Mechanical Synthesis of COF Nanosheet Cluster and Its Mixed Matrix Membrane for Efficient CO₂ Removal

Changchang Zou, Qianqian Li, Yinying Hua, Bihang Zhou, Jingui Duan,* and Wanqin Jin*†

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Jiangsu National Synergetic Innovation Centre for Advanced Materials, Nanjing Tech University, Nanjing 210009, China

Supporting Information

ABSTRACT: Covalent organic framework (COF) membranes used for selective removal of CO₂ were believed as an efficient and low-cost solution to energy and environmental sustainability. In this study, the amide modified COF nanosheet cluster with a 2D structure was facilely prepared through solid reaction, exhibiting good adsorption-based CO₂ selectivity (223 at 273 K and 90 at 298 K) toward N₂. Remarkably, the mixed matrix membrane (MMM) that consists of a lesser amount of COF filler (1 wt %) shows promising CO₂/N₂ gas selectivity (∼64). In addition, the competitive adsorption prompts the selectivity to ∼72 under an equimolar CO₂/N₂ mixture, which surpasses the values of all reported COF membranes. It is worth to note that the binary gas separation is stable during 120 h.

KEYWORDS: solid reaction, covalent organic framework, morphology transformation, mixed matrix membrane, CO₂/N₂ gas separation

INTRODUCTION

As the primary anthropogenic greenhouse gas, CO₂ is changing the global climate. The development of efficient selective carbon capture and storage (CCS), is, therefore, a scientific challenge of the highest order.1,2 Currently, a variety of methods, such as chemisorption with amide solvent, physical adsorption with porous adsorbents, and membrane technology, have been proposed for CO₂ capture.3,4 However, due to the group of benefits in lower energy consumption, ease of operation, environmental friendliness, and mechanical simplicity, the membrane-based process was believed as one of the most promising technologies in CCS.5–11

Due to its low cost, good mechanical simplicity, high scalability, and water resistance, an organic polymer (cellulose acetate) membrane was first reported for gas separation in 2001.12 Since then, various organic membranes have begun to draw widespread attention for feasible usage in gas separation.13–16 However, polymeric membranes are often limited by a permeability and selectivity trade-off. In parallel to the development of polymeric membrane, inorganic membranes with good separation performance are expensive, brittle, and difficult to upscale.17 Due to the integrated advantages of size/shape selectivity of functional fillers and the processability/mechanical stability of polymers, MMMs that consist of functional inorganic fillers, such as carbon tubes, mesoporous silicon, zeolites, metal organic frameworks, and porous metal oxides, were developed as an alternative solution to overcome these limitations.7,14,18,19 Despite those, the majority of MMMs usually suffer the poor compatibility between constituents, leading to decreased separation behavior, as the gas molecules bypass the particles.18 Thus, the problems we now face are becoming practical, i.e., how to address the issue of filler agglomeration and precipitation during membrane preparation, and further boosting CO₂ separation by MMMs.14

The stability of a matrix solution during the fabricating process is important. Thus, some techniques, such as adding nonsolvents into the dope formulation, performing the spinning at high temperature, and optimizing the shear and elongational force, were developed to prepare homogeneous dispersions of inorganic porous fillers within a polymer solution.19–21 Further,
controlling the surface properties of fillers, according to the rule of similarity and intermiscibility, was believed as one of the most attractive ways. For examples, the controlling of metal organic frameworks (MOFs)/polymer compatibility is a little easier than that of the zeolite/polymer, as the organic ligands in MOFs are more similar to polymer chains, but zeolites are not. In contrast with well-designed porous MOFs, COFs are another new kind of crystalline porous materials, which are assembled by the linkage of organic moieties only in periodic networks through strong covalent bonds with light elements. Due to the diversity of organic building units and chemical reactions, more and more COF materials with tunable pore chemistry, robust stability, as well as good COF/polymer compatibility offer significant opportunity for advanced membrane preparation and application. Whereas, unlike popular 3D MOF structures, most of the reported COFs show 2D lamellar structures that derived from the packing of organic nanosheet by weak interactions. In other words, once the weak interaction was overcome, it is possible to prepare multilayered or even single layered COF nanosheets from bulk lamellar COFs. Therefore, the shorter transmission routes and functional pore properties will make 2D COF nanosheets extremely attractive for membrane-based separation purposes.

We are interested in porous material and membrane design for feasible applications. In the present study, the 2D COF structure with rich amide groups was selected as membrane filler, because of its facile synthesis and also the preferred channel for CO₂ transport (Scheme 1). Through solid reaction, the well prepared honeycomb-like COF nanosheet cluster (named as TpPa-1-nc) showed good adsorption-based CO₂ selectivity (223 at 273 K and 90 at 298 K) toward N₂. Remarkably, a single gas permeation experiment showed that the TpPa-1-nc incorporated MMM exhibited a high CO₂/N₂ ideal selectivity (∼64), which was further improved to ∼72 under an equimolar CO₂/N₂ mixture, as the preferred

Scheme 1. COF Structure with Rich Amide Group

Figure 1. IR (a) and PXRD (b) of synthesized TpPa-1 during process of solid reaction.
competitive adsorption. In addition, long-term test showed that mixture gas separation is stable in 120 h.

### EXPERIMENTAL MATERIALS

All the reagents were commercially available and used as received. Dried phloroglucinol, trifluoroacetic acid, hexamethylenetetramine, and p-phenylenediamine were purchased from J&K Chemicals. Polyether-block-amide (PEBA) was purchased from Arkema, France. Methanol and dichloromethane were purchased from Sinopharm Chemical Reagent Co., Ltd. FTIR spectra were recorded in the range of 4000–400 cm$^{-1}$ on a Nicolet iD5 ATR spectrometer. Powder X-ray diffraction (PXRD) patterns were collected using a Bruker AXS D8 Discover powder diffractometer equipped with a Cu Ka X-ray source at 40 kV, 40 mA. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker 500 FT-NMR spectrometer. Solid $^{13}$C CP-MAS NMR spectra were measured on a Bruker AVANCE III 400 MHz spectrometer. The morphologies of COF materials during solid reaction were examined by field emission

**Figure 2.** SEM images of TpPa-1 during solid reaction (after washing): 5 min (a, b), 15 min (c, d), 25 min (e, f), 35 min (g, h), 45 min (i, j), and 55 min (k, l).

**Figure 3.** TEM images of nanosheet from TpPa-1-nc (a, b). Pore size analysis (c, d).
scanning electron microscope (SEM, S4800, Hitachi) and transmission electron microscopy (TEM, JEOL JEM-2010 UHR). A thermogravimetric analyzer (TGA, STA 209 F1, NETZSCH) was used to determine the thermal stability of the MMMs with a heating rate of 10 °C·min⁻¹ in a N₂ atmosphere. Differential scanning calorimetry (DSC, Q2000, TA Instruments, USA) measurements were performed from −80 to −20 °C in a N₂ atmosphere to study the glass transition temperature (Tg) of the membranes. The gas adsorption isotherms of TpPa-1-nc were collected by BELSORP-mini II, Bel Inc., Japan.

**Synthesis of TpPa-1-nc.** COF material was synthesized through solid reaction by Schiff base aldehyde–amine condensation according to a previous report.²⁴ 1,3,5-Trifluorophosphogluconol and p-phenylenediamine were placed in a mortar and ground using a pestle at room temperature. As time passed, the color of materials changed from light yellow, yellow, orange, and then to dark red finally, indicating the formation of conjugated units (Figure S1). After 35 min, the reaction mixture was collected and washed for getting pure TpPa-1-nc.

**Preparation of MMMs.** PEBA polymer was selected to disperse TpPa-1-nc. A poly(vinylidine fluoride) (PVDF) ultrafiltration membrane was used as support (average pore size: 450 nm). A certain amount of TpPa-1-nc was dispersed in ethanol and water with a mass ratio of (7:3), followed by stirring of 10 min. Then, PEBA was added and heated with stirring and refluxing under 80 °C for 2 h. The mass ratio of PEBA to solvent is 5:95, while the contents of TpPa-1-nc in the polymer matrix varied from 0 to 2 wt %. The membrane was prepared by spin-coating the mixed solution on PVDF supports, which was prepared by being immersed in water for 24 h to infiltrate fully. The MMMs were then dried at room temperature for 24 h, then curing in the oven at 70 °C for another 12 h. A pristine PEBA membrane was also prepared using a similar process for comparison. TpPa-1-nc loading in MMMs was calculated using the following formula:

\[
W_{\text{COF}} = \frac{m_{\text{COF}}}{m_{\text{PEBA}}} \times 100\%
\]

**COF Characterization.** Solid reactions with a number of advantages ripple throughout many industries. Generally, during the initial process of grinding, the particles of starting material assembled together and then reacted with each other. Then, the continuous grinding will break the formed product particle into smaller sizes. Taking this in consideration, the grinding of solid reaction can not only offer the energy for reaction but also overcome the weak interaction of the layers during 2D COF formation.

In order to confirm our idea, small amount samples were collected at different reaction times (5, 15, 25, 35, 45, and 55 min). IR and PXRD were used to monitor the reaction process during 55 min (Figure 1). The new IR peaks around (1605, 1579, and 1286 cm⁻¹) and their gradual increased intensity showed the formation of C=N, C=C, and C=O bonds, respectively (Figure 1a). Meanwhile, the crystallinity of obtained TpPa-1 at different times was evaluated by the powder X-ray diffraction (PXRD). As shown in Figure 1b, the newly emerged and gradually enhanced diffraction peaks at 8° (2θ) matched with the reported data, demonstrating the successful preparation of TpPa-1.²° It should be noted that the PXRD peaks at high angle indicate the existence of partial unreacted starting materials.

After washing with methanol and dichloromethane (for starting material removal), the structure and morphology of TpPa-1 particles were investigated by PXRD and scanning electron microscopy (SEM), respectively. As shown in Figure S2, the absence of peaks around high angle reveal the complete removal of starting materials and phase purity of TpPa-1. The similar IR spectra between as-synthesized and TpPa-1-nc were collected by BELSORP-mini II, Bel Inc., Japan. The similar IR spectra between as-synthesized and TpPa-1-nc were collected by BELSORP-mini II, Bel Inc., Japan. As shown in Figure S2, the absence of peaks around high angle indicate the existence of partial unreacted starting materials.

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CO₂ and N₂ gas isotherms were collected to evaluate the permanent porosity of TpPa-1-nc. As shown in Figure 4a, CO₂ adsorption of TpPa-1-nc exhibits a type-I adsorption isotherm, characteristic of microporous material. On the basis of the CO₂ adsorption isotherm, the Brunauer–Emmett–Teller (BET) and Langmuir surface areas are...
around 255 and 436 m$^2 \cdot$g$^{-1}$, respectively. CO$_2$ uptake of TpPa-1-nc reached to 100.6 cm$^3 \cdot$g$^{-1}$ at 195 K/1 bar, while a trace amount of N$_2$ (4.2 cm$^3 \cdot$g$^{-1}$) uptake was observed. Interestingly, similar adsorption trends were also found at 273 and 298 K (Figure 4b). In light of these obvious adsorption gaps, gas selectivity of TpPa-1-nc was calculated by determining the Henrys law constants (Table S1). As expected, the CO$_2$/N$_2$ gas selectivity is as high as 223 at 273 (90 at 298 K), which can be explained by high CO$_2$ adsorption heat toward TpPa-1-nc (35 kJ$\cdot$mol$^{-1}$) (Figure 4c). In addition, the calculated pore size distribution from the CO$_2$ isotherm (273 K) matches well with the TEM result (Figure S10).

**Membrane Characterization.** The thermogravimetric results showed that all MMMs started to decompose around 380 °C, indicating high thermal stability (Figure S11). PXRD of a series of MMMs (peak around 11°) confirmed the integrity of the TpPa-1 skeletal structure after membrane fabrication (Figure S12). To further unveil the uniform distribution of TpPa-1-nc within membranes, SEM images of the surface and cross-section of MMMs were collected (Figure 5). The continuous membrane surfaces showed gradually increased granular protuberances without interfacial voids or pinholes, following the increased ratio of TpPa-1-nc in the PEBA matrix. The thicknesses of the MMMs are around 2.6–2.8 μm on the support, while the TpPa-1-nc can be found clearly inside the membrane (Figure 5d, inset).

**Gas Permeation Tests.** Before measurements, the as-prepared MMMs were activated to remove guest molecules at 60 °C under vacuum for 24 h. In addition, to guarantee the reliability of results, the measurements were repeated at least three times for each point. Unlike the defined ideal selectivity above (from single gas adsorption isotherms), the selectivity defined from membrane-based technology is the ratio of permeabilities, $S_{A/B} = P_A/P_B$. Permeabilities ($P$) were determined using a CO$_2$/N$_2$ gas pair at 25 °C, 3 bar. As displayed in Figure 6, the MMMs exhibited gradually improved permeability of both CO$_2$ and N$_2$ accompanying the increase of TpPa-1-nc loading. This is because CO$_2$ and N$_2$ can diffuse freely through the TpPa-1-nc channel. In addition, differential scanning calorimetry measurements showed that the glass transition temperature ($T_g$) increased from −47.5 °C for pristine PEBA to −45.2 °C for 1 wt % MMM (Figure S13). This means TpPa-1-nc could disrupt the inherent organization of the polymer chains, and enhance the accessible free volume in the matrix for gas molecule transmission. Among these five MMMs, the ideal gas selectivity increases with TpPa-1-nc loading, and reaches to 64 at the loading of 1 wt %, which is a 56% improvement than that of the pure PEBA membrane. This is because the increased permeability of CO$_2$ is more rapid than that of N$_2$ when the TpPa-1-nc loading is lower than 1 wt %. Principally, the nature properties of high polarizability and quadrupole moment lead CO$_2$ molecules themselves...
to aggregate and permeate into the membrane; then, the generated CO₂ concentration gradient was manifested by amide modified TpPa-1-nc, and thus resulted in facilitated CO₂ transport within the MMM. With the loading above 1 wt %, increased permeability of CO₂ became slower than that of N₂, and thus leads to decreased selectivity. This is because more nonselective interface defects (space between nanosheets in a cluster) were generated when a larger amount of TpPa-1-nc was added into the matrix. Despite the uniform distribution of TpPa-1-nc in polymer solution, such kinds of interface defects cannot be fully filled by polymer chains.

Generally, the permeation selectivity result from mixture gas test is higher than that of single gas test, as the competitive adsorption and diffusion will occur inside the functional membrane. Thus, in light of high CO₂/N₂ separation factor from a single gas test, we then performed CO₂/N₂ mixture (1:1) separation on the MMM with 1 wt % COF filler at room temperature. As shown in Figure 7, the average separation factor increased to ~72, 12.5% higher than the calculated ideal separation factor (~64). More importantly, such mixture gas separation is stable in 120 h. To the best of our knowledge, the separation factor of the CO₂/N₂ mixture by TpPa-1-nc MMM (1 wt %) surpasses the value of all COF-based membranes. In contrast with other PEBA supported MMMs, TpPa-1-nc MMM (1 wt %) has a competitive advantage in CO₂/N₂ separation, even though it is hard to make a direct quantitative comparison due to different sample loading and operation conditions (Table 1).

Additionally, binary gas separation experiments by TpPa-1-nc MMM (1 wt %) were also explored at different temperatures (from 20 to 60 °C). As shown in Figure 8, high temperature leads to increased gas permeance, because higher temperature promotes the motion of polymer and weakens the interaction between a permeating molecule and a polymer molecule, and then results in the reduced transfer resistance for faster diffusion. However, due to the higher ratio of increased N₂ permeability, the reduced selectivity was observed at high temperature. Despite those, the gas selectivity remains as high as 45 at 40 °C, revealing the high possibility for selective CO₂ removal under feasible condition.

### CONCLUSIONS

In summary, the unique morphology change from amorphous COF particle to honeycomb-like COF nanosheet cluster was first observed during solid reaction. The functional amide group and uniform micropore make such a COF cluster achieving good surface area and CO₂/N₂ adsorption selectivity. More importantly, the PEBA-based MMM with 1 wt % COF nanosheet cluster showed the highest separation factor (~72) for an equimolar CO₂/N₂ mixture in all COF-based membranes. Gas separation is stable during 120 h. Thus, the excellent performance of energy saved MMMs along with easily prepared COF filler holds great promise for scale up selective CO₂ removal from N₂.

### ASSOCIATED CONTENT

Supporting Information

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**The value was calculated according to the reported CO₂ permeance and membrane thickness.

Figure 6. Gas permeability and CO₂/N₂ separation factor of MMMs with varied TpPa-1-nc loadings at 298 K.

Figure 7. Long-term test of equimolar CO₂/N₂ mixture separation on TpPa-1-nc MMM (1 wt %) at room temperature.

Figure 8. Effect of temperature on separation performance of MMM-1.0.

**Table 1. Separation Performance of CO₂/N₂ by PEBA Supported MMMs with Varied Fillers**

### AUTHOR INFORMATION

Corresponding Authors

*E-mail: duanjingui@njtech.edu.cn (J.D.).
*E-mail: wqjin@njtech.edu.cn (W.J.).
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REFERENCES


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