

## Supporting Information for

# Gas Separation Membrane with CO<sub>2</sub>-Facilitated Transport Highway Constructed from Amino Carrier Containing Nanorods and Macromolecules\*\*

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## 1. Experimental

### Materials and Chemicals:

N-vinylformamide (NVF) was purchased from Aldrich Inc., distilled under vacuum and stored at -15 °C. 2, 2'-azobis (2-methylpropion-amidine) dihydrochloride (AIBA) purchased 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 using. Aniline was purchased from Kewei Chemical Reagent Co. Ltd. (Tianjin, China) and distilled under reduced pressure to purify before use. Hydrochloric acid (HCl), ethanol, ammonium peroxydisulfate (APS) and

acetone purchased from Kewei Chemical Reagent Co. Ltd. (Tianjin, China) were of analytical grade and used as received. Deionized water having a conductivity of less than 12  $\mu\text{s}/\text{cm}$  was produced by a reverse osmosis system.

### **Synthesis of Polyvinylamine:**

The polyvinylamine (PVAm) was synthesized through the polymerization of NVF monomer in deionized water with AIBA as an initiator at 52 °C for 5 h under N<sub>2</sub> atmosphere and then the acidic hydrolysis of poly (N-vinylformamide) at 70 °C for 2 h. After acidic hydrolysis, the products were precipitated in excess ethanol and then purified using anion exchange resin. Finally, the PVAm was obtained after dried in a vacuum oven.

### **Synthesis of Modified PANI Nanorods:**

Modified PANI nanorods were synthesized through dispersion polymerization of aniline using APS as an oxidant and PVP (K25) as a steric stabilizer in 1 M HCl solution at 0 °C. After polymerization, the products were isolated through several acetone precipitation and wash steps. Finally, the products were dedoped with ammonia water, washed several times and then dried under a vacuum. The modified PANI nanorods were dispersed in deionized water with stir and ultrasonic treatment to prepare 2.0 wt% aqueous dispersion.

### **Preparation of Gas Separation Membranes:**

The PVAm-PANI coating solutions were prepared by mixing PVAm aqueous

solutions, PANI nanorods aqueous dispersion and deionized water. In the coating solutions, the mass content of PVAm kept at 2.0 wt%, and the mass ratio of PANI:PVAm ( $m_{\text{PANI}}/m_{\text{PVAm}}$ ) was 0.2. The nanocomposite membranes were prepared by casting PVAm-PANI coating solution on PSf ultrafiltration membrane with a pre-set wet coating thickness by a coating applicator (an accuracy of  $\pm 10 \mu\text{m}$ ), and then dried at 30 °C and 40% relative humidity for 24 h. The obtained membrane was marked as PVAm-PANI/PSf nanocomposite membranes. For comparison, pure PVAm membrane was also prepared with pure PVAm aqueous coating solutions. The wet coating thickness of the active layer was kept as 50 or 200  $\mu\text{m}$ .

#### **Characterization Techniques of Modified PANI nanorods and Membrane:**

The chemical composite and morphology of modified PANI nanorods were examined by fourier transform infrared spectroscopy (FTIR, FTS-6000, Bio-Rad) and transmission electron microscopy (TEM, JEM-100 CX, JEOL), respectively.

The surface chemical composite of the membrane was characterized by attenuated total reflectance fourier transform infrared (ATR-FTIR, FTS-6000, Bio-Rad). The tested samples, i.e. PVAm film and PVAm-PANI film, were obtained by dropping the coating solution on silicone rubber substrate, then drying under 30 °C and 40% relative humidity for at least 24 h and finally peeling from the substrate.

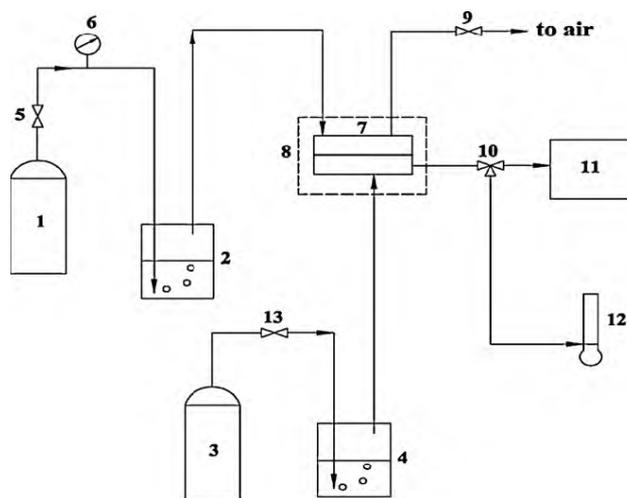
The scanning electron microscopy (SEM) cross-sectional image was performed on a Nova NanoSEM 430 (FEI, USA) instrument. For the cross-sectional observation,

the membrane sample was prepared by peeling away the polyester backing fabric, then frozen in liquid nitrogen and fractured. The membrane fragment was then coated with a nanometer scale gold layer by a sputter-coating machine.

X-ray diffraction (XRD) characterization was carried out to investigate the crystallinity of the films. XRD spectra were collected by X-ray diffractometer (XRD, D/MAX-2500, Japan) using Cu K $\alpha$  radiation ( $\lambda=0.1542$  nm) with  $2\theta$  scanned between  $5^\circ$  and  $80^\circ$  under an 8 kW power. The crystallinity was estimated by Jade 5.0 software according to the XRD spectrum.

The gas permselectivity of the membrane was characterized by a set of test equipments <sup>[S1]</sup> shown in Figure S1 using CO<sub>2</sub>/N<sub>2</sub> mixed gas (15/85 by volume). Prior to contacting the membrane, the feed gas and the sweep gas (H<sub>2</sub>) were humidified with water vapor. The flow of outlet sweep gas was measured using a soap film meter and its composition was analyzed by a gas chromatograph equipped with a thermal conductivity detector. The downstream pressure in the apparatus was maintained at the atmosphere pressure. Permeation experiments were carried out at 22 °C with a feed pressure varying from 0.11 to 1.5 MPa, and steady state permeation was assumed to have been reached when the sweep gas flow rate and its composition no longer changed with time. The gas permeances of CO<sub>2</sub> and N<sub>2</sub> were calculated through the steady sweep gas flow rate and composition. All error bars represent the standard errors of the performances of three membranes prepared under the same conditions. In addition, it has been suggested that the effect of back-diffusion of H<sub>2</sub> on data analysis

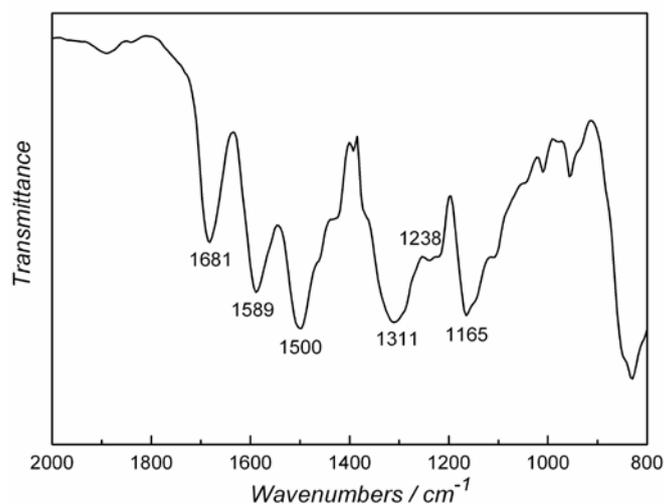
could be neglected.<sup>[S1]</sup>



**Figure S1.** Schematic representation of gas permeation apparatus: (1) feed gas cylinder; (2) sweep gas cylinder; (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.

## 2. FTIR Spectrum of Modified PANI Nanorods:

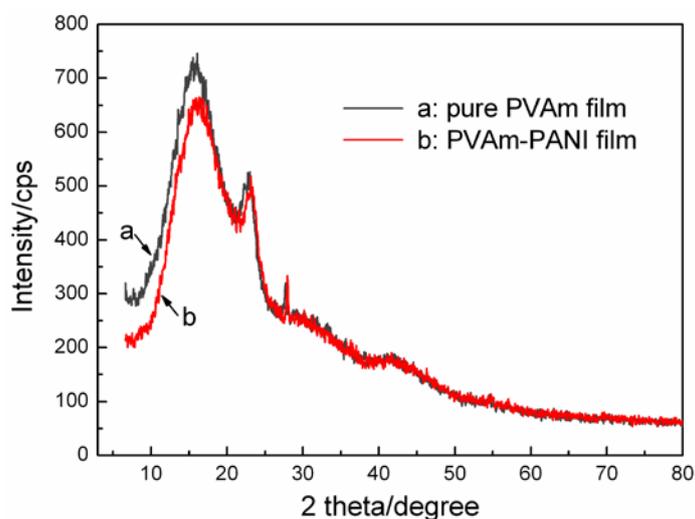
Figure S2 shows the FTIR spectrum of modified PANI nanorods. The bands at 1589 and 1500  $\text{cm}^{-1}$  are attributed to C=C stretching for quinoid ring and benzenoid ring of PANI.<sup>[S2]</sup> The absorption bands at 1311 and 1288  $\text{cm}^{-1}$  are ascribed to C–N stretching mode of the benzenoid ring of PANI, and the bands at 1165  $\text{cm}^{-1}$  are due to the aromatic C–H bending.<sup>[S2]</sup> The peak at 1681  $\text{cm}^{-1}$  is assigned to the carbonyl absorption of PVP. Thus, the FTIR spectrum of modified PANI nanorods is consisting of the characteristic peaks of PANI and PVP.



**Figure S2.** FTIR spectrum of the modified PANI nanorods

### 3. XRD Spectra of pure PVAm film and PVAm-PANI film:

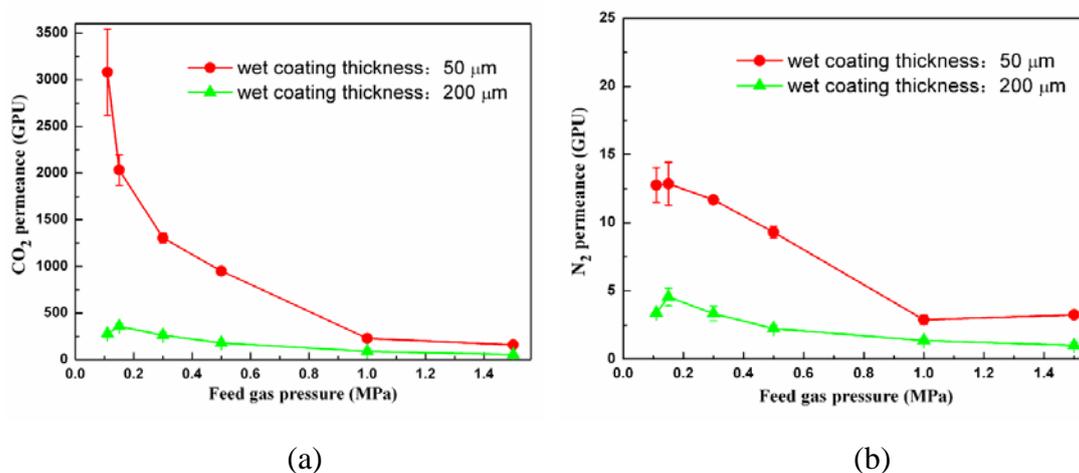
Figure S3 shows the XRD diffraction spectra of pure PVAm film and PVAm-PANI film. The diffraction intensities of the film decreased with the addition of modified PANI nanorods. Through the estimation of Jade 5.0 software, the crystallinity decreased from 28.2% to 17.8% with the incorporation of modified PANI nanorods.

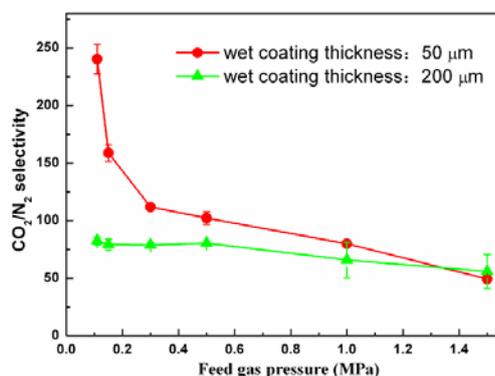


**Figure S3.** XRD spectra of pure PVAm film and PVAm-PANI film.

#### 4. Effect of Wet Coating Thickness on the Performance of PVAm-PANI/PSf Nanocomposite Membrane:

Figure S4 displays that the gas permselectivity of PVAm-PANI/PSf nanocomposite membrane prepared with different wet coating thickness. With increasing feed pressure, the CO<sub>2</sub> permeance of the thinner one drops more rapidly than that of the thicker one. Even though, both CO<sub>2</sub> permeance and CO<sub>2</sub>/N<sub>2</sub> selectivity of the membrane with 50 μm wet coating thickness are obviously higher than those of the membrane with 200 μm wet coating thickness. This indicated that the ultra-thin membrane preparation is favorable for the optimization of CO<sub>2</sub> separation performance of PVAm-PANI/PSf nanocomposite membrane.





(c)

**Figure S4.** Effects of wet coating thickness on gas permeance and selectivity of PVAm-PANI/PSf membrane, (a) CO<sub>2</sub> permeance, (b) N<sub>2</sub> permeance, (c) CO<sub>2</sub>/N<sub>2</sub> selectivity.  $m_{\text{PANI}}/m_{\text{PVAm}}$  in casting solution: 0.2

### 5. Performance Comparison with Other Membranes Reported in the Literature:

Table S1 presents the performance of PVAm-PANI/PSf nanocomposite membrane obtained in this work and the performance of other membranes reported in the literature. It can be seen that the membranes reported in the literature have a CO<sub>2</sub> permeance about 300–1000 GPU and have a CO<sub>2</sub>/N<sub>2</sub> selectivity of about 40–110. Compared with these membranes, PVAm-PANI/PSf nanocomposite membrane shows excellent CO<sub>2</sub> permeance as well as CO<sub>2</sub>/N<sub>2</sub> selectivity.

**Table S1.** Performance comparison of the membrane obtained in this work with other membranes in the literature

Membrane	Feed gas (CO <sub>2</sub> vol.%)	$R_{\text{CO}_2}$ (GPU)	$\alpha$	Permeate side	$P_{\text{CO}_2}$ (P)	Reference
PVAm-PANI/PSf	CO <sub>2</sub> /N <sub>2</sub> (15%)	3080	240	0.1 MPa, H <sub>2</sub> as sweeping gas	0.02 (0.11)	This work

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PVAm-EDA/PSf	CO <sub>2</sub> /N <sub>2</sub> (20%)	607	106	0.1 MPa, H <sub>2</sub> as sweeping gas	0.02 (0.11)	[S3]
Polaris™	CO <sub>2</sub> /N <sub>2</sub> (13%)	1000	50	0.022 MPa, vacuum	0.014(0.11)	[S4]
PVAm/PPO	CO <sub>2</sub> /N <sub>2</sub> (10%)	365	60	0.01 MPa, vacuum	0.02 (0.2)	[S5]
PEO-PBT/PEG-D BE (PAN-PDMS)	CO <sub>2</sub> /N <sub>2</sub> (28%)	730	40	0.11 MPa, no sweeping gas	0.14 (0.5)	[S6]

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$P_{\text{CO}_2}$ —CO<sub>2</sub> partial pressure of the feed gas (MPa);  $P$ —feed gas pressure (MPa). The prepared conditions of PVAm-PANI/PSf nanocomposite membrane: the mass ratio of PANI/PVAm in the coating solution: 0.2; wet coating thickness: 50 μm.

## References

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