

Supporting Information

Mixed Matrix Membranes Incorporating a Facile In Situ Synthesized PEI-g-ZIF-8 for CO₂ Separation

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Figure S1 shows the FTIR spectra of PEI, ZIF-8 and PEI-g-ZIF-8 nanoparticles. The peak at 1340 cm^{-1} in the curve of PEI belongs to the in-plane bending vibration of methenyl C-H. The characteristic absorption peak of ZIF-8 at 421 cm^{-1} , attributing to Zn-N stretch vibration mode, was observed in the curves of both ZIF-8 and PEI-g-ZIF-8. It is worth pointing out that the Zn-N bond characteristic peak of PEI-g-ZIF-8 is weaker than that of ZIF-8, owing to the alleviated formation of Zn-mim-Zn bonds when crystal cells connect together. The wide absorption bands in the range of 650 to 1500 cm^{-1} can be attributed to the vibration modes of the imidazolate in ZIF-8¹. In the curve of PEI-g-ZIF-8 spectrum, the weak doublet at 813 and 833 cm^{-1} belongs to the N-H bending and wagging vibration of primary amino groups, owing to the extra primary amino groups in the PEI chains exposed on the surface of PEI-g-ZIF-8 nanoparticles, while no such doublet can be observed in the ZIF-8 curve. In addition, there is a characteristic peak at 3277 cm^{-1} (N-H stretching vibration of primary and secondary amino groups) and a weak peak at 3348 cm^{-1} (doublet for N-H stretching vibration of primary amino groups) in the absorption bands of PEI but no such peaks for ZIF-8. After modified by PEI, a new broad peak at 3237 cm^{-1} in the absorption bands of PEI-g-ZIF-8 is observed, indicating that PEI chains are grafted into the ZIF-8 nanoparticles. Another proof is that the peak at 1381 cm^{-1} , attributing to methylene groups of PEI, becomes stronger in PEI-g-ZIF-8 curve compared with ZIF-8.

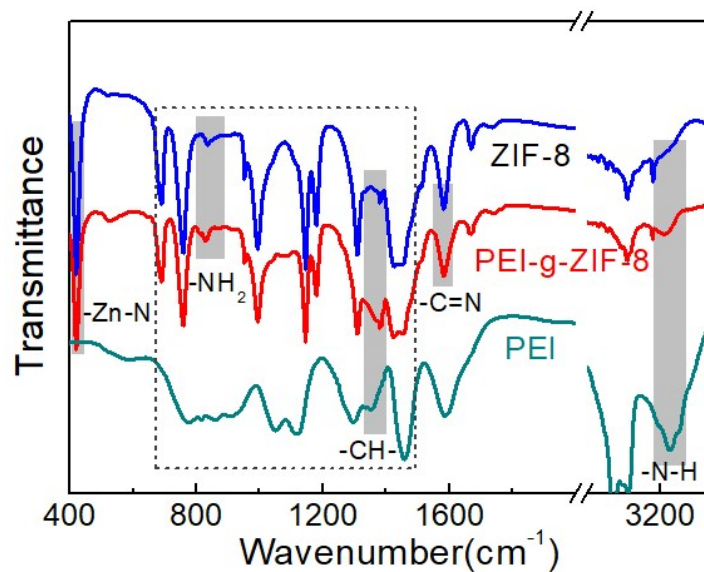


Figure S1. FTIR spectra of PEI, ZIF-8 and PEI-g-ZIF-8 nanoparticles.

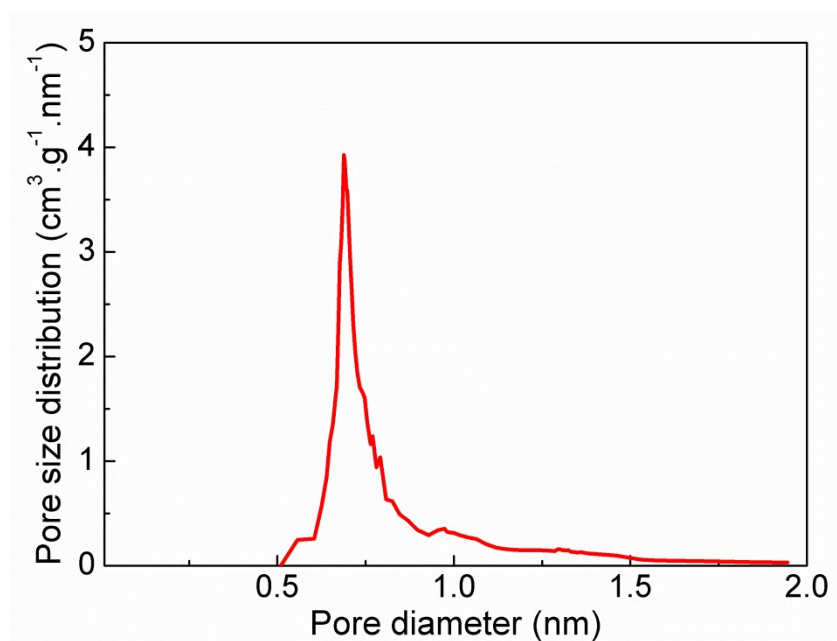


Figure S2. The pore size distribution of PEI-g-ZIF-8 nanoparticles.

The FTIR spectroscopy was also investigated to examine the change of film surface functionalities. Figure S2 shows the FTIR spectra of PVAm film and PVAm/PEI-g-ZIF-8 film in the frequency region from 650 cm^{-1} to 3000 cm^{-1} . Peaks in the spectrum of the PVAm/PEI-g-ZIF-8 film combine the characteristic bands of both PEI-g-ZIF-8

and PVAm. On one hand, compared with the characteristic peak at 833 cm^{-1} for PEI-g-ZIF-8, the peak slightly shifts to 814 cm^{-1} for PVAm/PEI-g-ZIF-8 film, demonstrating the formation of hydrogen bond between PEI-g-ZIF-8 and PVAm chains. On the other hand, the strong sharp peak at 1585 cm^{-1} for PEI-g-ZIF-8 and a similar peak at 1566 cm^{-1} for PVAm/PEI-g-ZIF-8 film could be attributed to the C=N vibration mode, also indicating an increased amount of hydrogen bond.

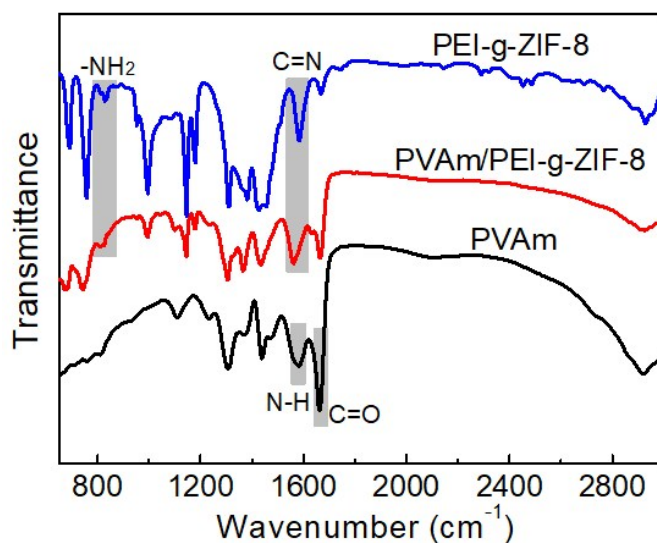


Figure S3. FTIR spectra of PEI-g-ZIF-8 nanoparticles, PVAm film and PVAm/PEI-g-ZIF-8 film.

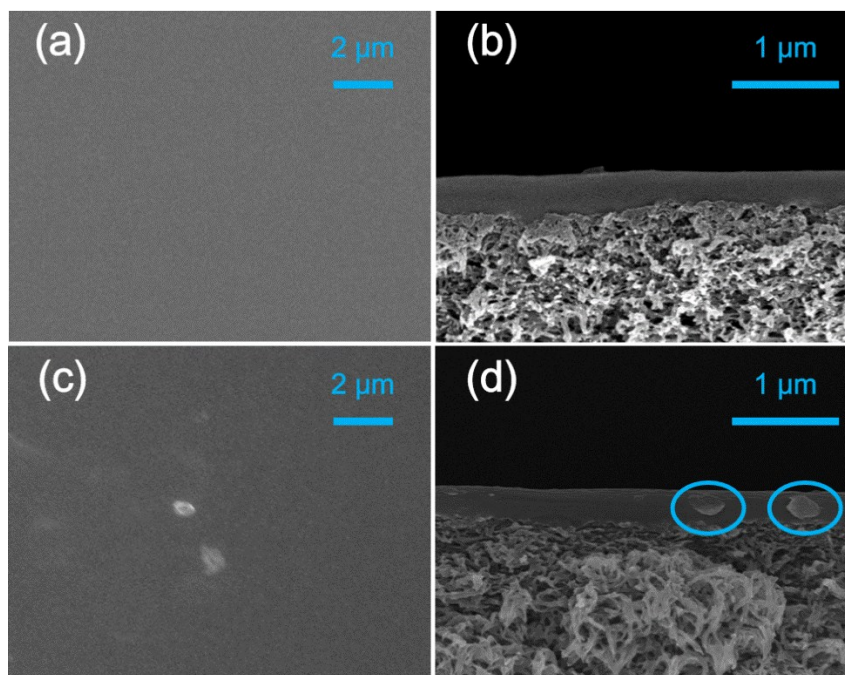


Figure S4. Surface and cross sectional SEM images of PVAm/mPSf (a, b) and PVAm/ZIF-8/mPSf (c, d) membranes. Wet coating thickness: 100 μm . MP_{NPs} : 20.0 wt%.

In this work, we employed three different contents of PEI and made a comparison of the separation performance of their corresponding MMMs under 0.30 MPa feed gas pressure. The PEI-g-ZIF-8 nanoparticles were denoted as PEI-g-ZIF-8(5:40:0.5), PEI-g-ZIF-8(5:40:1) and PEI-g-ZIF-8(5:40:2) with the molar ratios of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Hmim and PEI as 5:40:0.5, 5:40:1 and 5:40:2, respectively. As can be seen from Table S1, the MMMs fabricated by using PEI-g-ZIF-8(5:40:1) nanoparticles have the highest separation performance. Compared with the MMMs fabricated by using PEI-g-ZIF-8(5:40:1), the CO_2 permeance and CO_2/N_2 selectivity of the MMMs fabricated by using PEI-g-ZIF-8(5:40:0.5) decreased by 18.4% and 18.0% respectively, while the MMMs by using PEI-g-ZIF-8(5:40:2) resulted 21.6% and 23.3% decrease of CO_2 permeance and CO_2/N_2 selectivity, respectively. On one hand, a smaller amount of PEI is insufficient to improve the CO_2 absorption and permeate property for PEI-g-ZIF-8 nanoparticles. On the other hand, since the porous structure of ZIFs is sensitive to the ligand content, an excessive mass of PEI may

partly block the pores, resulting in the decrease of membrane separation performance. Thus, in this work we chose the optimal molar ratio of Zn^{2+} :Hmim:PEI as 5:40:1 to synthesize PEI-g-ZIF-8 nanoparticles.

Table S1 Separation performance of PVAm/PEI-g-ZIF-8/mPSf membranes using PEI-g-ZIF-8 nanoparticles synthesized with different molar ratios of $Zn(NO_3)_2 \cdot 6H_2O$, Hmim and PEI. Wet coating thickness for the MMMs: 100 μm . MP_{NPs} : 16.7 wt%.

Molar ratio (Zn^{2+} :Hmim:PEI)	PEI-g-ZIF-8	PVAm/PEI-g-ZIF-8/mPSf membranes	
		CO ₂ permeance	CO ₂ /N ₂ selectivity
5:40:0.5	PEI-g-ZIF-8(5:40:0.5)	1624 \pm 132	65.5 \pm 1.9
5:40:1	PEI-g-ZIF-8(5:40:1)	1990 \pm 148	79.9 \pm 2.0
5:40:2	PEI-g-ZIF-8(5:40:2)	1560 \pm 150	61.3 \pm 2.4

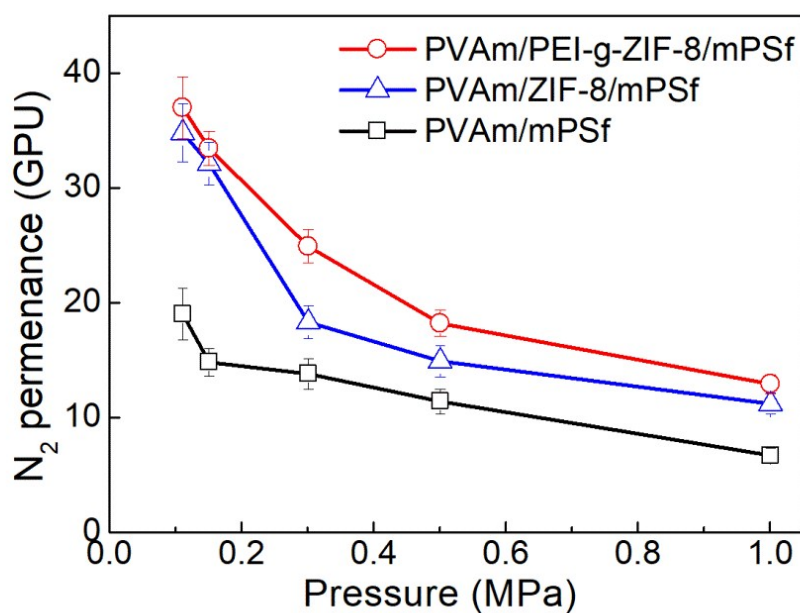


Figure S5. N₂ permeance of different MMMs based on mPSf substrate. Wet coating thickness for MMMs: 100 μm . MP_{NPs} : 16.7 wt%. Feed gas: CO₂/N₂ (15/85 vol.%) mixed gas. Feed gas pressure: 0.30 MPa.

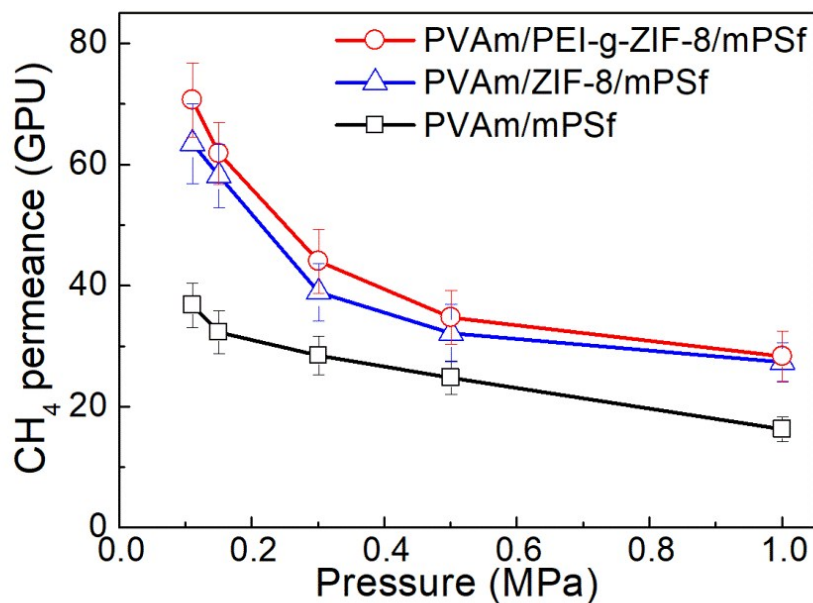


Figure S6. CH₄ permeance of different MMMs based on mPSf substrate. Wet coating thickness for MMMs: 100 μm. MP_{NPS} : 16.7 wt%. Feed gas: CO₂/CH₄ (10/90 vol.%) mixed gas. Feed gas pressure: 0.30 MPa.

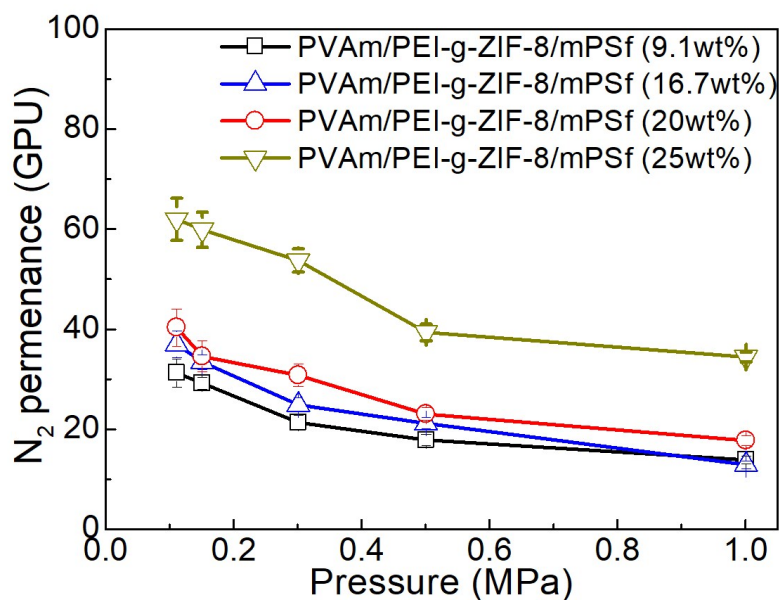


Figure S7. N₂ permeance of MMMs with different PEI-g-ZIF-8 loadings. Wet coating thickness for MMMs: 100 μm. Feed gas: CO₂/N₂ (15/85 vol.%) mixed gas. Feed gas pressure: 0.30 MPa.

Literature Cited

1. A. Samadi-Maybodi, S. Ghasemi and H. Ghaffari-Rad, *Sensors and Actuators B-Chemical*, 2015, **220**, 627-633.