Supporting Information

Experimental section

1 Materials

Poly(vinylidene fluoride) (PVDF) microfiltration membranes with an average pore size of 0.22 μm were purchased from Beihua Liming Co. Ltd. (Beijing, China). And the thickness of PVDF membrane is 0.1mm. Vinyltriethoxysilane (VTES, density of 0.904 g/ml) of analytical grade was obtained from Tianjin Chemical Reagent Institute (Tianjin, China). Polydimethylsiloxane (PDMS) (107#RTV), ethanol (purity>99.7%) and heptane of analytical grade (purity>95%), were supplied by Beijing Chemical Co. Ltd. Dibutyltin dilaurate (DBTL) of chemical grade was purchased from Fuchen Chemical Reagent Factory (Tianjin, China). Deionized water was made by a Direct-Q3 water purification system (EMD Millipore Corp., USA) and used in all experiments.

2 Membrane Preparation

The procedure for the preparation of the PVTES composite membranes is as follows. In order to prevent coating solution from intruding micro-pores in PVDF membrane, PVDF porous membrane as support layer was firstly wetted with ethanol due to the hydrophobic property of PVDF, then immersed in water. After about 10 minutes, the PVDF was placed on a clean glass plate and excess water on the surface was wiped off quickly with a filter paper. So that, water was introduced into micro-pores in PVDF membrane. Meanwhile, a coating solution was prepared from VTES, solvent n-heptane and catalyst DBTL with a 5/10/0.2 weight ratio, and then somicated at room temperature for 10 minutes for coating. Then the coating solution was casted on the pre-treatment PVDF membrane, after that the film was introduced

into a vacuum oven at 60 ºC for 24 hours to complete the crosslinking.

3 Membrane characterization

3.1 Scanning electron microscope (SEM)

The surface and cross-sectional morphological studies of PVTES membranes were performed on an FEI Quanta 200 SEM at a voltage of 10 kV. The cured samples were placed into liquid nitrogen for 5 min and then fractured into two pieces to create fresh surfaces. The fractured surfaces of all samples were placed in scanning electron microscope after they were coated with gold. Membrane thickness can be measured by SEM.

3.2 Fourier transform infrared (FTIR)

FTIR were used to determine membrane surface and polymer groups of reaction production. FTIR spectra of the samples were recorded in the 500-4000cm^{-1} range using a JIR-7000 spectrometer (JEOL) at 4 cm^{-1} resolution. Infrared spectra of the solid samples were measured using KBr pellet technique with a Nicolet AVATAR 360FT infrared analyzer. IR spectra of membrane specimens were carried out on a Nicolet NEXUS 670 Spectrometer by ATR (attenuated total reflection).

3.3 Solid-state ^{29}Si nuclear magnetic resonance (^{29}Si NMR)

Solid-state ^{29}Si NMR spectra measurements were recorded on a Bruker AV 300 spectrometer (4 mm specimen tube) at 59.62 MHz. An ambient temperature of 20 °C was fixed during measurements. The solid-state ^{29}Si NMR chemical shifts in parts per million (ppm) were referenced relative to tetremthylsilane (TMS). The sample for the ^{29}Si NMR measurement should be grinded into powder with a mortar.

3.4 X-ray diffraction (XRD)

Crystal area and amorphous area of the composite membrane were confirmed by

XRD. XRD spectra were obtained at room temperature using an X'PertPROX-ray diffractometer (PANalytical B.V., Netherlands). The diffractograms were measured at a scanning speed of 8º/min in the 2θ range of 3-90º using Cu Kα radiation (λ= 0.154 nm) monochromated by means of a nickel filter, a tube voltage of 40 kV and a tube current of 40 mA.

3.5 Mechanical properties Test

The tensile strength of the PVTES/PVDF, PDMS/PVDF and PVDF membranes were measured by a universal testing machine (Shimadzu AGS-100A, Japan) equipped with a 5 kg load cell. Before the test, the membranes were cut into $10*3$ mm^2 strips. The cross-head speed was controlled at 2 mm/min. An average value of the tensile strength was calculated by measuring three samples for each batch of the membranes.

3.6 Measurement of contact angle (CA)

Contact angle measurements are indicative for the surface chemistry of composite membrane surface. Contact angles were measured by a contact angle tester (HARKE-SPCAX1, China) at room temperature. A 2 μl portion of the pure water was dropped onto the sample surface at different locations. An average value of contact angle was calculated by measuring three samples for each batch of the membranes.

4 Pervaporation measurement

Pervaporation (PV) measurements were carried out on a homemade apparatus, schematically shown in Figure S1. The membranes were mounted in a stainless steel membrane module with an effective membrane area of 55.4 cm^2 and sealed with viton o-rings. The feed was circulated from the feed tank to membrane module with an YZ1515X peristaltic pump (Baoding Longer Precision Pump Co., Ltd., China). The temperature of the feed tank was controlled with a HH-4 thermostatic water bath (Jintan Ronghua Instrument Manufacture Co. Ltd., China). A 2XZ-2 vacuum pump (Shanghai Deying Vacuum & Lighting Equipment Co. Ltd., China) was used to

maintain the downstream pressure of the permeate side at 30 mmHg. The permeate was condensed in a liquid nitrogen trap. Before the experiment, the system was performed for 2 h to reach a steady state. After that, the permeate was collected every 1h by exchanging the cold trap periodically. The ethanol concentration of feed solution and permeate were analyzed by gas chromatography (Agilent 7890A, USA). Weight of permeate was determined by an electronic balance (OHAUS AR2130, USA). All values of fluxes and separation factors were means of triplicate measurements.
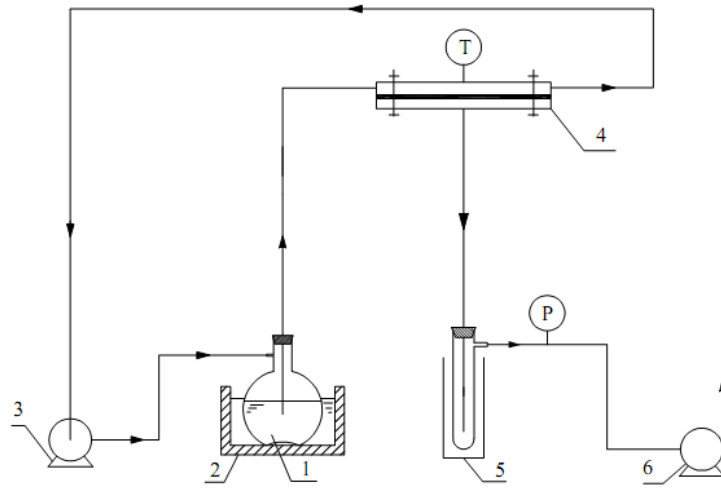
1. Feed solution tank; 2. Constant water tank; 3. Peristaltic pump; 4. Membrane cell; 5. Cold trap; 6.Vacuum pump

Figure S1. Schematic diagram of the pervaporation system.

The permeation flux (J) and the separation factor (α) are calculated using the following equation:

$$J = \frac{m}{At} \tag{1}$$

where m denotes the weight of permeate (g), A is membrane area (m^2) and t is the permeation time (h).

$$\alpha = \frac{Y_E/Y_W}{X_E/X_W} \tag{2}$$

where X_W, X_E and Y_W, Y_E are the weight fractions of water and ethanol in the feed and permeate, respectively.