_2O: 35 H_2O. The synthesis sol was aged at ambient temperature for 24h with

stirring. The seeded support tube was sealed at both ends and placed vertically in a Teflon autoclave filled with the aged synthesis sol. The secondary growth was carried out at 423 K for 1~4 h. The resultant membrane was thoroughly washed with water and dried at 373 K for several hours.

Characterizations

The morphologies of the Zeolite T seeds and membranes were observed by scanning electron microscopy (SEM) using a QUANTA 450 at an acceleration voltage of 30 kV after a layer of gold coating. The X-ray diffraction (XRD) patterns were collected from a Philips Analytical X-ray diffractometer using Cu Kα radiation (30 mA and 40 kV).

FEI Tecnai G2 F30 (S)TEM equipped with TWIN pole piece (Cs=2 mm) and a Schottky field emission electron gun operating at 300 kV with extraction voltage of 4,000 V was used for bright-field TEM imaging for zeolite T crystals. Low-dose setup of the microscope was used to minimize damage of the zeolite T sample. Selected area electron diffraction patterns were acquired with an integration time of 10 s at a camera length of 1.9 m on a Gatan 4 k × 4 k Ultrascan CCD at a 2 × 2 binning to yield a final 2 k × 2 k pixel2 image. Dry powder zeolite sample was dispersed by sprinkling on a 400 mesh Cu TEM grid (TedPella) with carbon supported thin film on holey carbon layer.

Pervaporation measurement

The properties of zeolite T membranes were evaluated by pervaporation separation of 90 wt. % isopropanol/water solution by using a laboratory-scale batch PV experimental apparatus as shown in Fig.S2. Acetic acid was added into 90 wt. % isopropanol/water mixtures to test acid stability of the prepared zeolite T membranes. The pH of the separation solution was controlled to be 5, tested by pH meter（Shanghai Yueping CO. Ltd）. The feed solution was stirred vigorously to minimize the effect of concentration polarization. And the temperature of the feed was controlled constant by thermostat water bath at 348 K. The inside of the membranes was connected to a vacuum pump and the permeate was collected by a cold trap cooled by liquid nitrogen. The pressure on the permeate side was keep around 100 Pa. The concentrations of the feed and permeate were tested on a gas chromatograph (GC) using a GC7890T. The separation performance of membranes was evaluated by the permeation flux (Q, $kg \cdot m^{-2} \cdot h^{-1}$) and the separation factor (S.F., α). The permeation flux was calculated by the mass of the permeate in a given time interval. The membrane S.F. was defined as:

$$\alpha_{A/B} = (Y_A / Y_B) / (X_A / X_B) \qquad (1)$$

where X_A and X_B denote the mass fraction of components A and B respectively in the

feed side , respectively; Y_A and Y_B the mass fractions of components A and B in the permeate that is collected by a cold trap cooled by liquid N_2 , respectively; A and B represent for water and isopropanol component , respectively.

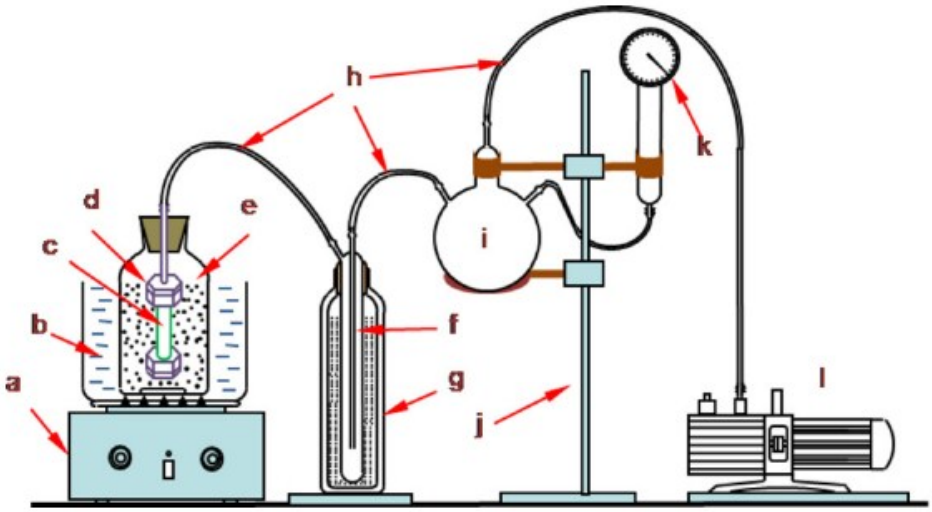

Figure S2: Experimental apparatus for pervaporation unit: (a) magnetic stirring apparatus, (b) thermostat water bath, (c) membrane tube, (d) membrane modules, (e) stock bottle, (f) cold trap, (g) liquid nitrogen, (h) silicone vacuum tube, (i) vacuum buffer tank, (j) iron stand, (k) vacuum manometer, and (l) vacuum pump.

3. Results and Discussion

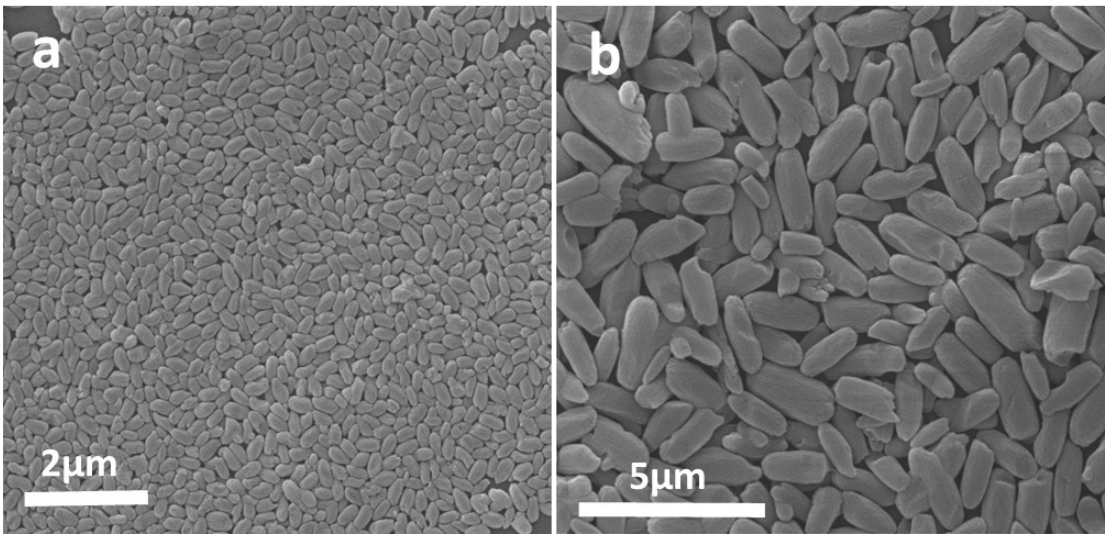

Fig. S3 SEM images of the seeds a) 600 nm, b) 2μm.

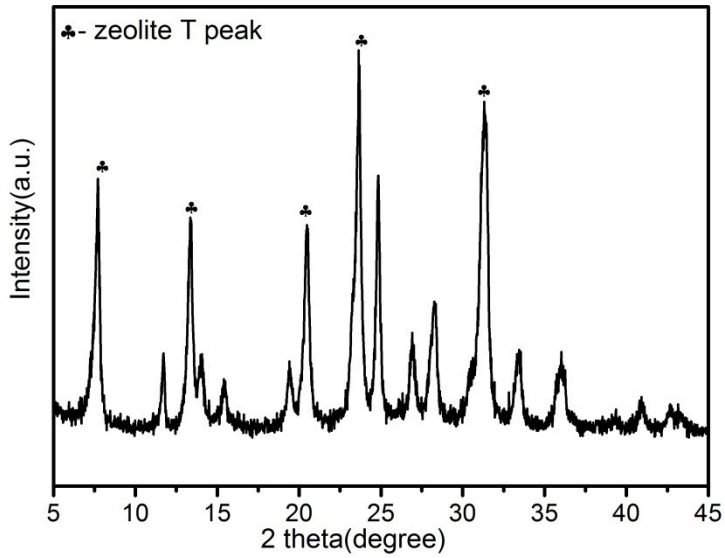

Fig. S4 XRD pattern of zeolite T seeds (2μm).

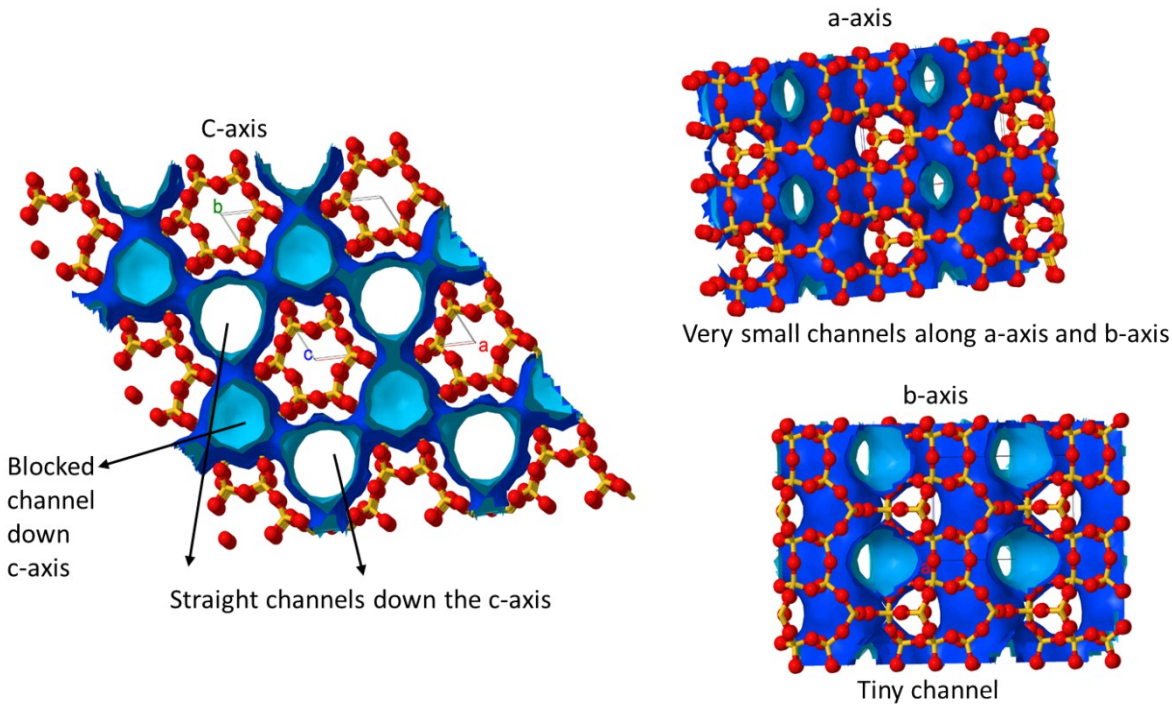

Fig. S5 Simulated framework of zeolite T crystal in different axis.

In zeolite T structure, each erionite cage involves a large pore (12-ring) completely blocked by 6-ring channels. Thus, a single unit cell of erionite is a "dead-end" to the large pore of offretite, forcing diffusion through 8-ring channel in the a- or b-direction and leading to the shape-selectivity. Therefore, small amount of erionite intergrown in offretite is expected to convert offretite despite the offretite can sorb large molecules into zeolite. The erionite were only a small portion of the zeolite T structure, but these erionite cages are the controlling "bottleneck" factor in diffusion due to the "dead-end" effect [2].The pore window size of channels running along a- or b-axis is about 0.31 nm. In contrast, the 12-ring pore channel in c-orientation is completely blocked by 6-

ring channels of erionite cage, and the opening for the molecular permeation is very small around 0.25 nm. The molecule kinetic diameter [3] of isopropanol and water are 0.47 and 0.30 nm, separately. Therefore, the preferred orientation for the water molecular permeation is a- or b-axis, the obtained a- or b-oriented membrane is favorable for achievement of high pervaporation performance of the M1.

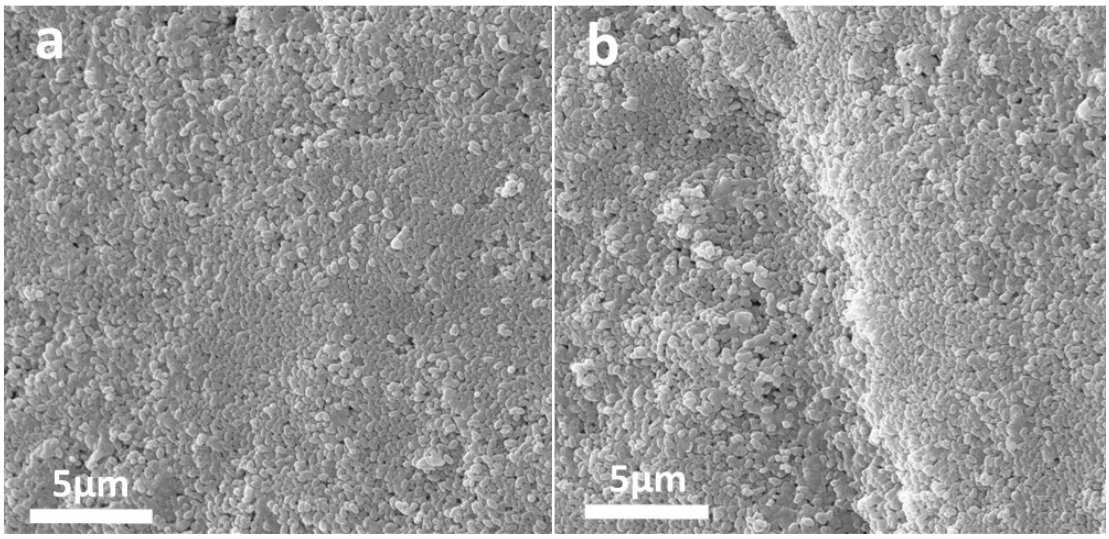

Fig. S6 Top view: SEM images of top view seed layer made by VTHDC method on HF support (a) and b) are different magnification).

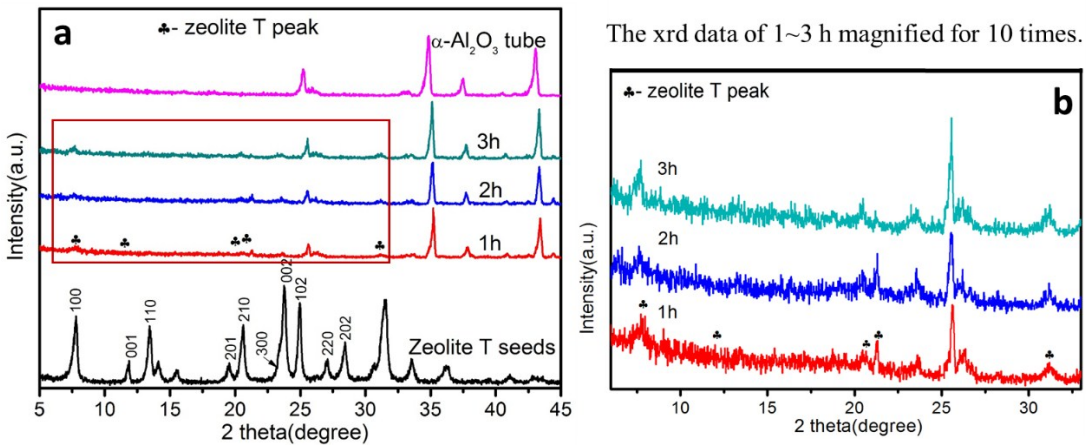

Fig. S7 XRD patterns of a) zeolite T membrane for different crystallization time 1~3 h b) 1-3 h crystallization time for zeolite T magnified 10 times from the marked region in a.

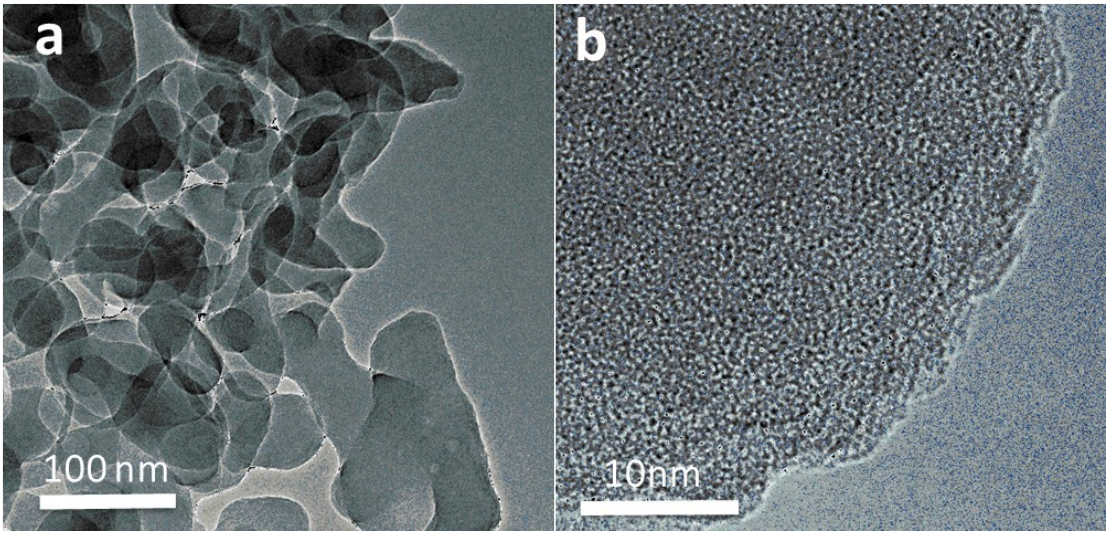

Fig. S8 Different magnifications of BF-TEM image of the sample collected from the bottom of autoclave for the membrane M1 growth using the Tecnai F30 (FEI).

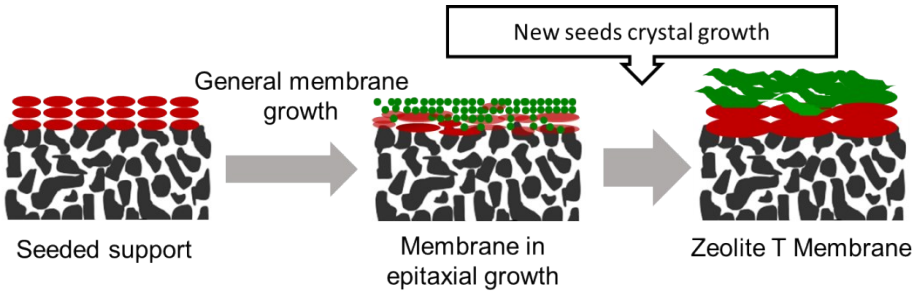

Fig. S9 Schematic of zeolite T membrane growth mechanism.

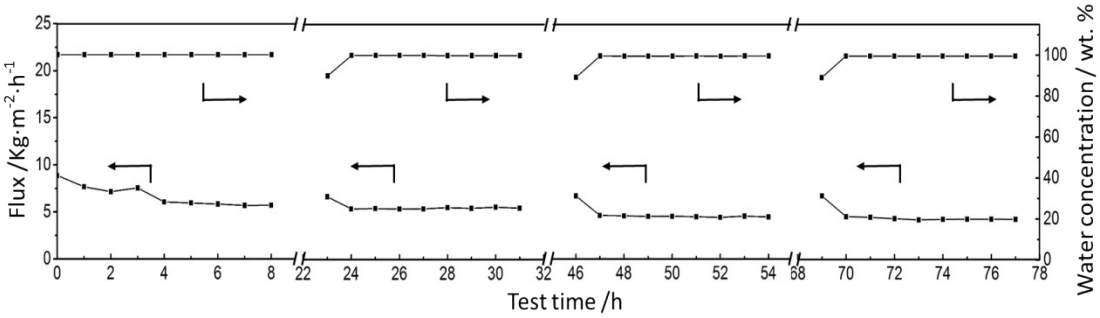

Fig. S10 Pervaporation performance of zeolite T membrane M1 as a function of operation time for a 90 wt. % isopropanol solution (added Acetic, pH 5) mixture at 348 K. The horizontal axis breaks in the figure indicate periods during which the membrane was immersed in the solution at 348 K (without vacuum pumping but other conditions are exactly the same with those during the pervaporation measurement).

The water flux decreased from the initial value of 5.9 kg•m^{-2}•h^{-1} to a steady-state of 4.7 kg•m^{-2}•h^{-1} after 70 h, and almost remained the same until the investigated period of 100h. Moreover, the water permeate concentration remained above 99.8 wt. % through the experiment. Acetic acid was not detected in the permeate. Because acetic acid absorbed on the membrane surface and affected the adsorption coverage of water and isopropanol, the total flux declined and permeate side water content decreased during the initial stabilization period after the soak time.

Table S1 PV properties for 90 wt. % isopropanol solution at 348 K of zeolite T membranes prepared by VTHDC method on HF support.

Membrane No.	Flux/ (kg·m^{-2}·h^{-1})	Separation factor, α
1	16.6 ± 0.1	7 ± 55
2	10.1 ± 0.1	94 ± 55
3	8.6 ± 0.1	90 ± 55

Table S2 Comparison of PV performance of zeolite T membranes for90 wt. % isopropanol aqueous solutions at 348 K.

Support	Synthesis Temperature (K)	Synthesis time(h)	Membr. thickness (μm)	Flux ($kg.m^{-2}.h^{-1}$)	αw/o	Ref.
Al_2O_3	423	4	3~4	5.9	>10000	This work
HF	423	4	3~4	9.8	3870	This work
Al_2O_3	373	30	4~5	2.52	10000	[1]
Mulite	423	20	~38	3.10	3400	[4]
Mulite*	423	6	~11	4.43	8200	[5]*
Stainless steel*	423	6	5	6.7	5300	[6]*
YSZ HF	378	40	~12	7.36	>10000	[7]

***:** The Zeolite T membrane on stainless steel or Mulite tube was obtained from a synthesis solution containing fluoride ion that is not environmentally friendly.

Table S3 PV properties for 90 wt. % isopropanol solution at 348 K of zeolite T membranes prepared by VPVS method on HF support and VTHDC method on alumina support.

Membrane No.	Support	Flux/ ($kg \cdot m^{-2} \cdot h^{-1}$)	Separation factor, α
M1-1	Alumina	6.0 ± 0.2	>10000
M1-2	Alumina	5.9 ± 0.2	>10000
M2-1	HF	9.7 ± 0.1	3900 ± 55
M2-2	HF	9.8 ± 0.1	3790 ± 50

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