Pebax Mixed-Matrix Membrane with Highly Dispersed ZIF-8@CNTs to Enhance CO₂/N₂ Separation

Yahui Zhang, Yuping Tong,* Xinyu Li, Shoujie Guo, Hailong Zhang, Xi Chen, Kun Cai, Linghe Cheng, and Weiwei He*

ABSTRACT: In this work, zeolitic imidazolate frameworks (ZIF-8) and carboxylated carbon nanotubes (CNTs) were compounded to prepare a kebab-like one-dimensional linear composite, ZIF-8@CNTs. The mixed-matrix membrane (MMM) for separating carbon dioxide is prepared by embedding it into the polymer matrix Pebax-1657. The results indicated the successful synthesis of the ZIF-8@CNT composite. The combination of ZIF-8 and carboxylated CNTs avoided the aggregation of ZIF-8 in the polymer, increased the free volume of the MMM, and enhanced the CO₂ adsorption performance and CO₂/N₂ separation performance. In addition, the interaction between CNTs and ZIF-8 provided a fast transport channel for CO₂ molecules and improved the mechanical properties of the MMM. The 5 wt % ZIF-8@CNT MMM showed the best separation performance with a CO₂ permeability of 225.5 Barrer and a CO₂/N₂ selectivity of 48.9, which exceeded the Robeson upper limit in 2008. The combination of high permeability and selectivity made Pebax/ZIF-8@CNT MMMS promising for industrial CO₂ separation applications.

1. INTRODUCTION

An increase in the concentration of CO₂ in the atmosphere will lead to an aggravation of the global greenhouse effect.1–4 Membrane gas separation technology is considered an effective way to separate CO₂. Compared with the traditional gas separation technology (such as gas distillation or cryogenic condensation purification), the membrane gas separation technology has many advantages, such as low energy consumption, high efficiency, environmental protection, simple operation, and easy scaling.5–8 Polymers have become a common material for membrane manufacturing because of their low cost and easy processing.9 However, for most commercial polymer membranes (such as polysulfone, polyimide, and Pebax-1657), a trade-off relationship exists between the permeability and selectivity known as the Robeson upper bound. The use of mixed matrix membranes (MMMs) composed of organic polymers and inorganic particles has been recognized as an effective method for simultaneously improving membrane permeability and selectivity.10–14 Many materials, such as metal organic frameworks (MOFs), carbon nanotubes (CNTs), graphene and graphene oxide (GO), and zeolites and their derivatives, have been used to prepare highly permeable and selective MMMS.15–20 MOFs are highly ordered crystalline microporous materials formed by the self-assembly of transition-metal cations and organic-linking agents. Because of their adjustable pore size, high porosity, specific surface area, and relatively good thermal stability and chemical stability, MOFs are considered as the ideal choice for fillers.21–23 Zeolitic imidazolate frameworks (ZIFs) are a typical representative of the MOF structure. They are porous crystals with a three-dimensional structure formed by combining metal ions (Zn, Co, etc.) with imidazole tetrahedra. Their pore size is 11.6 Å, and their crystallographically determined pore size is 3.4 Å. They have high thermal and chemical stability and have become a suitable filler for preparing MMMS.24,25 Shadi Meshkat et al. improved the permeability of CO₂ by filling ZIF-67 with a smaller pore size into Pebax-MH-1657, which increased by 130% (162 Barrer) compared with that of the original Pebax membrane (70 Barrer), while Pebax/ZIF-8 had a lower growth rate (85%) (130 Barrer).26 Naifi and Hägg used ZIF-8 as the filler, and the synthesized ZIF-8/6FDA-Durene diamine MMM resulted in a significant increase in gas...
Jameh et al. used modified ZIF-8 nanoparticles to prepare the MMM Pebax 1074/ZIF-8. After modifying the nanoparticles with ethylenediamine (ED), the loading of ZIF-8 nanoparticles in the mixed matrix film was increased to 30 wt % without any agglomeration. The adsorption and permeability to CO2 and CH4 of the MMM are higher with modified ZIF-8 nanoparticles than with unmodified ZIF-8 nanoparticles.

However, the current mixed matrix film prepared with ZIF-8 as a filler has some problems. First, ZIF-8 will have irreversible agglomeration during the film drying process; second, when the amount of filler ZIF-8 increases, the probability of forming particle agglomerates in the polymer matrix will increase, resulting in an increase in interface pores. Finally, the mixed matrix film prepared with ZIF-8 as a filler often does not have good mechanical stability. In response to these problems, Li et al. prepared MWCNTs@ZIF-8 composite materials by adding CNTs during the synthesis of ZIF-8, which improved the aggregation problem of ZIF-8 in the polymer matrix and the mechanical stability of the mixed matrix film. This has improved, to a certain extent, the problems of the combination of ZIF-8 and MMMs, but due to the large particle size and small specific surface area of ZIF-8, the gas adsorption capacity is restricted. Therefore, there is still a lot of work to be done on how to improve the gas adsorption capacity of ZIF-8 in the MMM. Therefore, we prepared ZIF-8 with a particle size of about 50 nm and successfully combined with CNTs to form ZIF-8@CNTs. It is expected that the prepared MMM can have good gas separation performance.

Because their polar ether groups lead to enhanced CO2 solubility selectivity, polymers based on poly (ethylene oxide) (PEO) have recently gained growing attention. However, PEO suffers from high crystallinity and low mechanical strength when used alone in a membrane. Among the most well-known PEO-containing polymers, poly(ether-block-amide) (PEBAX) is a block copolymer composed of a rubbery PEO block that interacts with CO2 and a glassy block of polyamide (PA), providing mechanical strength. It is a MMM polymer suitable for substrate selection. In the present work, the CNTs were acidified to produce carboxyl groups on the surface, which facilitated ZIF-8 binding. As shown in Figure 1, in the process of ZIF-8 synthesis, oxidized CNTs were added to prepare the kebab-like one-dimensional linear composite material ZIF-8@CNTs. Then, this material was embedded in the Pebax matrix to prepare the Pebax/ZIF-8@CNT MMM. The combination of CNTs and ZIF-8 can effectively change the aggregation of ZIF-8 nanoparticles in the mixed matrix film so that ZIF-8 and CNTs have better dispersibility in this film. The incorporation of CNTs can serve as a channel for gas molecule diffusion, improve the mechanical strength of the MMM, and reduce the adverse effect of rigid PA segments on CO2 permeability.

2. RESULTS AND DISCUSSION

2.1. Characterization of ZIF-8 and ZIF-8@CNTs. The morphology and structure of the nanofillers were characterized via scanning electron microscopy (SEM) and transmission electron microscopy (TEM). As shown in Figures 2 and 3.
understand the morphological changes between them. TEM further proves that 50 nm sized ZIF-8 is grown on the outer surface of CNTs. This is due to carboxylated CNTs providing numerous nucleation sites for the growth of ZIF-8. This strong interaction causes ZIF-8 to completely cover the surface of the CNTs.16

Phase identification of ZIF-8 and ZIF-8@CNT composite materials was performed using X-ray diffraction (XRD). As shown in Figure 4a, the diffraction patterns of ZIF-8@CNTs and pure ZIF-8 are basically identical. ZIF-8 still maintains a good crystal structure after inserting CNTs, and ZIF-8 has limited growth on CNTs and does not affect the synthesis of ZIF-8. In addition, because of the low intensity of CNTs, no diffraction peak of CNTs was found, which is consistent with previous reports.39

Thermogravimetric analysis of ZIF-8 and ZIF-8@CNT is shown in Figure 4b with increasing temperature,40 in which a negligible mass loss of ZIF-8 particles occurs below 400 °C. Above 400 °C, the quality of ZIF-8 particles gradually decreases with increasing temperature. At these temperatures, the main component of the residue is ZnO, with a mass of 26.9%. The thermogravimetric curve of ZIF-8@CNT particles is not much different from that of ZIF-8 particles. Below 200 °C, with the increase in temperature, the quality of ZIF-8@CNT decreases slightly. At the same time, the imidazole are removed due to the collapse of ZIF-8 at high temperature, and a constant mass transition occurred at 600 °C. Starting at 700 °C, the quality of the residue stabilized and reached a value of 21.6%.

Figure 4c-d shows the N₂ adsorption and desorption isotherms of ZIF-8 and ZIF-8@CNT nanoparticles. Because the doped CNTs occupy the structure of ZIF-8, the specific surface area of ZIF-8@CNTs, 1078.511 m²/g, is slightly smaller than that of ZIF-8, 1876.028 m²/g.
Fourier transform infrared (FTIR) spectroscopy was used to analyze the chemical structure of ZIF-8 and ZIF-8@CNTs. As shown in Figure 4e, the peak at 1580.2 cm$^{-1}$ corresponds to the C=N stretching vibration, and the peaks at 1177.6 and 996.4 cm$^{-1}$ belong to the C=N stretching vibration. The absorption bands at 3134.7 and 2927.7 cm$^{-1}$ represent the aromatic and aliphatic C–H stretches of imidazole, respectively. The results show that ZIF-8 and its derivatives have been successfully synthesized.

2.2. Characterizations of the Membranes. The morphology of the film was characterized via SEM. Compared with the pure Pebax film, we can see that as the ZIF-8@CNT filler increases, more and more aggregates will appear on the surface of the mixed matrix film, resulting in the interface defect. Figure 5c shows MMMs with a filler of 5 wt % ZIF-8@CNTs. Compared with Figure 5d,f, the filler, as shown in Figure 5c, has better interfacial compatibility with the polymer matrix. Figure 5f shows that when pure 5 wt % ZIF-8 is added, a lot of white particles appear on the surface of the MMMs. This is due to the irreversible self-aggregation of ZIF-8 in the polymer matrix during the drying process of the film. Although there are no obvious defects on the surface of the membrane, the aggregation of ZIF-8 will cause the decrease in the CO$_2$ adsorption and CO$_2$/N$_2$ selectivity of the MMMs.

The comparison chart (Pebax/ZIF-8@CNTs-5%) clearly shows that the aggregation problem of ZIF-8 and Pebax-1657 has been substantially improved because the composite of ZIF-8 and CNTs improves the dispersibility of ZIF-8. The oxygen-containing functional group in ZIF-8@CNTs provides compatibility between ZIF-8 and Pebax-1657 such that the filler does not appear to be stacked in the polymer matrix. At the same time, the addition of the filler increases the free volume of the MMM, and the interaction of the filler with this membrane improves the permeability of CO$_2$.

The microstructure and crystallization characteristics of the pure Pebax-1657 film and mixed matrix film were analyzed via XRD. As shown in Figure 6a, the crystallinity and topology of ZIF-8 and ZIF-8@CNTs in the polymer matrix remain unchanged. The pure Pebax-1657 film is a semicrystalline copolymer, showing a PA6 peak at 23.9°, which is consistent with that reported in the ref 41. From the XRD patterns of MMMs with identical fillers and different qualities, it is shown that the PA6 peak intensity changes slightly, and the gas separation performance of the MMM is barely affected by the crystallinity of Pebax.

As shown in Figure 6b, the thermal decomposition temperature of the pure Pebax film is near 400 °C. The addition of ZIF-8 reduces the thermal decomposition temperature and weight loss rate of the Pebax film. However, the addition of ZIF-8@CNTs not only reduces the thermal decomposition temperature of the Pebax thin film but also results in a slightly higher weight loss rate than that of the Pebax thin film, which is caused by the carbon contained in the filler ZIF-8@CNTs being converted into CO$_2$ and escaping.

The surface structure and morphology of the mixed matrix film were further analyzed using AFM images. As shown in Figure 7, the fillers added are 1 wt % ZIF-8@CNTs (a,b), 5 wt % ZIF-8@CNTs (c,d), and 5 wt % ZIF-8 (e,f). It can be seen from Figure 7a–d that when the filler is 1 wt % ZIF-8@CNTs and 5 wt % ZIF-8@CNTs, the dark and bright areas of the AFM image are evenly distributed, which shows that when the filler is 1 and 5 wt % low content of ZIF-8@CNTs, the problem of particle aggregation on the surface of the mixed matrix film has been improved. As shown in Figure 7e,f, the...
filler is 5 wt % ZIF-8. From the figure, we can see that many bright areas have whiter colors, which indicates that there are aggregations on the surface of the mixed matrix film and areas with large height gaps. Therefore, from the AFM image of the mixed matrix film, we can know that when the filler is pure ZIF-8, there will indeed be aggregation on the surface of the mixed matrix film, but this phenomenon has been improved after adding CNTs.

2.3. CO₂/N₂ Separation Performance. In this work, MMMs of ZIF-8@CNTs with different loadings were prepared to study the effect of ZIF-8@CNTs on the separation performance of Pebax-1657 matrix gas, as shown in Figure 8.
The experiment was performed at 35 °C and 0.5 MPa, and the sweep gas flow rate is 5 mL/min. The figure shows that with the increase in ZIF-8@CNTs, the permeability of CO2 first increases and then decreases, and the selectivity of CO2/N2 continues to increase. When the loading of ZIF-8@CNTs reaches 5 wt %, the CO2 permeability reaches its highest value of 225.5 Barrer, and the CO2/N2 selectivity at this time is 48.9. Because of the different dynamic diameters of CO2 and N2, the adsorption of CO2 by ZIF-8 nanoparticles is faster than that of N2. The permeation process of CO2 in the ZIF-8 particles is the adsorption of CO2 by the ZIF-8 particles such that the occupied sites in the ZIF-8 particles are saturated, and then, the CO2 is discharged through diffusion. The addition of CNTs can make the ZIF-8 particles better dispersed and improve the mechanical strength of the mixed matrix film. This may be because the introduction of ZIF-8@CNTs improves the mixed matrix, and the free volume of the membrane increases the permeability of CO2. When the loading of ZIF-8@CNTs increases from 1 to 5 wt %, the CO2 permeability continues to increase. At a lower content of ZIF-8@CNTs, ZIF-8@CNTs may reduce the accumulation of polymer chains and reduce the resistance to gas diffusion. On the other hand, the carboxyl group of the oxidized CNT has a strong CO2 adsorption capacity and a smooth inner surface, which becomes a bridge between adjacent ZIF-8 particles and improves the transmission speed of CO2 in the Pebax matrix. Effectively reducing the transmission barrier of the Pebax matrix improves the permeability of CO2. This result also proves the key role of CNTs in the mixed matrix film. When the loading of ZIF-8@CNTs continues to increase, the CO2 permeability begins to decrease. This is because increasing the content of ZIF-8@CNTs increases the proportion of the impermeable area occupied by the filler, which prevents or hinders gas transmission and reduces the CO2 permeability. As the filler increases, the polymer chains on the filler surface are hardened, resulting in a decrease in permeability. When the loading of the filler is increased again, the probability of particle agglomerations in the MMM will increase, resulting in an increase in the interface pores of the MMM. At this time, the gas permeability will increase due to the interface pores, but the selectivity will be lower. The permeability of N2 continues to increase with increasing loading of ZIF-8@CNTs, and the permeability of CO2 decreases after 5%, which leads to a decrease in the CO2/N2 separation performance. In general, the CO2 permeability and CO2/N2 selectivity of the Pebax/ZIF-8@CNT MMM are 205.1 and 124.8% higher than those of the pure Pebax membrane, respectively.

![Figure 8](https://doi.org/10.1021/acsomega.1c00493)

**Figure 8.** Effect of the filler loading on mixed gas permeability and selectivity of (a) Pebax/ZIF-8@CNT MMMs and comparison of pure membrane and MMMs (b,c) (5 bar and 35 °C).

Table 1 shows the effect of fillers on the measured mechanical properties of membranes. CNTs effectively improve the mechanical properties of pure Pebax and the stability of the membrane. This result can be attributed to a substantial load transfer across the nanotube−matrix interface.

### 2.4. Compared with Other Studies and the Upper Bound.

Table 2 lists the gas separation performances of Pebax/ZIF-8@CNT MMMs and other MMMs previously reported. The novel structure of combining MOFs and CNTs for gas separation is different from those of other studies. It is
shown that Pebax/ZIF-8@CNT MMMs have a good balance performance. However, because of the difference in the polymer matrix and test conditions, a direct comparison with previously reported MMMs is difficult.

As shown in Figure 9, the gas separation performances of the Pebax/ZIF-8@CNT MMMs are much higher than that of the pure Pebax membranes. The results show that ZIF-8@CNTs can effectively improve the gas separation performance of the membrane. In addition, the ideal CO2/N2 separation performance of 8 MMMs of Pebax/ZIF-8@CNTs exceeds Robeson's upper limit (2008). The results indicate that the Pebax/ZIF-8@CNT MMM may be a potential candidate for the actual carbon dioxide capture process.

3. CONCLUSIONS

In this study, we successfully synthesized the one-dimensional linear composite material ZIF-8@CNTs. By embedding the nanoparticles in Pebax, we provided an effective strategy for preparing MMMs. Carboxylated CNTs provided many nucleation sites for ZIF-8, which enabled the ZIF-8 particles to grow successfully on the surface of the functional CNTs. The compatibility between ZIF-8@CNTs and Pebax effectively improved the permeability and selectivity of the MMM to CO2/N2. In addition, the inserted CNTs helped improve the mechanical properties and stability of the mixed matrix film. Compared with the reported MMM, Pebax/ZIF-8@CNTs have an excellent gas separation performance, exceeding the upper limit of 2008 Robeson.

4. EXPERIMENTAL SECTION

4.1. Materials. The Pebax-MH-1657 copolymer [comprising 40 wt % Nylon 6 PA6 segment and 60 wt % polyethylene oxide (PEO) segment] was supplied by Arkema (France). Zinc nitrate hexahydrate [Zn(NO3)2·6H2O], ethanol, nitric acid, and sulfuric acid were purchased from Sinopharm Holdings (China) Co., Ltd. 2-Methylimidazole (MeIm) was obtained from Shanghai Macleans Biochemical Technology Co., Ltd. (Shanghai, China).

4.2. Synthesis of ZIF-8 and ZIF-8@CNT Nanometer Materials. 1.2978 g of 2-Melm and 0.5866 g of Zn(NO3)2·6H2O were dissolved in 60 mL of methanol. After stirring for 1 h at room temperature, the crystals were separated by centrifugation and washed three times in methanol. The product was dried under vacuum at 100 °C overnight. The ZIF-8@CNT particles were synthesized by the typical procedure. Pretreatment of CNTs improves hydrophilicity. With stirring in an oil bath at 50 °C, CNT was added to (H2SO4/HNO3 = 3:1) mixed acid for treatment for 20 h. Then, the samples were collected, washed with deionized water to neutrality, and dried under vacuum at 80 °C overnight. The pretreated 120 mg of CNTs was dispersed in a methanol solution containing 1.2978 g of 2-Melm in 30 mL by ultrasonic stirring, and the solution was mixed with a methanol solution containing 0.5866 g of Zn(NO3)2·6H2O in 30 mL and stirred at room temperature for 1 h. After the reaction, the crystals were separated by centrifugation and washed three times in methanol. The product was dried under vacuum at 100 °C overnight.

4.3. Membrane Preparation. Pure Pebax-1657 and MMMs were prepared using the solvent evaporation technology. Pure Pebax-1657 particles (0.45 g) were dissolved in a mixed solvent of 10 mL (70% ethanol and 30% water) and stirred at 85 °C for 8 h. A homogeneous mixed solution was obtained by stirring and ultrasonic treatment, and then, the mixed solution was poured into a glass Petri dish and dried in an oven at 50 °C for 10 h. The preparation method of the MMM is basically the same as that of pure Pebax-1657. 10 mL of mixed solvent was used to dissolve Pebax-1657 particles in 2/3 of the solvent, and the filler was dispersed in 1/3 of the solvent by ultrasonic treatment. After stirring the Pebax-1657

Table 2. Comparison of the Gas Separation Performances of Pebax/ZIF-8@CNTs

| membrane              | operation conditions | PCO2 (Barre) | αCO2/N2 | ref.  |
|-----------------------|----------------------|--------------|---------|-------|
| ZIF-8–90/Pebax1657    | 0.1 MPa, 20 °C       | 99.7         | 59.6    | 41    |
| Pebax/ZIF-8@GO-6      | 0.1 MPa, 25 °C       | 249          | 47.6    | 42    |
| Pebax-1657 nanocomposite | 0.2 MPa, 31 °C       | 100          | 65      | 43    |
| ZIF-90/PI             | 0.2 MPa, 25 °C       | 720          | 27      | 44    |
| MIL-53(Al)/Matrimid   | 0.2 MPa, 35 °C       | 40           | 95.2    | 45    |
| Cd–6F/PI              | 0.2 MPa, 25 °C       | 37.8         | 35.1    | 46    |
| SO3H-MCM-41/SPEEK     | 1 MPa, 25 °C         | 21.0         | 22.9    | 47    |
| MIL-101(Cr)/SPEEK     | 0.1 MPa, 30 °C       | 31           | 37      | 48    |
| Pebax1657/ZIF-8@CNTs-5% | 0.5 MPa, 35 °C       | 225.2        | 49.1    | this work |

“MMMs with those of previously reported MMMs.
particles in an oil bath at 85 °C for 8 h, the filler was added. It was stirred and sonicated to obtain a uniform mixed solution. The loadings of the filler in MMMs were adjusted to 1, 3, 5, 8, 10, and 15 wt % for the purposes of this study based on eq 1

\[ \phi = \frac{M_{\text{filler}}}{M_{\text{filler}} + M_{\text{Pebax}}} \]  

where \( M_{\text{filler}} \) and \( M_{\text{Pebax}} \) are the mass of the filler and Pebax in the MMMs, respectively. The thickness of the prepared film is about 80–100 μm.

4.4. Characterizations. The crystal structure of the filler and mixed matrix film was characterized by XRD (Bruker D8 ADVANCE diffractometer) using monochromatic Cu Kα radiation (\( \lambda = 1.5418 \) Å). SEM images of the filler and mixed matrix film were recorded on the FEI Nova Nano SEM machine (FEI, USA). TEM images were captured on a Tecnai G2 F20 U-TWIN electron microscope with an accelerating voltage of 200 kV. Thermal analysis (STA 409 PC/4/A, NETZSCH, Germany) was used to measure the thermal stability of the filler at a rate of 10 °C min\(^{-1}\) in the temperature range from room temperature to 800 °C, and the thermal stability of the mixed matrix film was measured at a rate of 10 °C min\(^{-1}\) in the temperature range from room temperature to 800 °C. FTIR spectroscopy of the particles was measured with a thermoelectric Nicolet 6700 spectrometer in the wavenumber range of 500–4000 cm\(^{-1}\). A ASAP2060 machine was used to derive the BET specific surface area of ZIF-8 and its derivatives from the 77 K nitrogen adsorption isotherm.

4.5. Gas Permeation Experiments. As described elsewhere, a constant pressure/variable volume permeation system is used to measure the gas permeation of the membrane.\(^{38}\) The device is shown in Figure 10. The equation of permeability calculation is as follows

\[ p_i = \frac{Q_i l}{\Delta p_i S} \]  

where \( \Delta p_i \) is the pressure difference between the feed side and permeate side (cm Hg), \( S \) is 10 cm\(^2\) which is the effective area of the membrane, \( Q_i \) is the downstream volumetric of gas \( i \) (cm\(^3\) (STP)/S), and \( l \) is the thickness of the membrane (cm). The ideal selectivity (\( \alpha_{ij} \)) for two gases is determined as

\[ \alpha_{ij} = \frac{P_i}{P_j} \]  

where \( P_i \) and \( P_j \) are the permeability of gases \( i \) and \( j \), respectively. The gas separation performance was measured three times to ensure the accuracy of the data.

AUTHOR INFORMATION

Corresponding Authors
Yuping Tong – School of Materials and Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045 Henan, P. R. China; orcid.org/0000-0002-0526-0907; Email: yptong_zz@163.com
Weiwei He – Key Laboratory of Micro-Nano Materials for Energy Storage and Conversion of Henan Province, Institute of Surface Micro and Nano Materials, College of Chemical and Materials Engineering, Xuchang University, Xuchang 461000 Henan, P. R. China; Henan Joint International Research Laboratory of Nanomaterials for Energy and Catalysis, Xuchang University, Xuchang 461000 Henan, China; orcid.org/0000-0002-3495-9514; Email: heweixuc@gmail.com

Authors
Yahui Zhang – School of Materials and Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045 Henan, P. R. China; Key Laboratory of Micro-Nano Materials for Energy Storage and Conversion of Henan Province, Institute of Surface Micro and Nano Materials, College of Chemical and Materials Engineering, Xuchang University, Xuchang 461000 Henan, P. R. China
Xinyu Li – School of Materials and Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045 Henan, P. R. China
Shoujie Guo – Key Laboratory of Micro-Nano Materials for Energy Storage and Conversion of Henan Province, Institute of Surface Micro and Nano Materials, College of Chemical and Materials Engineering, Xuchang University, Xuchang 461000 Henan, P. R. China
of Surface Micro and Nano Materials, College of Chemical and Materials Engineering, Xuchang University, Xuchang 461000 Henan, P. R. China; Henan Joint International Research Laboratory of Nanomaterials for Energy and Catalysis, Xuchang University, Xuchang 461000 Henan, China

Hailong Zhang — School of Materials and Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045 Henan, P. R. China

Xi Chen — School of Materials and Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045 Henan, P. R. China

Kun Cai — Key Laboratory of Micro-Nano Materials for Energy Storage and Conversion of Henan Province, Institute of Surface Micro and Nano Materials, College of Chemical and Materials Engineering, Xuchang University, Xuchang 461000 Henan, P. R. China; Henan Joint International Research Laboratory of Nanomaterials for Energy and Catalysis, Xuchang University, Xuchang 461000 Henan, China

Linghe Cheng — School of Materials and Engineering, North China University of Water Resources and Electric Power, Zhengzhou 450045 Henan, P. R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00493

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is supported financially by the National Natural Science Foundation of China (21875085), the Program for Innovative Research Team (in Science and Technology) in Henan Province (19IRTSTHN026), and the Program for Zhongyuan Leading Talents of Science and Technology Innovation in Henan Province (204200510016).

REFERENCES

(1) Ho, M. T.; Allinson, G. W.; Wiley, D. E. Reducing the cost of CO2 capture from flue gases using membrane technology. Ind. Eng. Chem. Res. 2008, 47, 1562–1568.
(2) Ma, M.; Hansen, H. A.; Valenti, M.; Wang, Z.; Cao, A.; Dong, M.; Smith, W. A. Electrochemical reduction of CO2 on compositionally variant Au-Pt bimetallic thin films. Nano Energy 2017, 42, 51–57.
(3) Li, X.; Guo, T.; Zhu, L.; Ling, C.; Xue, Q.; Xing, W. Charge-modulated CO2 capture of C/N nanosheet: Insights from DFT calculations. Chem. Eng. J. 2018, 338, 92–98.
(4) Wang, S.; Li, X.; Wu, H.; Tian, Z.; Xin, Q.; He, G.; Peng, D.; Chen, S.; Yin, Y.; Jiang, Z.; Guiver, M. D. Advances in high permeability polymer-based membrane materials for CO2 separations. Energy Environ. Sci. 2016, 9, 1863–1890.
(5) Xiao, Y.; Chung, T.-S. Grafting thermally labile molecules on cross-linkable polyimide to design membrane materials for natural gas purification and CO2 capture. Energy Environ. Sci. 2011, 4, 201–208.
(6) Sanders, D. F.; Smith, Z. P.; Guo, R.; Robeson, L. M.; McGrath, J. E.; Paul, D. R.; Freeman, B. D. Energy-efficient polymeric gas separation membranes for a sustainable future: A review. Polymers 2013, 5, 4729–4761.
(7) Jomekian, A.; Bebbahani, R. M.; Mohammadi, T.; Kargari, A. CO2/CH4 separation by high performance co-cast ZIF-8/Pebax 1657/PES mixed matrix membrane. J. Nat. Gas Sci. Eng. 2016, 31, 562–574.
(8) Zhang, C.; Wu, B.-H.; Ma, M.-Q.; Wang, Z.; Xu, Z.-K. Ultrathin metal/covalent–organic framework membranes towards ultimate separation. Chem. Soc. Rev. 2019, 48, 3811–3841.
(9) Pazani, F.; Aroujalian, A. Enhanced CO2-selective behavior of Pebax-1657: A comparative study between the influence of graphane-filled fillers. Polym. Test. 2020, 81, 106264.
(10) Dai, Z.; Deng, J.; Peng, K.-J.; Liu, Y.-L.; Deng, L. Pebax/PEG Grafted CNT-hybrid membranes for Enhanced CO2/N2 Separation. Ind. Eng. Chem. Res. 2019, 58, 12226–12234.
(11) Atash Jameh, A.; Mohammadi, T.; Balbhtian, O. Preparation of PEBAX-1074/modified ZIF-8 nanoparticles mixed matrix membranes for CO2 removal from natural gas. Sep. Purif. Technol. 2020, 231, 115900.
(12) Jomekian, A.; Bebbahani, R. M.; Mohammadi, T.; Kargari, A. High speed spin coating in fabrication of Pebax 1657 based mixed matrix membrane filled with ultra-porous ZIF-8 particles for CO2/CH4 separation. Korean J. Chem. Eng. 2017, 34, 440–453.
(13) Zhang, Y.; Seong, J. G.; Do, Y. S.; Lee, W. H.; Lee, M. J.; Guiver, M. D.; Lee, Y. M. High-strength, soluble polyimide membranes incorporating Tröger’s Base for gas separation. J. Membr. Sci. 2016, 504, 55–65.
(14) Surya Murali, R.; Ismail, A. F.; Rahman, M. A.; Sriidhar, S. Mixed matrix membranes of Pebax-1657 loaded with 4A zeolite for gaseous separations. Sep. Purif. Technol. 2014, 129, 1–8.
(15) Lu, C.; Wang, D.; Zhao, J.; Han, S.; Chen, W. A Continuous Carbon Nitride Polyhydron Polymer for High-Performance Flexible Supercapacitors. Adv. Funct. Mater. 2017, 27, 1606219.
(16) Yang, Y.; Ge, L.; Rudolphi, V.; Zhu, Z. In situ synthesis of zeolitic imidazolate frameworks/carbon nanotube composites with enhanced CO2 adsorption. Dalton Trans. 2014, 43, 7028–7036.
(17) Wei, J.; Hu, Y.; Liang, Y.; Kong, B.; Zhang, J.; Song, J.; Bao, Q.; Simon, G. P.; Jiang, S. P.; Wang, H. Nitrogen-doped nanoporous carbon/graphene nanosandwiches:synthesis and application for efficient oxygen reduction. Adv. Funct. Mater. 2015, 25, 5768–5777.
(18) Nafisi, V.; Hågg, M. B. Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO2 capture. J. Membr. Sci. 2014, 459, 244–255.
(19) Wang, Z.; Wang, D.; Zhang, S.; Hu, L.; Jin, J. Interfacial Design of Mixed Matrix Membranes for Improved Gas Separation Performance. Adv. Mater. 2016, 28, 3399–3405.
(20) Li, T.; Pan, Y.; Peinemann, K.-V.; Lai, Z. Carbon dioxide selective mixed matrix composite membrane containing ZIF-7 nanofillers. J. Membr. Sci. 2013, 425–426, 235–242.
(21) Brozek, C. K.; Dinča, M. Cation exchange at the secondary building units of metalorganic frameworks. Chem. Soc. Rev. 2014, 43, 5456–5467.
(22) Qiu, S.; Xue, M.; Zhu, G. Metalorganic framework membranes: from synthesis to separation application. Chem. Soc. Rev. 2014, 43, 6116–6140.
(23) Erucar, I.; Keskin, S. High CO2 selectivity of an amine-functionalized metal organic framework in adsorption-based and membrane-based gas separations. Ind. Eng. Chem. Res. 2013, 52, 3462–3472.
(24) Cai, W.; Lee, T.; Lee, M.; Cho, W.; Han, D.-Y.; Choi, N.; Yip, A. C. K.; Choi, J. Thermal structure transitions and carbon dioxide adsorption properties of zeolitic imidazolate framework-7 (ZIF-7). J. Am. Chem. Soc. 2014, 136, 7961–7971.
(25) Karagiardis, O.; Lalonde, M. B.; Bury, W.; Sarjeant, A. A.; Farha, O. K.; Hupp, J. T. Opening ZIF-8: a catalytically active zeolitic imidazolate framework of sodalite topology with unsubstituted linkers. J. Am. Chem. Soc. 2012, 134, 18790–18796.
(26) Meshkat, S.; Kallaguiene, S.; Rodrigue, D. Comparison between ZIF-67 and ZIF-8 in Pebax® MH-1657 mixed matrix membranes for CO2 separation. Sep. Purif. Technol. 2020, 235, 116150.
(27) Nafisi, V.; Hågg, M. B. Gas separation properties of ZIF-8/6FDA-durene diamine mixed matrix membrane. Sep. Purif. Technol. 2014, 128, 31–38.
(28) Li, X.; Yu, S.; Li, K.; Ma, C.; Zhang, J.; Li, H.; Chang, X.; Zhu, L.; Xue, Q. Enhanced gas separation performance of Pebax mixed matrix membranes by incorporating ZIF-8 in situ inserted by multiwalled carbon nanotubes. Sep. Purif. Technol. 2020, 248, 117080.
UiO-66-polyether block amide mixed matrix membranes for CO2 absorption in both C and X bands. 

| Year | Authors | Journal | Title |
|------|---------|---------|-------|
| 2020 | Liu, Z.; Shi, Q.; Xiao, P.; Yang, Y.; Zhang, T.; Chen, Y. | Greenhouse Gases: Sci. Technol. | Synergistically assembled MWCNT/graphene foam with highly efficient microwave heating. |
| 2020 | Dong, L.; Chen, M.; Li, J.; Shi, D.; Dong, W.; Li, X.; Bai, Y. | Microporous Mesoporous Mater. | Metal-organic framework-graphene oxide composites: A facile method to highly improve the CO2 separation performance of mixed matrix membranes. |
| 2020 | Yu, B.; Cong, H.; Li, Z.; Tang, J.; Zhao, X. S. | J. Appl. Polym. Sci. | Pebax-1657 nano-composite membranes incorporated with nanoparticles/colloids/carbon nanotubes for CO2/N2 and CO2/H2 separation. |
| 2020 | Bae, T.-H.; Lee, J. S.; Qiu, W.; Koros, W. J.; Jones, C. W.; Nair, S. | Sep. Purif. Technol. | A high-performance gas separation membrane containing submicrometer-sized metal–organic framework crystals. |
| 2020 | Hsieh, J. O.; Balkus, K. J.; Ferraris, J. P.; Musselman, I. H. | Microporous Mesoporous Mater. | MIL-53 frameworks in mixed-matrix membranes. |
| 2020 | Lin, R.; Ge, L.; Diao, H.; Rudolph, V.; Zhu, Z. | J. Membr. Sci. | Propylene/propane selective mixed matrix membranes with grape-branched MOF/CNT filler. |
| 2020 | Pan, X.; Zhang, J.; Xue, Q.; Li, X.; Ding, D.; Zhu, L.; Guo, T. | J. Membr. Sci. | Mixed Matrix Membranes with Excellent CO2 Capture Induced by Nano-Carbon Hybrids. |
| 2020 | Chen, H.; Huang, Z.; Huang, Y.; Zhang, Y.; Ge, Z.; Qin, B.; Liu, Z.; Shi, Q.; Xiao, P.; Yang, Y.; Zhang, T.; Chen, Y. | Carbon | Synergistically assembled MWCNT/graphene foam with highly efficient microwave absorption in both C and X bands. |
| 2020 | Shen, J.; Liu, G.; Huang, K.; Li, Q.; Guan, K.; Li, Y.; Jin, W. | J. Membr. Sci. | UiO-66-polymer block amide mixed matrix membranes for CO2 separation. |
| 2021 | Zhang, W.; Ding, R.; Yang, K.; Dai, Y.; Yan, X.; He, G. | ACS Omega | ZIF-8 nanoparticles with tunable size for enhanced CO2 capture of Pebax based MMMs. |

Enhanced permeation performance of polyether-polyamide block copolymer membranes through incorporating ZIF-8 nanocrystals. 

High-performance polymeric membrane materials for CO2 separations. 

Improved membrane performance. 

Metal-organic framework-graphene oxide composites: A facile method for gas separation. 

Mixed matrix membranes composed of sulfonated poly (ether ether ketone) and a sulfonated metal–organic framework.