

Polymer/metal-organic framework junctions in polyamide membrane via *in-situ* amine etching for stable CO₂/N₂ selectivity at elevated pressures

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ABSTRACT: Polyamide thin-film composite (PA-TFC) membranes with ultrathin selective layers, fabricated via facile interfacial polymerization process, are fascinating for CO₂/N₂ separation. But they always suffer from drastic deterioration of CO₂/N₂ selectivity at elevated pressures due to CO₂-induced swelling of polymer chains. Herein, we report an *in-situ* amine etching strategy to construct robust polyamide/polyethyleneimine (PEI)-functionalized ZIF-8 (PA/PEI-ZIF-8) junctions within PA-TFC membranes. In this strategy, PEI-ZIF-8 colloid was sprayed onto triethylenetetramine (TETA)-preimpregnated polysulfone substrates prior to interfacial polymerization, leading to controllable etching of PEI-ZIF-8 particles into Zn-imidazole clusters and ultra-small PEI-ZIF-8 nanocrystals. These etched species subsequently coordinated with TETA, forming highly integrated PA/PEI-ZIF-8 junctions with enhanced interfacial compatibility. Benefiting from the high porosity of PEI-ZIF-8 nanocrystals and excellent interfacial compatibility, the optimized composite membrane realizes a CO₂ permeance of 478 GPU (GPU = gas permeance unit) and a CO₂/N₂ selectivity of 60.3. Notably, owing to the rigidity of PEI-ZIF-8 nanocrystals and coordination interactions between PEI-ZIF-8 and polyamide chains, the PA/PEI-ZIF-8 junctions effectively improve the anti-swelling property of composite membranes. Contrary to reduced CO₂/N₂ selectivity of pristine PA membrane at elevated pressures, the CO₂/N₂ selectivity of composite membrane remains stable as the feed gas pressure increases from 1 to 4 bar. This work provides a novel strategy for fabricating robust PA-TFC membranes for pressurized CO₂ separation.

KEYWORDS: polyamide composite membranes, metal-organic frameworks, PEI-ZIF-8 nanoparticles, *in-situ* amine etching, CO₂ separation

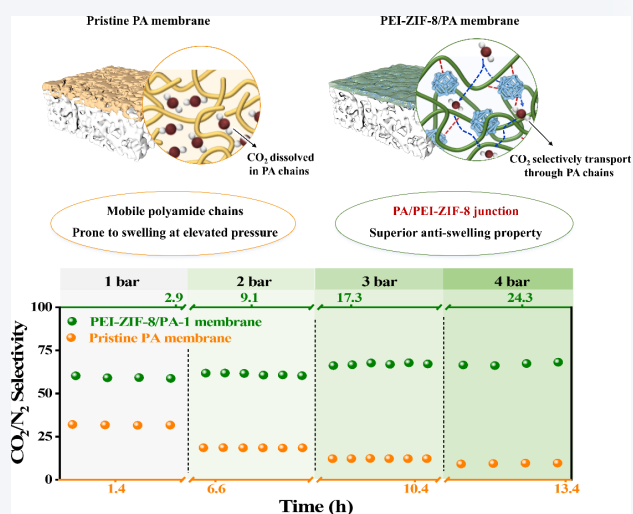
1 Introduction

Membrane gas separation process has emerged as a promising

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approach for CO₂ capture, owing to its low energy consumption compared with traditional gas separation technologies such as cryogenic distillation, solvent absorption, and adsorption [1, 2]. Among various membranes, polyamide (PA)-based facilitated transport membranes have attracted considerable attention due to their exceptional CO₂ separation performance [3, 4]. These membranes typically feature ultrathin selective layers (usually below 200 nm) and abundant amino groups, which contribute to a superior CO₂ facilitated transport capability [5, 6]. Although PA membrane fabricated via the classic “water-before-oil” interfacial

polymerization (IP) approach has been widely commercialized in the field of reverse osmosis (RO) membrane, nanofiltration (NF), and forward osmosis (FO) processes [7–10], its application in CO₂ separation lags behind.

Some efforts have been devoted toward enhancing CO₂ separation performance based on the conventional “water-before-oil” IP approach, such as surfactant-assisted IP [11, 12], introduction of porous nanofillers [13, 14], prolonged polymerization time, elevated reaction temperatures [15], creation of Turing structures [16, 17], and electrospraying-assisted IP [18]. Among these strategies, the introduction of porous nanofillers, such as metal-organic frameworks (MOFs) [19], covalent organic frameworks (COFs) [20], carbon materials [21], and boron nitride [22], has been considered as an effective approach. These nanofillers not only provide fast and selective transport pathways for CO₂ through their well-defined pore structure and functionalized surfaces but also modulate the cross-linking network of PA matrix. For example, Li et al. developed a polyamide thin-film nanocomposite (PA-TFN) membrane modified with porous graphene (PG) nanosheets [23]. The uniformly distributed PG nanosheets in membrane provided high-efficiency molecular sieving pathway for CO₂, leading to simultaneous increase in CO₂ permeance and CO₂/N₂ selectivity by approximately 21.0% and 20.8%, respectively. Excluding the intrinsic pore structures provided by nanofillers, the introduction of nanofillers can also tailor the chain packing of the polyamide matrix. Awad et al. developed a high-performance CO₂ separation membrane by incorporating carbide-derived carbon (CDC) into the PA layer [21]. The CDC fillers disrupted chain packing of polyamide and increased the fractional free volume, enhancing CO₂ permeance by 88% and CO₂/CH₄ selectivity by 49% compared with the pristine membrane.

However, most PA-based composite membranes always suffer from poor stability under pressurized conditions, mainly due to the inherent flexibility of PA chains and poor filler-matrix interfacial compatibility, which render the PA matrix susceptible to CO₂-induced swelling under elevated pressures [24–26]. This phenomenon, commonly referred to as CO₂ plasticization, originates from the strong affinity of CO₂ molecules toward polar functional groups within polymer membranes. At high feed gas pressures, excessive sorbed CO₂ molecules penetrate into the

polymer matrix and act as molecular spacers, weakening intermolecular interactions such as hydrogen bonding and increasing the interchain spacing as well as the free volume of the polymer. Consequently, the segmental mobility of the polymer chains increases significantly, accompanied by relaxation of the originally rigid structure. This process results in a substantial loss of selectivity and facilitates the permeation of both target and non-target gas molecules, ultimately leading to a considerable reduction, or even complete loss of selectivity [27, 28]. Improving the anti-swelling properties of polymeric membranes therefore remains a critical challenge. Various strategies have been developed to address this issue [29], including physical or chemical cross-linking [30–32], incorporation of rigid moieties [33–35], and optimization of polymer chain orientation [36]. Among these strategies, incorporating rigid nanofillers with ideal interfacial compatibility is an effective approach to suppress membrane swelling and maintain structural integrity [37]. For example, Yaghi et al. reported that the construction of polymer-COF junctions, where polymer chains thread through the pores of COF nanocrystals forming the strong interfacial interaction, considerably enhanced mechanical robustness of polymers, leading to simultaneous improvements in strength, ductility, and toughness of composite materials [38]. Similarly, Li et al. developed polyethylene oxide@ZIF-8 (PEO@ZIF-8) mixed matrix membranes (MMMs) through a dormancy and double-activation strategy [39]. The strong interfacial interaction between PEO and ZIF-8 nanocrystals effectively restricted polymer chain mobility, achieving stable CO₂/CH₄ separation performance. These reports indicate that the construction of ideal polymer-filler interfacial interaction is effective for enhancing the anti-swelling property of composite membranes.

We herein developed PA-TFN membranes with PA/PEI-ZIF-8 (PEI = polyethyleneimine) junctions via an *in-situ* amine etching approach during IP process. As schematically illustrated in Fig. 1, polysulfone (PSF) substrate was pre-impregnated by triethylenetetramine (TETA) aqueous solution. Polyethyleneimine functionalized ZIF-8 (PEI-ZIF-8) colloid containing nanoparticles (average size around 25 nm) were first sprayed onto surface of TETA-impregnated substrate. During this process, PEI-ZIF-8 nanoparticles were etched by TETA and partially decomposed, yielding Zn-imidazole coordination clusters and residual PEI-ZIF-8

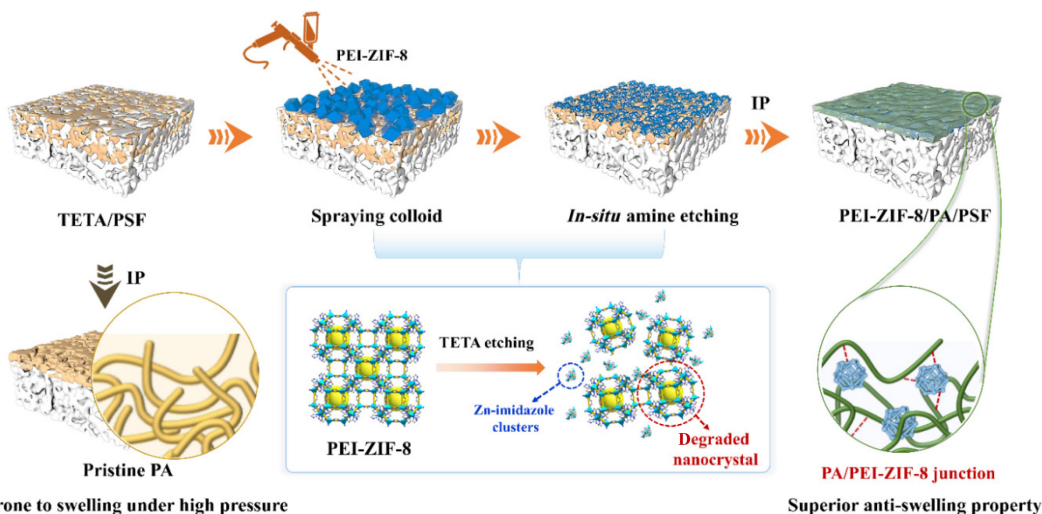


Figure 1 Schematic illustration of the preparation for PEI-ZIF-8/PA composite membranes (IP represents the polycondensation reaction between TETA and TMC monomers at the two-phase interface, as depicted in Fig. S1 in the ESM). Compared with pristine PA membrane, the construction of PA/PEI-ZIF-8 junction via *in-situ* amine etching endows the PEI-ZIF-8/PA/PSF composite membrane with superior anti-swelling property.

nanocrystals with small particle size. The Zn-imidazole clusters subsequently entered the aqueous phase and coordinated with TETA monomers, thereby modulating the subsequent IP reaction with trimesoyl chloride (TMC), producing a smooth and ultrathin PA layer. Simultaneously, the residual PEI-ZIF-8 nanoparticles were uniformly embedded within the nascent PA matrix. Importantly, the etching process created additional intracrystalline and interfacial mesopores within the nanoparticles, which facilitated deeper infiltration of PA chains and promoted the formation of a tightly interlocked PA/PEI-ZIF-8 junctions, effectively restricting polymer segment mobility and enhancing the rigidity of the composite membrane. The resulting composite membrane is anticipated to exhibit superior anti-swelling properties and stable CO₂ separation performance under elevated feeding pressures, offering a practical and scalable route for the development of high-performance and pressure-resistant gas separation membranes.

2 Experimental

2.1 Preparation of PEI-ZIF-8 colloid

The colloid was prepared in accordance with a modified method reported by Jiao et al. [40]. 2-Methylimidazole (2-MeIm, 1.624 g) and polyethyleneimine (PEI, 0.3 g) were respectively dissolved in 30 and 20 mL of methanol. The above two solutions were mixed and stirred for 5 min. A solution containing methanol (50 mL) and Zn(NO₃)₂·6H₂O (0.736 g) was subsequently added and stirred for 1 h. The resulting PEI-ZIF-8 nanoparticles were separated by centrifugation at a speed of 9800 r·min⁻¹. The final product was dispersed in methanol (37 mL) and the concentration of PEI-ZIF-8 colloid was estimated to be 6 mg·mL⁻¹.

2.2 Fabrication of PEI-ZIF-8/PA membranes

PSF ultrafiltration membrane substrate was immersed in deionized water for 12 h and washed with water before use. The substrate was immersed in an aqueous solution containing 0.3 wt.% of TETA and 0.4 wt.% of Na₂CO₃ for 10 min. After removing the excess aqueous solution, the TETA/PSF substrate was dried in the atmosphere. Then, the PEI-ZIF-8 colloids with different concentrations of 0.06, 0.6, 1, 2, and 6 mg·mL⁻¹ were respectively sprayed onto TETA/PSF substrate. After the membranes dried at room temperature for 2 h, the hexane solution with 0.7 wt.% of TMC was poured onto the membrane surface. After 3 min of interfacial polymerization, hexane solution was removed. 15 mL of hexane solution was used to wash the resulting membranes for three times. After 12 min of further heating at 70 °C for densification, the polyamide composite membranes were kept away from light at room temperature. The as-prepared polyamide composite membranes were denoted as PEI-ZIF-8/PA-*x*, where *x* indicated the concentration of PEI-ZIF-8 colloid that sprayed onto TETA/PSF substrate.

2.3 Gas separation measurement

Single gas, CO₂/N₂ (50/50 vol.%), and CO₂/CH₄ (50/50 vol.%) mixed gas separation performances were tested via constant pressure/variable volume method using a custom-made permeation cell. The effective permeation area of all membranes was 0.785 cm². The separation performance was both tested at 25 °C with a feed gas pressure of 1 bar (excluding the pressure specially stated). Each feed gas flow rate was controlled at 10 mL·min⁻¹ for gas permeation tests, and argon was used as the sweep gas. Both the test gas and

sweep gas passed through gas bubblers filled with water. All the data were recorded after the stabilization of the gas permeation. The permeated gas composition was measured by an online gas chromatograph (A91, PANNA, China).

The gas separation permeance (P_i) and separation factor (α_{ij}) were calculated by Eq. (1)

$$P_i = Q_i / A \Delta p_i \quad (1)$$

where Q_i is the permeation rate of component *i* (mol·s⁻¹), *A* is the effective membrane area (m²), Δp_i is the transmembrane pressure difference of component *i* (Pa), and P_i of each gas is gas permeance unit (1 GPU = 3.35 × 10⁻¹⁰ mol·m²·s⁻¹·Pa⁻¹).

The selectivity of the mixture gas was calculated by Eq. (2)

$$\alpha_{ij} = P_i / P_j \quad (2)$$

where P_i and P_j refer to the permeance of components *i* and *j*, respectively.

3 Results and discussion

3.1 In-situ amine etching PEI-ZIF-8 nanoparticles

PEI-ZIF-8 nanoparticles were synthesized via a one-pot method at room temperature and subsequently dispersed in methanol for membrane fabrication. As shown in Fig. 2(a), the diffraction peaks of PEI-ZIF-8 match well with the simulated pattern of ZIF-8, confirming the presence of the characteristic sodalite (SOD) topology [41, 42]. No additional peaks corresponding to crystalline impurities were detected, indicating the high purity of the synthesized PEI-ZIF-8. The porous structure of PEI-ZIF-8 nanoparticles was further analyzed using N₂ adsorption-desorption isotherms at 77 K (Fig. 2(b)). Both PEI-ZIF-8 and pristine ZIF-8 exhibit typical Type I isotherms, indicative of a microporous structure [43]. The Bernauer-Emmett-Teller (BET) specific surface area of PEI-ZIF-8 was calculated to be 1288.2 m²·g⁻¹, which is lower than that of pristine ZIF-8 (1615.1 m²·g⁻¹). A decrease in total pore volume was also observed (Table S1 in the Electronic Supplementary Material (ESM)), probably attributed to the incorporation of PEI. All the above results generally confirm the successful integration of PEI within the ZIF-8 framework.

Transmission electron microscopy (TEM) was employed to examine the morphology and particle size of PEI-ZIF-8 nanoparticles. As displayed in Fig. 2(c), PEI-ZIF-8 nanoparticles exhibit a uniform quasi-spherical morphology with an average diameter of approximately 25 nm, which is notably smaller than that of pristine ZIF-8 nanoparticles (~45 nm, Fig. S2 in the ESM). The reduced particle size is mainly ascribed to the grafting of PEI chains, which coordinate with Zn²⁺ ions and inhibit the coordination between Zn²⁺ and 2-MeIm, thereby restraining crystal growth [44]. The nanoparticles display well-defined boundaries without observable aggregation, consistent with their colloidal stability. This observation is further supported by the Tyndall effect of PEI-ZIF-8 dispersion in methanol (inset of Fig. 2(c)). Such good dispersibility is crucial for achieving a homogeneous deposition of nanoparticles in the subsequent membrane fabrication. Generally, the above results verify the successful synthesis of microporous PEI-ZIF-8 with a particle size around 25 nm. As anticipated, spraying the stable PEI-ZIF-8 colloid onto a PSF support yields a uniform and continuous nanoparticle layer (denoted as PEI-ZIF-8/PSF), as

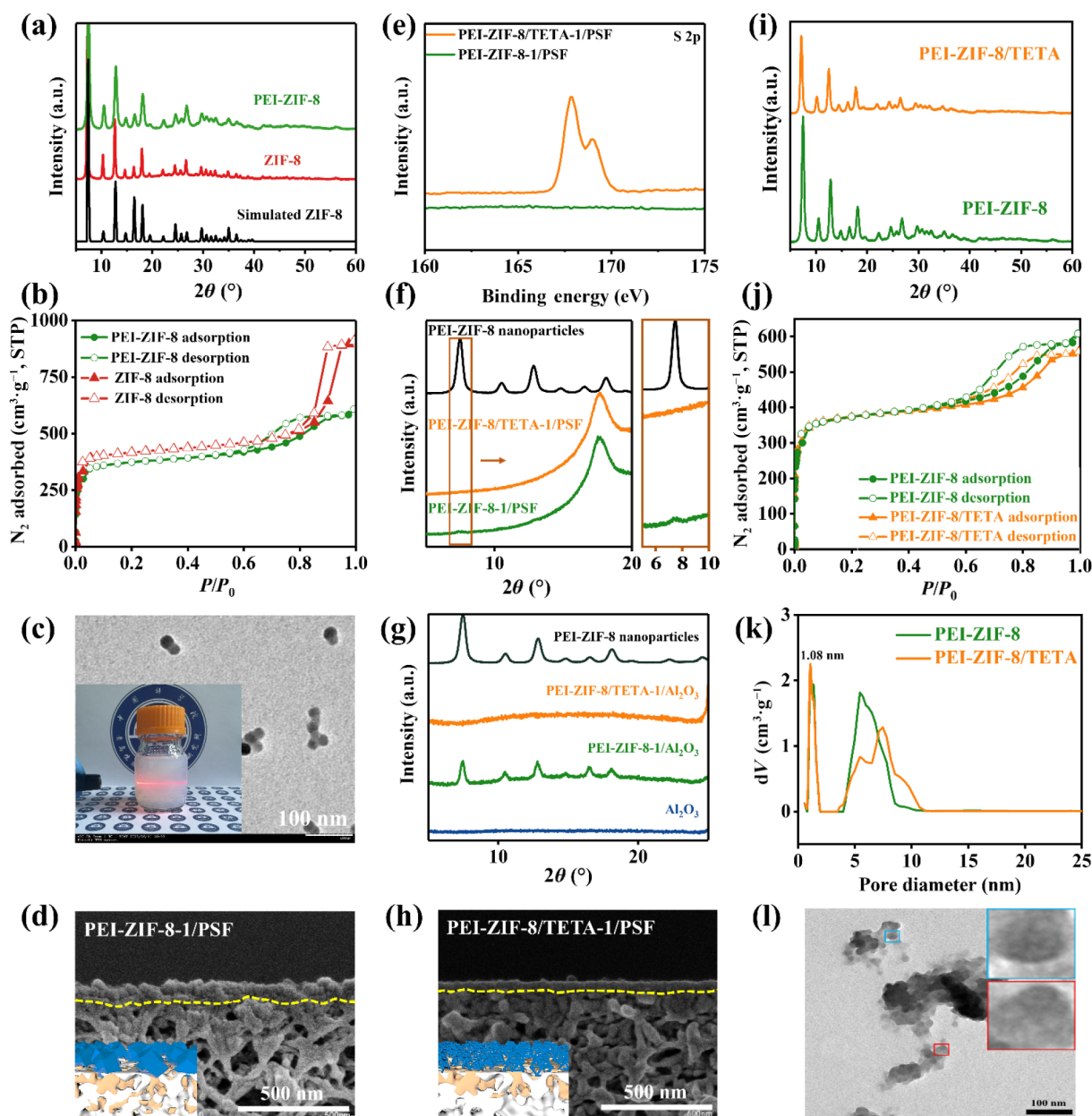


Figure 2 (a) XRD patterns of PEI-ZIF-8, synthesized ZIF-8 nanoparticles, and simulated ZIF-8. (b) N_2 adsorption–desorption isotherms at 77 K of PEI-ZIF-8 and ZIF-8 nanoparticles. (c) TEM image of PEI-ZIF-8 nanoparticles (inset is the Tyndall effect of PEI-ZIF-8 colloid). (d) The cross-sectional SEM image of PEI-ZIF-8-1/PSF membrane. (e) High-resolution XPS S 2p spectra of PEI-ZIF-8-1/PSF and PEI-ZIF-8/TETA-1/PSF membranes. (f) XRD patterns of PEI-ZIF-8 nanoparticles, PEI-ZIF-8-1/PSF membrane, and PEI-ZIF-8/TETA-1/PSF membrane. (g) XRD patterns of PEI-ZIF-8 nanoparticles, Al_2O_3 substrate, PEI-ZIF-8-1/ Al_2O_3 membrane, and PEI-ZIF-8/TETA-1/ Al_2O_3 membrane. (h) The cross-sectional SEM image of PEI-ZIF-8/TETA-1/PSF membrane. (i) XRD patterns, (j) N_2 adsorption–desorption isotherms at 77 K, and (k) pore size distribution of PEI-ZIF-8 nanoparticles and PEI-ZIF-8/TETA solid. (l) TEM image of PEI-ZIF-8/TETA solid.

clearly observed in the corresponding cross-sectional scanning electron microscopy (SEM) image (Fig. 2(d)). This homogeneous deposition layer provides an ideal platform for the subsequent IP reaction, ensuring the effective incorporation and uniform distribution of nanoparticles within the PA matrix.

For the fabrication of polyamide composite membrane, PEI-ZIF-8 colloid was sprayed on the surface of PSF substrate that pre-impregnated with an aqueous TETA solution. In this stage, the pre-adsorbed TETA monomers competitively coordinate with the Zn^{2+} , initiating a controlled etching process of PEI-ZIF-8 nanoparticles. As shown in Figs. 2(d) and 2(h), and Fig. S3 in the ESM, different from PEI-ZIF-8/PSF, the cross-sectional and surface SEM images of

the PEI-ZIF-8/TETA/PSF sample show very flat surface without distinct particles, which indicates that the presence of TETA triggers the etching and corresponding decomposition of PEI-ZIF-8 into Zn-imidazole coordination clusters and residual PEI-ZIF-8 nanocrystals with small particle size. The etching behavior was further investigated using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) techniques. In the XPS spectra (Fig. 2(e)), the S 2p peak at approximately 165 eV, characteristic of the PSF substrate, is absent in the PEI-ZIF-8/PSF sample, indicating complete surface coverage by the PEI-ZIF-8 nanoparticle layer. In contrast, a distinct S 2p peak can be clearly observed in the spectrum of PEI-ZIF-8/TETA/PSF, which is attributed to the

degradation of the PEI-ZIF-8 framework and thus corresponding destruction of PEI-ZIF-8 nanoparticle layer. XRD was used to analyze the structure of degraded PEI-ZIF-8. As shown in Fig. 2(f), both the PEI-ZIF-8/PSF and PEI-ZIF-8/TETA/PSF samples exhibited no obvious diffraction peak due to the interference from the amorphous broad peak of the PSF substrate. Only the weak diffraction peak at 7.5° assigned to PEI-ZIF-8 nanoparticles presents in the PEI-ZIF-8/TETA/PSF, but disappears in the PEI-ZIF-8/TETA/PSF sample, suggesting that the crystal structure of PEI-ZIF-8 nanoparticles was disrupted via TETA etching. To eliminate the interference of PSF substrate, crystalline α - Al_2O_3 was employed as an alternative substrate for XRD analysis. As illustrated in Fig. 2(g), the XRD pattern of PEI-ZIF-8/ Al_2O_3 displays distinct diffraction peaks corresponding to the crystalline PEI-ZIF-8 phase, which completely disappear in the pattern of PEI-ZIF-8/TETA/ Al_2O_3 . The obvious difference may be due to the decomposition of PEI-ZIF-8 nanoparticles on the PSF substrate into smaller and highly dispersed nanocrystals via TETA etching.

To further elucidate the structural evolution of PEI-ZIF-8 during the etching process, PEI-ZIF-8 nanoparticles were treated with an aqueous TETA solution at a concentration identical to that used in membrane fabrication, yielding the etched solid denoted as PEI-ZIF-8/TETA. High-resolution TEM (HRTEM) image reveals a significant morphological transformation. As shown in Fig. 2(l), PEI-ZIF-8/TETA exhibits a reduced size of approximately 16 nm compared with the PEI-ZIF-8 nanoparticles (Fig. 2(c)). The crystalline integrity after etching was assessed by XRD (Fig. 2(i)). The diffraction pattern of PEI-ZIF-8/TETA matches well with that of the PEI-ZIF-8 nanoparticles, indicating that the crystal core is predominantly preserved during the etching process. N_2 adsorption-desorption isotherms provide further insight into the pore structure evolution (Fig. 2(j) and Table S1 in the ESM). Both PEI-ZIF-8 and PEI-ZIF-8/TETA exhibit Type I isotherms characteristic of microporous materials. The micropore volume of PEI-ZIF-8/TETA ($0.507 \text{ cm}^3 \cdot \text{g}^{-1}$) remains comparable to that of PEI-ZIF-8 ($0.484 \text{ cm}^3 \cdot \text{g}^{-1}$), which is mainly due to the retention of microporous crystal core. Although the mesopore volume of PEI-ZIF-8/TETA decreases slightly (Table S1 in the ESM), the mesopore size distribution shifts toward larger pore sizes, as shown in the pore size distribution profiles that are calculated using the density functional theory (DFT) method (Fig. 2(k)), which is favorable for the penetration of PA chains into the mesoporous structure. The initial mesopores in PEI-ZIF-8 are primarily originated from interparticle voids arising from nanoparticle aggregation [45]. After the TETA etching, the enlarged mesopores appear in PEI-ZIF-8/TETA, providing enough space for PA chains infiltration, contributing to the construction of PA/PEI-ZIF-8 junctions. These structural changes induced by TETA etching are pivotal for membrane fabrication and performance based on the following considerations. First, the preserved micropores of residual PEI-ZIF-8/TETA nanocrystals provide well-defined and molecular-sieving pathways that can facilitate fast transport of gas molecules, thereby enhancing CO_2 permeance. Second, the enlarged mesopores are expected to provide rigid and dispersed nodes that anchor and cross-link the surrounding polyamide chains, enabling the successful construction of PA/PEI-ZIF-8 junctions, which can effectively restrict chain mobility and mitigate swelling at elevated pressures, leading to anti-plasticization property [38, 46].

3.2 Characterization of polyamide thin-film nanocomposite membranes

The etched PEI-ZIF-8/TETA/PSF substrate was further immersed into a TMC organic solution, generating the PA-TFN membrane, as illustrated in Fig. 1. The surface morphology and elemental distribution of the resulting composite membranes were characterized using SEM and corresponding energy-dispersive X-ray (EDX). As shown in Figs. 3(a) and 3(b), the pristine PA membrane exhibits a typical nodular surface structure with a top layer thickness of 90 nm [47, 48]. With an increase in concentration of the sprayed PEI-ZIF-8 colloid from 0.06 to $2 \text{ mg} \cdot \text{mL}^{-1}$, the nodular structure progressively become smaller, and the top layer thickness becomes thinner than those of pristine PA membrane, leading to the generation of smoother and ultrathin PA layers (Fig. 3(c)–3(j)). This morphological evolution is attributed to the formation of Zn-imidazole clusters during amine etching process, which provides more polyamide nucleation sites on the interface and reduces the diffusion rate of TETA via coordinating with TETA, promoting the formation of a thinner and more uniform PA layer. However, when the colloid concentration reaches $6 \text{ mg} \cdot \text{mL}^{-1}$, the top layer thickness dramatically increases to approximately 880 nm (Figs. 3(k)–3(l)). This is likely due to the formation of thick initial PEI-ZIF-8 nanoparticle layer, which limits the etching efficiency of TETA, leaving partially un-etched nanoparticles that interfere with the polyamide formation and lead to a thicker selective layer. EDX mapping of the PEI-ZIF-8/PA-1 composite membrane confirms the uniform distribution of Zn^{2+} throughout the PA layer (Fig. 3(m) and Fig. S4 in the ESM), indicating homogeneous dispersion of the etching species of PEI-ZIF-8 nanoparticles. In summary, the *in-situ* etching of PEI-ZIF-8 nanoparticle layer facilitates the formation of an ultrathin and continuous selective layer, which is highly favorable for fast gas transport.

The chemical structure and interfacial interactions of PEI-ZIF-8/PA-1 composite membrane were investigated through XPS and attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy. As shown in Fig. 4(a), the distinct Zn signals present in the composite membrane but absent in the pristine PA membrane, further confirming the successful incorporation of the PEI-ZIF-8. To investigate the evolution of the Zn^{2+} coordination environment throughout the fabrication process, high-resolution Zn 2p spectra were collected for the PEI-ZIF-8 nanoparticles, PEI-ZIF-8/TETA-1 membrane, and the final PEI-ZIF-8/PA-1 composite membrane (Fig. 4(b)). The Zn $2p_{3/2}$ and Zn $2p_{1/2}$ peaks for PEI-ZIF-8 appear at 1021.60 and 1044.67 eV, respectively [49], both of which remain virtually unchanged in the PEI-ZIF-8/TETA-1 membrane, indicating that the Zn-imidazole coordination is preserved after the amine etching, consistent with the formation of zinc-imidazole clusters and ultra-small PEI-ZIF-8 nanocrystals. In contrast, the Zn $2p_{3/2}$ and Zn $2p_{1/2}$ binding energies of PEI-ZIF-8/PA-1 composite membrane shift to higher values of 1021.79 and 1044.83 eV, respectively, suggesting the formation of new coordination interactions between Zn^{2+} and PA matrix [50]. Therefore, strong interfacial interaction between the inorganic nanoparticles and the PA matrix is formed, likely due to the construction of PA/PEI-ZIF-8 junction. The cross-linking degree of the PA network within pristine PA membrane and PEI-ZIF-8/PA-1 composite membrane was evaluated via high-resolution O 1s XPS spectra (Fig. 4(c)). The spectrum is deconvoluted into two peaks, including the peak at $\sim 531.5 \text{ eV}$ assigned to $\text{O}=\text{C}-\text{O}$ (carboxyl)

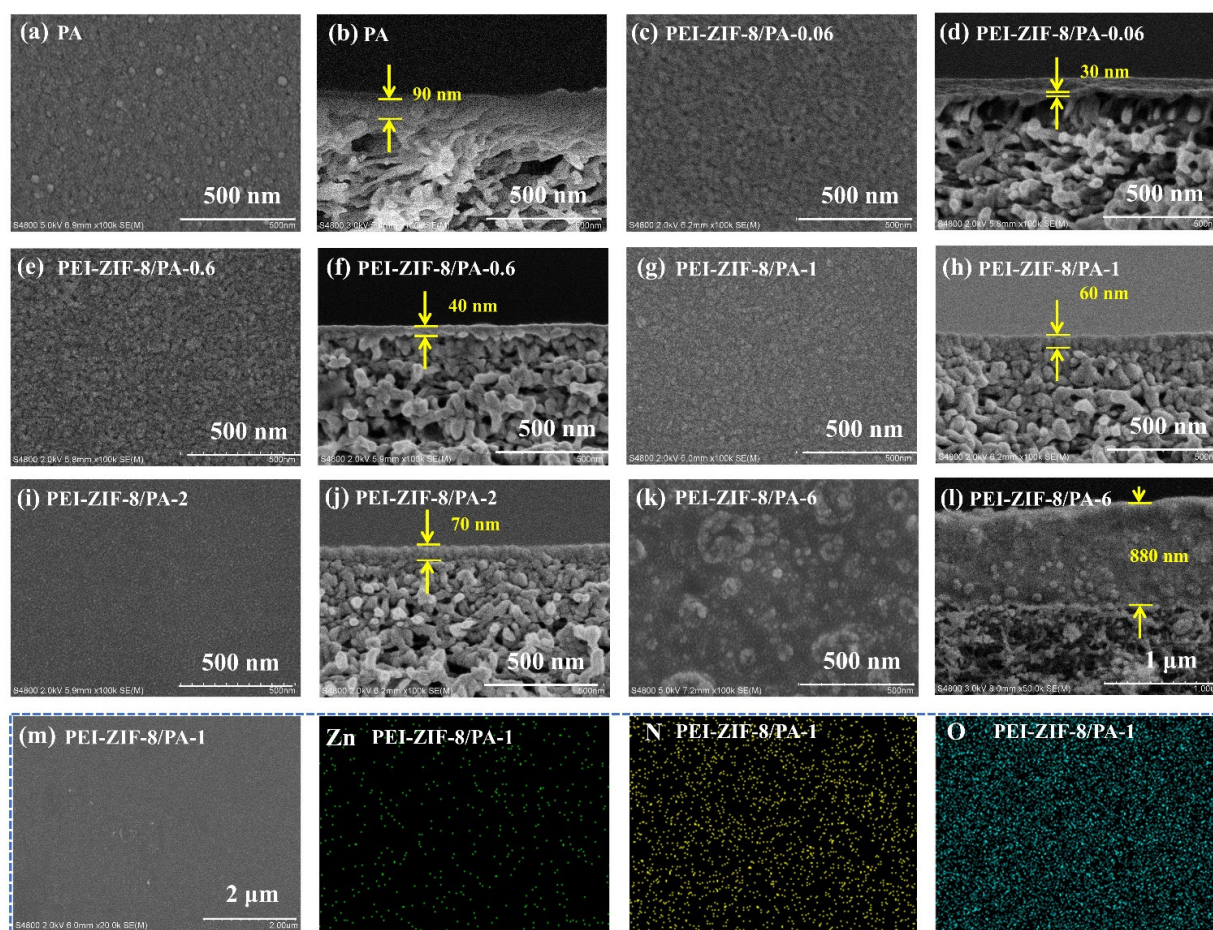


Figure 3 ((a)–(l)) The surface and cross-sectional SEM images of composite membranes: ((a) and (b)) PA, ((c) and (d)) PEI-ZIF-8/PA-0.06, ((e) and (f)) PEI-ZIF-8/PA-0.6, ((g) and (h)) PEI-ZIF-8/PA-1, ((i) and (j)) PEI-ZIF-8/PA-2, and ((k) and (l)) PEI-ZIF-8/PA-6. (m) Surface SEM image and corresponding EDX mappings of PEI-ZIF-8/PA-1 composite membrane.

groups and the peak at ~ 530.8 eV corresponding to N–C=O (amide) groups [51]. The ratio of the amide peak area decreases from 54.81% in the pristine PA membrane to 49.12% in the PEI-ZIF-8/PA-1 composite membrane, implying a lower cross-linking degree of composite membrane, which is conducive to facilitating gas diffusion [49]. ATR-FTIR spectroscopy was carried out to verify the interfacial interactions (Fig. S5 in the ESM). The characteristic amide I (C=O stretching) band for the pristine PA membrane appears at 1678 cm^{-1} [52], which shows a slight red shift to 1670 cm^{-1} in the PEI-ZIF-8/PA-1 composite membrane and a more pronounced shift to 1620 cm^{-1} in the PEI-ZIF-8/PA-6 composite membrane. These progressive red shifts are indicative of interaction between PA matrix and degraded PEI-ZIF-8 species, such as hydrogen bond and/or covalent bond between acyl chloride and amino groups from PEI-ZIF-8 [53]. Such interactions can effectively improve the compatibility between the filler and polyamide matrix, which contributes to ensure the high gas selectivity of composite membranes [54, 55].

The distribution of residual PEI-ZIF-8 nanocrystals in PEI-ZIF-8/PA-1 composite membrane was further investigated using HRTEM coupled with EDX mapping. To eliminate the interference from PSF substrate, free-standing films were prepared by dissolving the substrate in dichloromethane. As displayed in Fig. 4(d), the detached free-standing pristine PA film processes a smooth and continuous layer, with EDX mapping confirming the homogeneous

distribution of C, N, and O elements. In contrast, the detached free-standing PEI-ZIF-8/PA-1 film (Fig. 4(e)) exhibits a uniform dispersion of ultra-fine and dark spots throughout the polyamide matrix, which may originate from PEI-ZIF-8 nanocrystals and/or PA/PEI-ZIF-8 junctions, according to the Zn EDX mapping. The uniform dispersion without evident aggregation of these PEI-ZIF-8 nanocrystals and/or PA/PEI-ZIF-8 junctions mainly demonstrates the effectiveness of *in-situ* etching strategy. These results indicate that the *in-situ* amine etching of PEI-ZIF-8 plays a dual role in membrane fabrication: (i) The released Zn-imidazole clusters modulate the IP process via coordinating with TETA monomers, leading to the formation of a thinner selective layer with reduced cross-linking degree, and (ii) the uniformly embedded ultra-small PEI-ZIF-8 nanocrystals not only provide additional gas diffusion channels, but also generate PA/PEI-ZIF-8 junctions for suppressing chain mobility. The synergistic effect of both Zn-imidazole clusters and ultra-small nanocrystals is expected to endow polyamide composite membranes with stable and outstanding CO_2 separation performance, especially at elevated pressures.

3.3 Gas separation performance

The gas separation performance of pristine PA membrane and polyamide composite membranes fabricated with different concentrations of PEI-ZIF-8 colloid (0.06, 0.6, 1, 2, and 6 $\text{mg}\cdot\text{mL}^{-1}$) was evaluated utilizing a humidified CO_2/N_2 mixture with a volume

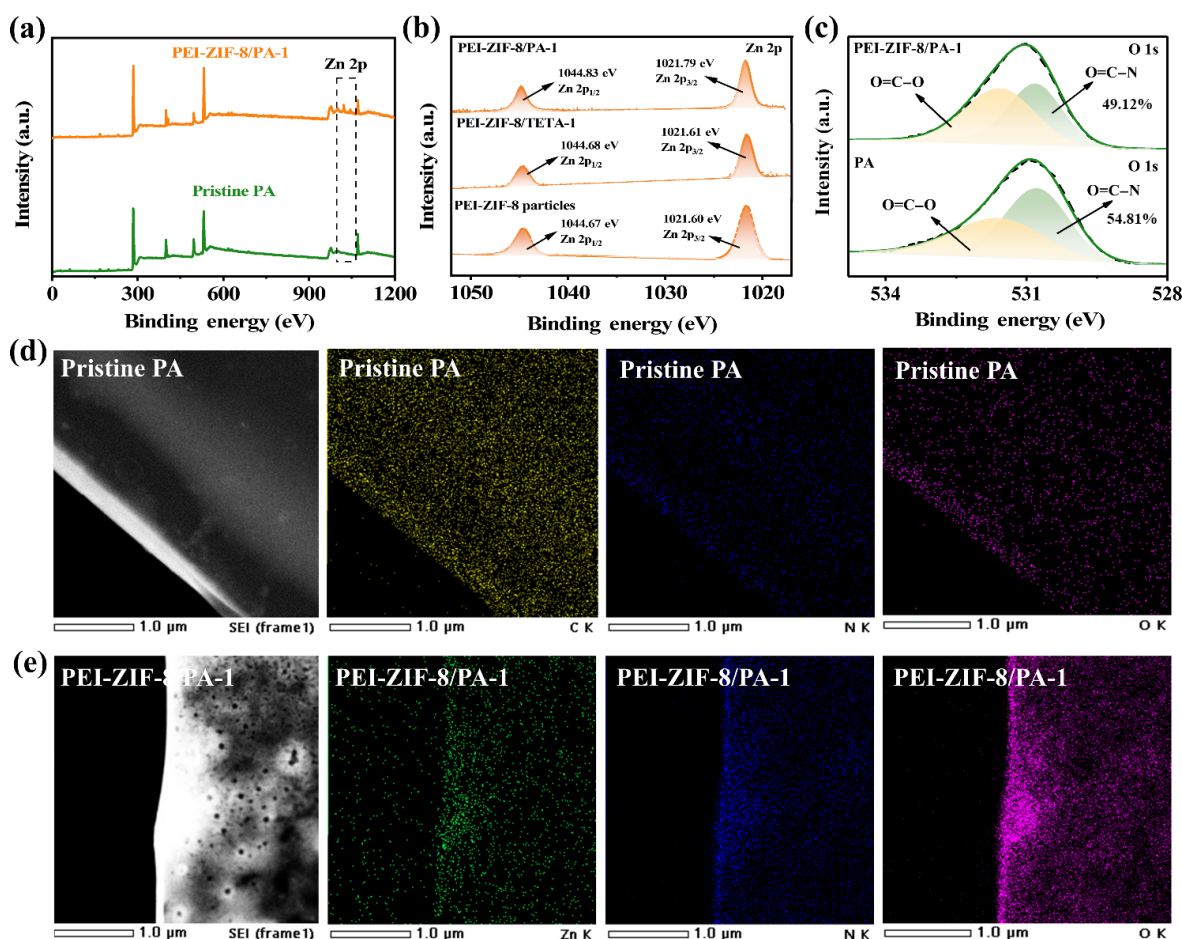


Figure 4 (a) Full-range XPS survey spectra of pristine PA membrane and PEI-ZIF-8/PA-1 composite membrane. (b) High-resolution XPS spectra of Zn 2p for PEI-ZIF-8 particles, PEI-ZIF-8/PA-1 membrane, and PEI-ZIF-8/PA-1 composite membrane. (c) High-resolution XPS spectra of O 1s for pristine PA and PEI-ZIF-8/PA-1 composite membranes. ((d) and (e)) TEM images and corresponding EDX mappings of (d) pristine PA membrane and (e) PEI-ZIF-8/PA-1 composite membrane.

ratio of 50/50 as the feed gas. As shown in Fig. 5(a), both the CO_2 permeance and CO_2/N_2 selectivity exhibit a pronounced volcano-shaped trend as the nanoparticle loading increases. The PEI-ZIF-8/PA-1 composite membrane, prepared with a PEI-ZIF-8 colloid concentration of $1 \text{ mg}\cdot\text{mL}^{-1}$, exhibits the best gas separation performance with a CO_2 permeance of 478 GPU and a CO_2/N_2 selectivity of 60.3, which are improved by 110% and 85%, respectively, compared to the pristine PA membrane, overcoming the trade-off effect of the traditional polymer membranes. A similar trend is observed in the mixed CO_2/CH_4 gas separation (Fig. S6 in the ESM). The remarkable improvement in CO_2 permeance for the PEI-ZIF-8/PA-1 membrane can be attributed to synergistic effects of the moderately reduced cross-linking degree of polyamide network and the accessible micropores of PEI-ZIF-8 nanocrystals, which provide fast and additional transport pathways for CO_2 molecules. Single gas permeation tests for H_2 , CO_2 , N_2 , and CH_4 were conducted and are displayed in Fig. 5(b). CO_2 shows a higher permeance than H_2 with a smaller kinetic diameter, suggesting that in addition to the solution-diffusion mechanism, CO_2 transport through the membrane also depends on the facilitated transport mechanism. Consequently, the ideal selectivities for CO_2/H_2 , CO_2/N_2 , and CO_2/CH_4 (Fig. 5(c)) significantly surpass the corresponding Knudsen selectivity.

To evaluate permeation separation stability, mixed-gas CO_2/N_2 separation tests were performed at elevated feeding pressures. As

shown in Fig. 5(d), the pristine PA membrane exhibits an obvious reduction in CO_2/N_2 selectivity from 31.7 to 9.4 as the feeding pressure increases from 1 to 4 bar over 13 h. The sharp decline in selectivity is mainly attributed to CO_2 -induced chain swelling, which is severe in PA-TFC membranes, where their ultrathin selective layer possesses relatively mobile surface polymer chains that readily sorb highly soluble CO_2 molecules. Excessive CO_2 sorption enhances chain segment mobility and accelerates polymer relaxation, thereby enlarging the transient free volume and ultimately deteriorating the gas-pair selectivity. In contrast, the CO_2/N_2 selectivity of the PEI-ZIF-8/PA-1 membrane remains stable, even showing a slight increase from 59.3 to 66.7 as the feeding pressure increases from 1 to 4 bar over 24 h, a phenomenon that was rarely reported for PA-based gas separation membranes [56]. This different behavior and corresponding transport mechanism are further clarified by analyzing the CO_2 and N_2 permeances at elevated pressures. The transport of N_2 through the PA layer primarily follows the solution-diffusion mechanism. As N_2 molecules exhibit relatively weak interactions with the membrane matrix, their diffusion through the membrane is governed primarily by the size disparity between the transient free volume elements and the molecular dimensions of N_2 . For the pristine PA membrane, N_2 permeance increases markedly at pressurized conditions (Fig. 5(e)), mainly due to the swelling of PA matrix induced by the dissolved CO_2 molecules, which permeate

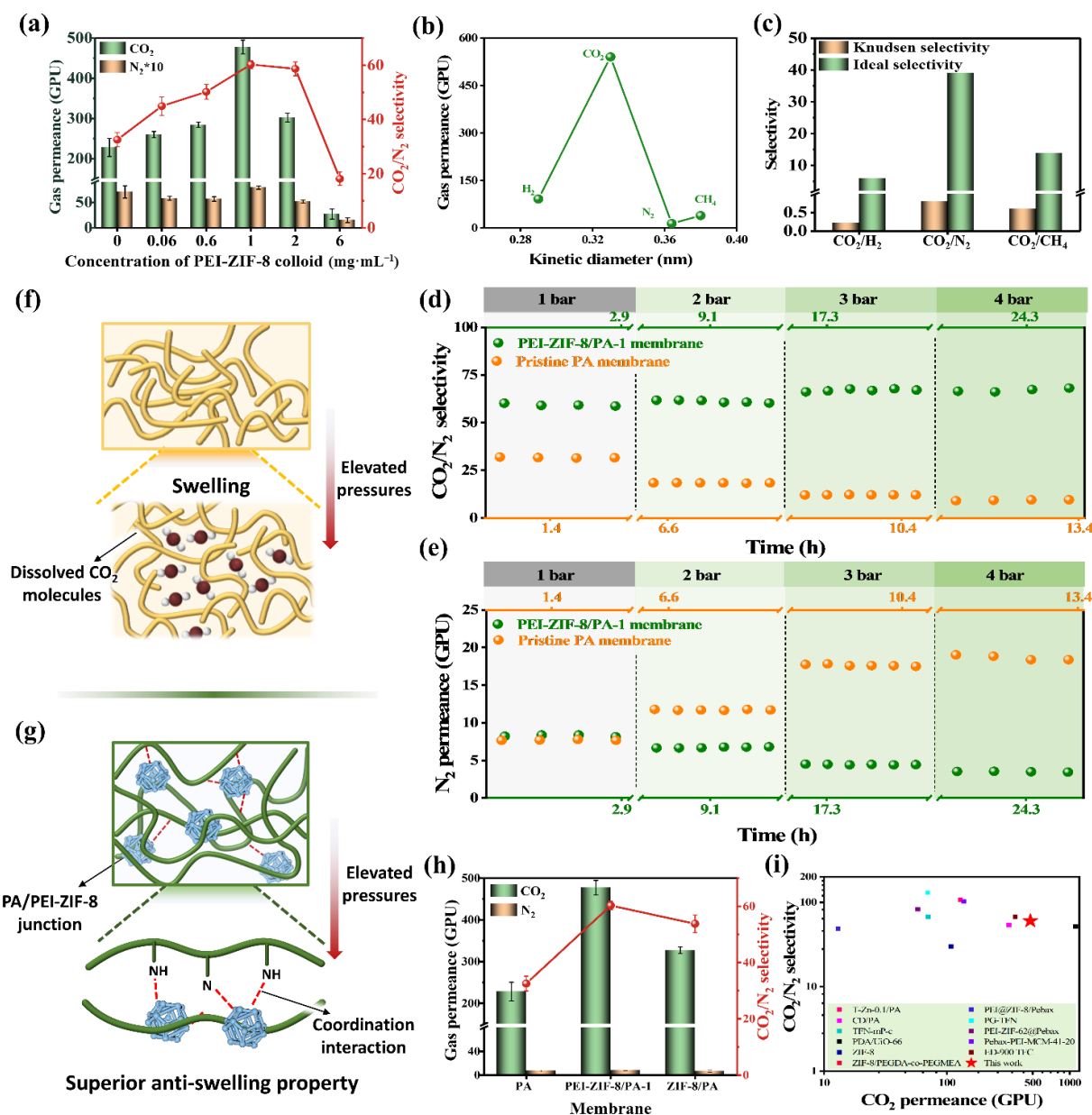


Figure 5 (a) Mixed CO₂/N₂ (50/50 vol.%) separation performance of pristine PA membrane and PEI-ZIF-8/PA composite membranes. (b) The single gas permeance of PEI-ZIF-8/PA-1 composite membrane. (c) The ideal selectivity and Knudsen selectivity of PEI-ZIF-8/PA-1 composite membrane. ((d) and (e)) The effect of feed pressure on (d) CO₂/N₂ selectivity and (e) N₂ permeance for pristine PA membrane and PEI-ZIF-8/PA-1 composite membrane. ((f) and (g)) The schematic illustration for microstructure of pristine PA and PEI-ZIF-8/PA composite membrane at elevated pressures. (h) The comparison of CO₂/N₂ mixed gas separation performance of PEI-ZIF-8/PA-1 composite membrane in this work with those of membranes reported in previous literatures that are provided in the ESM (Table S2 in the ESM).

and accumulate between chains, disrupting the interchain hydrogen bonds and thereby enhancing the chain mobility (Fig. 5(f)). Consequently, the enlarged transient free volume facilitates the diffusion and transport of N₂ molecules through the membrane. While N₂ permeance for PEI-ZIF-8/PA-1 composite membrane decreases with elevating pressures, a phenomenon predominantly stemmed from the construction of PA/PEI-ZIF-8 junction, which restricts the polyamide chain mobility and therefore suppresses membrane swelling (Fig. 5(g)), impeding the transmembrane transport of N₂ molecules. The transport of CO₂ through the PA layer primarily is dominated by the facilitated transport mechanism. Accordingly, the concentration and accessibility of amine carriers within the membrane play critical roles in governing

CO₂ transport performance. As shown in Fig. S7 in the ESM, CO₂ permeances for both pristine PA and PEI-ZIF-8/PA-1 membrane decline with increasing pressure, a behavior caused by carrier saturation at pressurized conditions, which is characteristic of the facilitated transport mechanism [57, 58]. For comparison, a ZIF-8/PA composite membrane was fabricated as a reference, using similar fabrication method excluding spraying ZIF-8 colloid on the TETA-pre-impregnated PSF substrate. The performance of ZIF-8/PA composite membrane remains inferior to that of the PEI-ZIF-8/PA membrane (Fig. 5(h)), highlighting the critical role of ideal interfacial compatibility, which not only stabilizes the membrane structure to enhance its resistance to swelling, but also prevents the formation of non-selective defects. In detail, the *in-situ* amine

etching not only realizes homogeneous filler dispersion but also constructs strong interfacial interactions including hydrogen bond, covalent bond between acyl chloride and amino groups from PEI-ZIF-8, and PA/PEI-ZIF-8 junctions, leading to both high CO₂ permeance and stable CO₂/N₂ separation. The PEI-ZIF-8/PA-1 membrane realizes a superior separation performance that surpasses the most PA-based membranes fabricated via “water-before-oil” IP process in previous literatures (Fig. 5(i)).

4 Conclusions

In conclusion, we successfully developed a high-performance and pressure-resistant polyamide thin-film nanocomposite membrane for CO₂ separation via an innovative *in-situ* amine etching strategy during IP process. The fabrication approach involved spraying PEI-ZIF-8 colloid onto the TETA pre-impregnated PSF substrate, constructing a favorable platform for the subsequent IP reaction. Via TETA etching, the sprayed PEI-ZIF-8 nanoparticle layer decomposed into Zn-imidazole clusters and ultra-small PEI-ZIF-8 nanocrystals, playing a dual role in the subsequent interfacial polymerization process. On the one hand, the Zn-imidazole clusters coordinated with TETA monomers, moderating the IP reaction between TETA and TMC monomers. On the other hand, the ultra-small PEI-ZIF-8 nanocrystals were uniformly embedded into the PA matrix, serving as cross-linking anchors for PA chains and forming PA/PEI-ZIF-8 junctions. Furthermore, the PEI-ZIF-8 nanocrystals retained their intrinsic microporous characteristics, providing additional diffusion pathways for gas molecules. The optimized membrane (PEI-ZIF-8/PA-1) realized a superior CO₂ permeance of 478 GPU and a CO₂/N₂ selectivity of 60.3, outperforming most of the polyamide composite membrane fabricated by similar “water-before-oil” IP approach. Notably, this membrane exhibited exceptional stability at elevated pressures, maintaining consistent CO₂/N₂ separation selectivity as the feed pressure increased from 1 to 4 bar. This fascinating anti-swelling property was attributed to the construction of PA/PEI-ZIF-8 junctions, which effectively restricted segmental mobility of PA chains, thereby suppressing membrane swelling. The proposed *in-situ* amine etching strategy offers a novel avenue for constructing rigidity-reinforced PA-TFN membrane with outstanding and stable CO₂ separation performance at elevated pressures, thereby advancing their potential for practical carbon capture applications.

Electronic Supplementary Material: Supplementary material (materials, fabrication of PEI-ZIF-8/TETA-*x* nanoparticles, characterization methods, TEM image of ZIF-8 nanoparticles, surface SEM images and corresponding EDX mappings of PEI-ZIF-8/PA-*x* composite membranes, ATR-FTIR spectra of PEI-ZIF-8 nanoparticles, pristine PA, PEI-ZIF-8/PA-1, and PEI-ZIF-8/PA-6 composite membranes, CO₂/CH₄ separation performance for PEI-ZIF-8/PA composite membranes, and the comparisons of separation performance) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908903>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

X. Q. Z.: Data curation, validation, investigation, writing manuscript. Y. X.: Data curation, validation, writing manuscript. X. L.: Data curation, validation. L. P.: Validation, investigation. X. J. S.: Manuscript review and editing, funding acquisition. C. L. J.: Supervision, funding acquisition, manuscript writing and review. H. Q. J.: Supervision, experimental design, project administration, funding acquisition, manuscript review. All the authors have approved the final manuscript.

Use of AI statement

None.

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