

Electronic Supplementary Material (ESI)

CO₂ separation enhancement of the membrane by modifying polymer with small molecule containing amine and ester groups

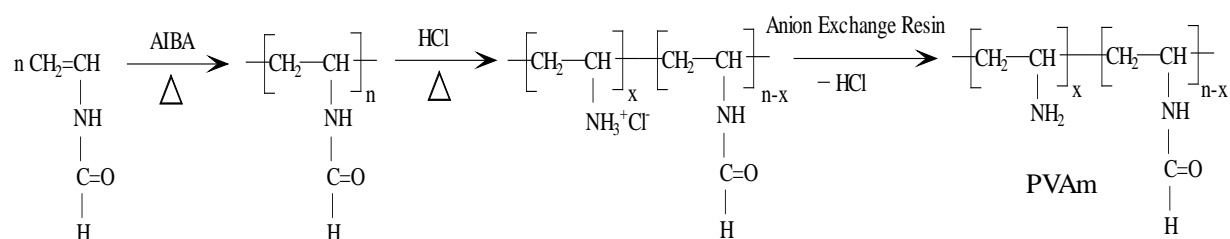
1. Material

N-vinylformamide (NVF) from Aldrich Inc. was distilled under vacuum and stored at -15 °C. 2, 2'-Azobis (2-methylpropion-amidine) dihydrochloride (AIBA) from Aldrich Inc. was recrystallized from ethanol and stored at -15 °C. The PSF ultrafiltration membrane with an average cut-off molecular weight of 6,000 was supplied by Vontron Technology Co., Ltd. (China). 201×7 strongly basic anion exchange resin was purchased from Chemical Plant of Nankai University (China) and regenerated before use. MC (99.0% purity) was obtained from Aladdin Reagent Co., Ltd. (China) and used without further purification. Ethanol and hydrochloric acid were of analytical grade and used as received.

2. Synthesis of the polymer

Polyvinylamine (PVAm) was synthesized according to the method reported in the literature.¹ The synthesis route of PVAm is shown in Fig. S1. 10g NVF monomer (0.14 mol) and a certain amount of AIBA were dissolved in 40ml deionized water. Then the polymerization of PNVF was carried out in a flask equipped with a stirrer at 50 ± 2 °C for 5h under nitrogen atmosphere. After polymerization, a colorless transparent viscous gel-like liquid was obtained. A certain concentration of hydrochloric acid was added into the flask and acidic hydrolysis was carried out at 70 ± 2 °C for 2 h. Then, the solution was poured into a large quantity of ethanol to

precipitate a white deposit. The deposit was dried in a vacuum oven at 60°C for 48h. The dried product, which is PVAm-HCl polymer, was dissolved in a certain amount of deionized water. The polymer solution was mixed with excessive strongly basic anion exchange resin and was further stirred for 2h. Finally, the PVAm aqueous solution was obtained by vacuum filtration of the mixture. The molecular weight of PVAm is 3.7×10^5 g/mol, which was measured with the viscosity method. The hydrolysis degree $\mu = x/n$, as shown in Scheme S1. The x/n can be calculated by the ¹H nuclear magnetic resonance (HNMR). As shown in Fig. S1, the peak around 2.15 ppm can be assigned to CH and CH₂ in the main chain; the peak around 7.95 ppm can be assigned to CHO.⁹ The integral quantities of the peaks are shown in the Fig. S1. By calculating, the hydrolysis degree is 58.33%. To confirm the result, the percentage composition of C (m_C%) and the percentage composition of N (m_N%) in the PVAm were measured by an elemental analyzer (Carlo Erba EA1110, Italy). The x and n can be calculated by the m_C% and m_N% in the PVAm. The m_C% is 53.14% and the m_N% is 25.84%. By calculating, the hydrolysis degree is 60.12%, which is close to 58.33%.



Scheme S1 Synthesis route of PVAm

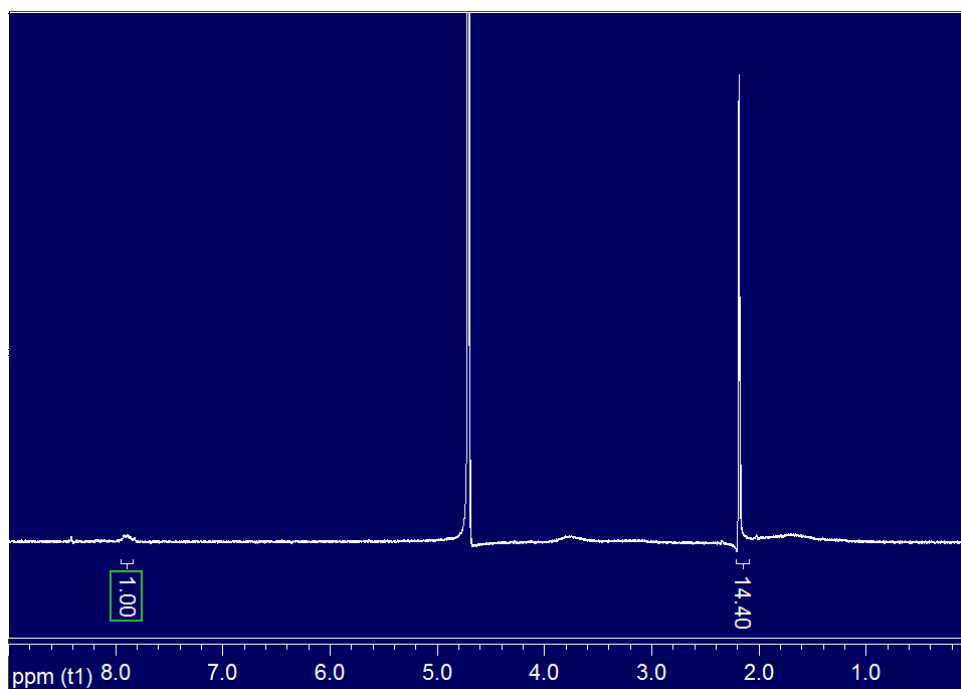


Fig. S1 1H nuclear magnetic resonance spectrum of PVAm

3. Preparation of the membranes and films

The PVAm-MC containing 0.02g/ml PVAm as well as 0.0266 g/ml MC was prepared by mixing PVAm aqueous solution with MC and deionized water. Then the mixtures were stirred for 12 hours and stood for 24 hours at room temperature (22°C). The PVAm-MC/PSF composite membrane was prepared by coating PVAm-MC on PSF ultrafiltration membrane with a pre-set wet coating thickness (the gap between substrate and coating knife) 50 μm by a coating applicator, followed by drying at 30°C and 40% relative humidity in an artificial climate chamber (Climacell 222R, Germany) for 24 hours. The PVAm/PSF composite membrane was also prepared with the same pre-set wet coating thickness, which has been reported in the previous work.¹ The cross-section of the PVAm/PSF composite membrane and the PVAm-MC/PSF composite membrane were characterized using scanning electron microscopy (SEM,

Nova Nano 430, FEI of USA), as shown in Fig. S2. The thicknesses of the PVAm and PVAm-MC active layer are both 281 ± 5 nm. The PVAm or PVAm-MC films were obtained by coating PVAm or PVAm-MC on silicone rubber substrate, then dried for 24 hours under the same temperature and relative humidity as the preparation of composite membranes, and finally were peeled from the silicone rubber substrate.

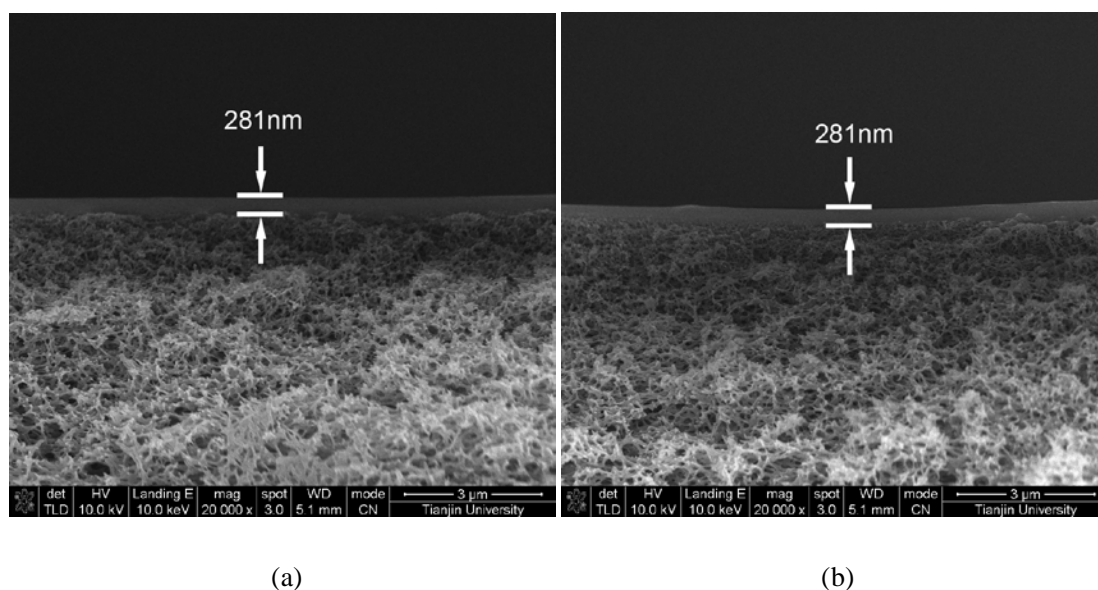


Fig. S2 SEM cross-sections of PVAm/PSF membrane (a) and PVAm-MC/PSF membrane (b)

with the same wet coating thickness $50 \mu\text{m}$

4. Gas permeation measurements

The permselectivity of the PVAm-MC/PSF composite membrane was measured by a set of test equipment, as shown in Fig. S2.² The membrane was mounted in a circular stainless steel cell (effective membrane area = 19.26 cm^2). Prior to contacting the membrane, the feed gas was saturated with water vapor by firstly being humidified by bubbling through water bottles at 40°C and then passing an empty

bottle at room temperature (22°C) to remove the condensate water. The sweep gas was humidified by passing through water bubblers at room temperature (22°C). In the laboratory testing process, the membrane area is small. Therefore, when the pressure difference between the feed side and the permeate side is low, the permeate gas flow rate is small. In this case, the sweep gas is necessary to transport the permeate gas to the gas chromatograph for analyzing the permeate gas composition. Moreover, the concentration polarization at the permeate interface of membrane has an obvious effect on the performance of the membrane, and the sweep gas is often used to avoid concentration polarization.^{5,7} The gas chromatograph used for analyzing the gas composition is equipped with a thermal conductivity detector (TCD). H₂ and He are both suitable carrier gas for TCD, because of their low molecular weight, low viscosity and high thermal conductivity. Considering that H₂ owns higher thermal conductivity and lower cost than He, we used H₂ as carrier gas for CO₂/N₂ and CO₂/CH₄ analysis. For CO₂/H₂ analysis, because H₂ need to be analyzed, we used He as carrier gas. In order to make the analysis of the permeate gas composition accurate, the same kind of gas was used as the sweep gas. Thus, we used H₂ as sweep gas for CO₂/N₂ and CO₂/CH₄ test, and used Ar as sweep gas for CO₂/H₂ test. The fluxes of gases were calculated from the sweep gas flow rate and its composition. The downstream pressure in the apparatus was maintained at atmosphere pressure. The gas permeance is customarily expressed in the unit of GPU. Permeation experiments were carried out at room temperature (22°C) with a feed pressure varying from 0.3 to 2.0 MPa, and steady state permeation was assumed to have reached when the sweep gas

flow rate and its composition no longer changed with time. All error bars presented represent standard errors of the performances of three membranes which were prepared under the same preparation condition. In addition, it has been proved that the effect of back-diffusion of the sweep gas on data analysis could be neglected.²

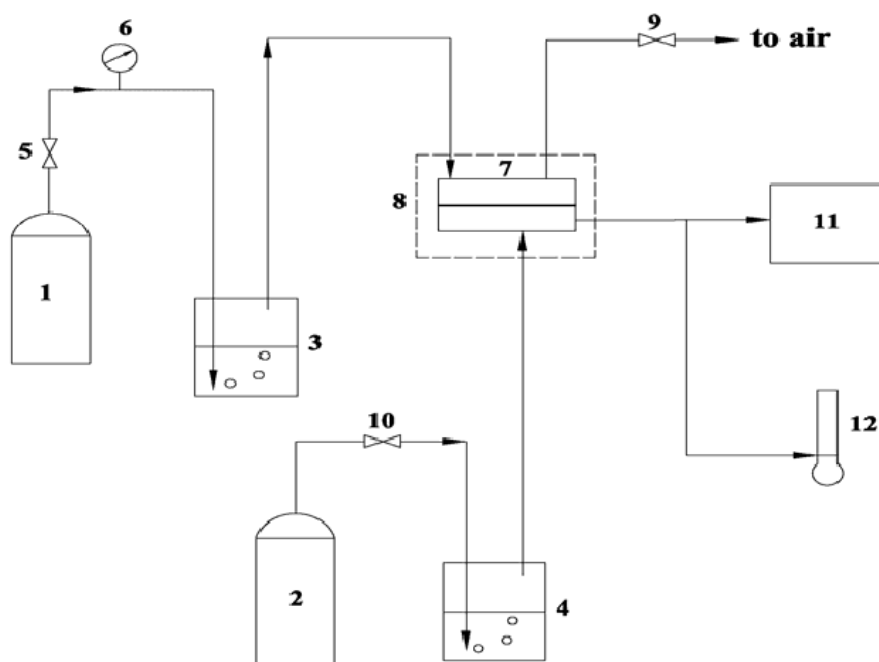
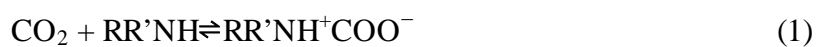
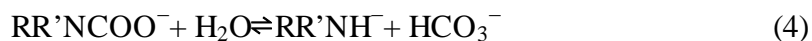


Fig. S3 Schematic representation of gas permeation apparatus: (1) feed gas; (2) sweep gas; (3)(4) humidifier; (5) pressure regulator; (6) pressure gauge; (7) membrane cell; (8) oven; (9)(10) flow regulating valve; (11) gas chromatograph; (12) soap-film flow meter.

In addition, the feed gas and sweep gas were saturated with water in the performance test for the reason that the presence of water vapor is expected to enhance CO₂ permeation of the membrane as following formulas.





where R' may be an H or other group. The reaction between CO₂ and amine group is defined by the zwitterion mechanism in formulas (1) to (4). Firstly, CO₂ reacts with amine group to form zwitterions as an intermediate. Then, the zwitterions are deprotonated by amine or H₂O to form the carbamate ions. The carbamate ions are unstable and could react with H₂O to form bicarbonate ions. And the saturated water was to make sure the humidity of the feed gas and sweep gas was constant.

5. The preparation of spiral wound membrane module and properties testing

The membrane element was prepared by ourselves. Firstly, we manufactured the central tube with stainless steel, which has equidistant holes on it. Then, we wound the membrane on the central tube, the two sides of the membrane was sealed by polyurethane adhesive. Finally, we waited for the solidification of polyurethane adhesive, which took about 48 hours. The length of the membrane element is 300mm, the diameter is 40mm. Take account of the safety of pressure vessel, the shell of the module was made by professional company. The spiral wound membrane module was fabricated by putting the membrane element into the shell. The membrane element and the spiral wound membrane module are shown in Fig. S3.

The properties of the modules were also tested by test equipment mentioned in front, as shown in Fig. S2. The difference is that the unit 7 (membrane cell) was replaced by the spiral wound membrane module. During the Industrial application of spiral wound membrane module, the feed gas pressure usually is high and the membrane area is large, which makes the permeate gas flow rate is large. Thus, the concentration polarization is not obvious. In this case, there may be no need to use sweep gas.

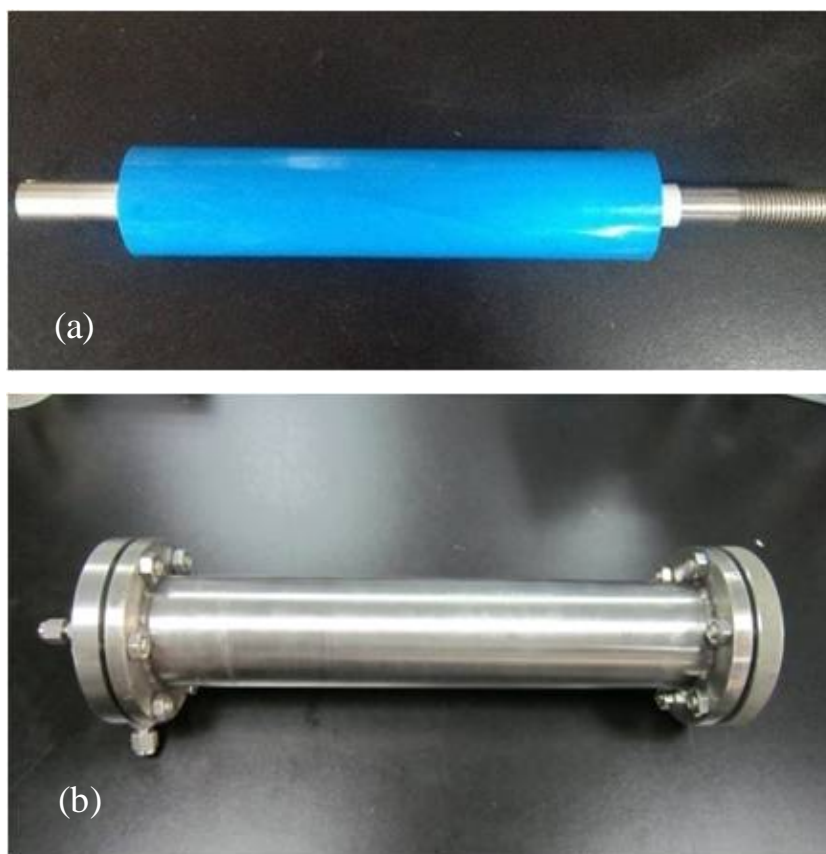


Fig. S4 (a) membrane element; (b) spiral wound membrane module.

6. Calculation of the introduced molecule concentration content in the PVAm-MC

The introduced molecule concentration α (mol molecule/g PVAm) can be

calculated according to the m_C/m_N in the PVAm-MC film as follows:

$$\frac{24 \times \alpha + m_C \%}{14 \times \alpha + m_N \%} = m_C / m_N$$

$m_C\%$ - the percentage composition of C in the PVAm;

$m_N\%$ - the percentage composition of N in the PVAm;

m_C/m_N - The mass ratio of C/N in the PVAm-MC.

When calculating the hydrolysis degree, the $m_C\%$ and $m_N\%$ in the PVAm have been measured by an elemental analyzer (Carlo Erba EA1110, Italy). The $m_C\%$ is 53.14% and the $m_N\%$ is 25.84%. The mass ratio of C/N (m_C/m_N) in the PVAm-MC film was 1.889, which was also measured by elemental analyzer. By the calculation, the introduced molecule concentration is 1.76×10^{-2} mol molecule/g.

7. Adsorption selectivity for PVAm and PVAm -MC

The $\text{CO}_2, \text{N}_2, \text{CH}_4$ and H_2 adsorption capacities of the pure PVAm and PVAm-MC were characterized by Brunauer–Emmett–Teller measurement using the single component of $\text{CO}_2, \text{N}_2, \text{CH}_4$ and H_2 gases at low pressure region (below 1 bar). The ideal adsorption solution theory (IAST) of Myers and Prausnitz has been reported to predict binary gas mixture adsorption.^{3,4} The adsorption selectivity [defined as $S_{\text{ads}}=(q_1/q_2)/(P_1/P_2)$, where q_i is the amount of i adsorbed and P_i is the partial pressure of i in the mixture] of the pure PVAm and PVAm-MC for CO_2/N_2 (20/80 by volume), CO_2/CH_4 (10/90 by volume) and CO_2/H_2 (40/60 by volume) were estimated from the experimental single-component isotherms, as shown in Fig. S4.

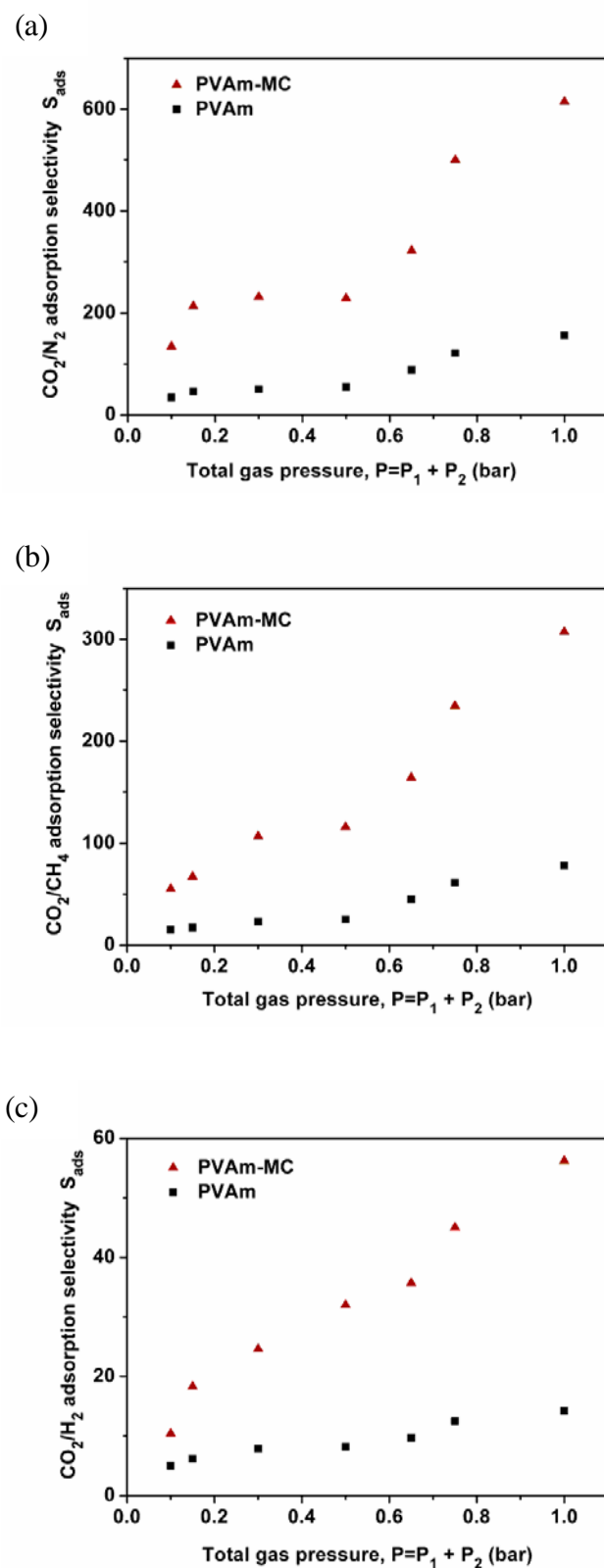
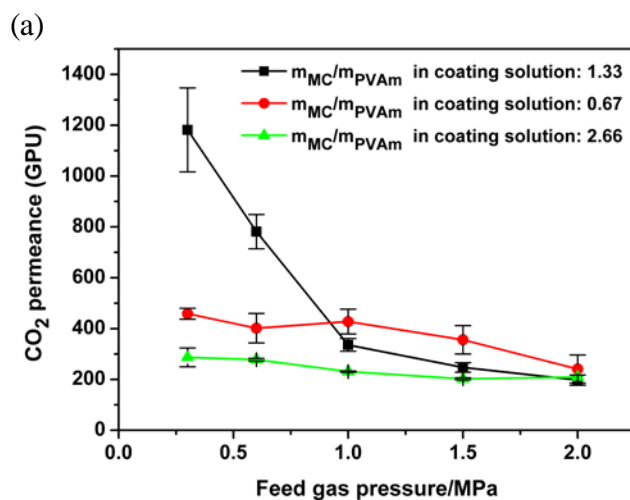


Fig. S5 IAST-predicted CO₂ adsorption selectivity of the pure PVAm and PVAm-MC: (a) CO₂/N₂; (b) CO₂/CH₄; (c) CO₂/H₂

8. The separation performance of PVAm-MC/PSF membrane with different mass ratio of MC/PVAm (m_{MC}/m_{PVAm})

We prepared PVAm-MC/PSF membrane with different m_{MC}/m_{PVAm} in coating solution. The concentration of PVAm is 0.02 g/ml and the m_{MC}/m_{PVAm} is 0.67, 1.33 and 2.66 respectively. The separation performance of PVAm-MC/PSF membrane for CO₂/N₂ with different m_{MC}/m_{PVAm} in coating solution is shown in Fig. S5. Comprehensively considering the CO₂ permeance and CO₂/N₂ selectivity, the PVAm-MC/PSF membrane with m_{MC}/m_{PVAm} in coating solution 1.33 shows the best separation performance. The explanation about the separation performance can be found in our previous work.^{1,8} Thus, in this communication, the PVAm-MC aqueous solution containing 0.02 g/ml PVAm as well as 0.0266 g/ml MC was prepared.



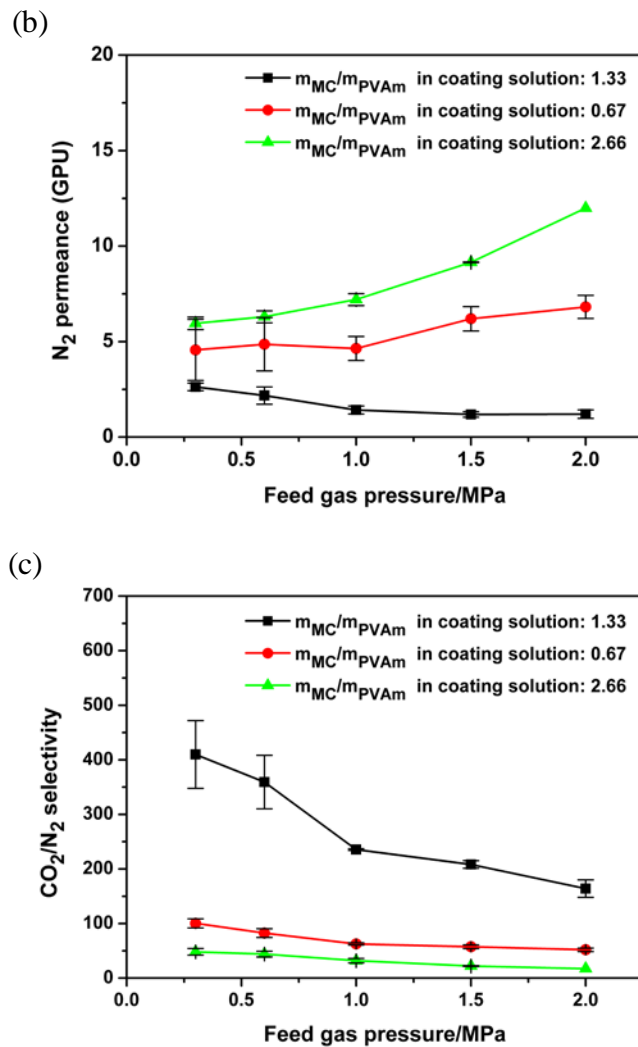


Fig. S6 The separation performance of PVAm-MC/PSF membrane with different m_{MC}/m_{PVAm} (a) CO₂ permeance; (b) N₂ permeance; (c) CO₂/N₂ selectivity. Feed gas: CO₂/N₂ (20/80 by volume).

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