Enhanced CO$_2$/N$_2$ separation performance by using dopamine/polyethyleneimine-grafted TiO$_2$ nanoparticles filled PEBA mixed-matrix membranes

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**ABSTRACT**

Mixed matrix membranes (MMMs) were fabricated by incorporating synthesized titanium dioxide (TiO$_2$) nanoparticles into polyether block amide (PEBA) matrix to fabricate TiO$_2$/PEBA MMMs for CO$_2$/N$_2$ separation. The mesoporous channels of TiO$_2$ increased the density of active sites with high accessibility and also facilitate the diffusion of CO$_2$ in the gas separation process. Furthermore, amine groups are grafted onto the TiO$_2$ fillers via one-step reaction with dopamine (DA) and polyethyleneimine (PEI). The modified TiO$_2$ fillers with abundant amine groups are conductive to transfer CO$_2$ owing to the reversible reaction occurred between CO$_2$ and amine groups. The effects of TiO$_2$ loading, DA/PEI modification on the morphology and CO$_2$/N$_2$ separation performance of the resulting TiO$_2$/PEBA MMMs were systematically studied. The results showed that the MMMs filled with 3 wt% DA-PEI-TiO$_2$ synthesized with DA/PEI mass ratio of 1/1 and PEI molecular weight of 1800 exhibited optimal separation performance with CO$_2$ permeability of 67 Barrer and CO$_2$/N$_2$ selectivity of 101, surpassing the 2008 Robeson upper-bound.

1. Introduction

The increase of CO$_2$ emission is a main source of global warming [1,2]. For now, CO$_2$ capture and storage (CCS) [3–5], a low operating cost and low energy consumption technology, in addition to its environmental application, is recognized as one feasible strategy to mitigate CO$_2$ emissions from diverse sources [6–8]. Membrane gas separation, a green technology, offers a number of benefits over other separation technologies in the terms of CO$_2$ capture, and plays an increasingly important role in reducing the environmental impacts and costs of many industrial processes.

Membrane materials are the core of membrane separation technology [9]. Although polymeric membranes are the dominant gas separation membranes, their broad application might be limited by the intrinsic trade-off between permeability and selectivity [10–12]. Alternatively, mixed matrix membranes (MMMs), containing fillers in polymer matrix, are regarded as a kind of promising membrane for gas separation, which provide a solution to overcome the trade-off for polymeric membranes [13,14]. MMMs can combine both the advantages of polymer and inorganic materials with respect to performance and processability [15]. Different types of fillers such as silica [16,17], zeolite [18–20], molecular sieve [21,22], titanium dioxide [23–26], carbon nanotubes [27,28], graphene oxide [29,30], and metal organic frameworks [31,32] have been applied to the fabrication of MMMs. It has been well demonstrated that the match of filler and matrix is crucial for the development of high-performance MMMs [33].

Polyamide-b-ethylene oxide (PEBA), a rubbery (polyamide (PA)-polyethylene oxide (PEO) copolymer, which is suitable for the CO$_2$ removal of from flue gas [34,35]. It is synthesized by two monomers including PA as rigid segment which provides high mechanical stability and stable structure for membranes and polyether (PE) block as soft and flexible segment which has etheric oxygen and provides high free volume within membranes [36]. The PEO part possesses a high affinity for CO$_2$ because the polar ether group can form polar interactions with CO$_2$ [37–39]. Moreover, rigid-soft structure of PEBA could enhance the interfacial interaction between polymer and filler particles [40]. Titanium oxide (TiO$_2$) is a potential candidate for the development of mixed matrix membranes due to its favorable physical properties, stability, low cost, and easy to synthesize [41,42]. Importantly, TiO$_2$ exhibits very high adsorption capacity and size-selective adsorption for certain gases (such as CO$_2$) [43], and its mesoporous channels further increase the density of active sites with high accessibility to facilitate the gas...
Diffusion. Meanwhile, incorporation of CO₂-facilitated transport fillers (e.g. amine-functionalized TiO₂) into polymeric membranes is an efficient approach to enhance gas separation performance due to the reversible reaction between CO₂ and facilitated transport groups [38, 44, 45]. Our previous work demonstrated that amine modification of UiO-66 MOF fillers could not only enhance CO₂ sorption but also improve the filler dispersion in the matrix.

In this study, TiO₂ nanoparticles were synthesized via a solvothermal method and used as filler to be incorporated into PEBA matrix to fabricate TiO₂/PEBA MMMs for CO₂/N₂ separation. To enhance CO₂ preferential sorption in the MMMs, the TiO₂ fillers were grafted with amine groups via one step reaction with dopamine (DA) and polyethyleneimine (PEI) as shown in Fig. 1. DA plays a bridging role between TiO₂ and PEI, and PEI chain contains plenty of amine groups that is beneficial to improve the gas separation performance through the reversible reaction between amine groups and CO₂. Therefore, the synergistic effect of DA and PEI of the modified TiO₂ nanofillers is expected to enhance the gas separation performance of the PEBA membrane. Effects of TiO₂ loading, amine modification and modification conditions of the TiO₂ fillers on the membrane morphology and separation performance were investigated. Moreover, the influence of operating temperature and long-term stability of the TiO₂/PEBA MMMs were studied, as well.

2. Experimental

2.1. Materials

For the synthesis of mesoporous TiO₂, titanium isopropoxide and Poly(Ethyleneimine) (PEI, molecular weight Mw = 600, 1800 and 10,000, 99%) were supplied by Adamas. Acetone and hydrochloric acid were purchased by Shanghai Lingfeng Chemical Reagent Co. Ltd., 4-(2-aminoethyl)benzene-1,2-diol (dopamine, DA) was provided Yuancheng Technology Development Co., Ltd., ethanol was obtained by Wuxi City Yasheng Chemical Co. Ltd., PEBAX 1657 was purchased from Arkema, France. N₂ and CO₂ with purity 99.999% was supplied by Nanjing Special Gases Company. Deionized water was used in all the experiments. All the materials were used without further purification.

2.2. Preparation of mesoporous unmodified and modified TiO₂

The preparation of TiO₂ were carried out following the procedures as described in previous study [46]. For TiO₂, 1 ml of titanium isopropoxide was mixed with 60 ml of anhydrous acetone. The mixture was stirred at ambient conditions for 30 min and then transferred to a Teflon-lined stainless-steel autoclave (125 ml volume), and heated at 200 °C for 12 h. After synthesis, the white precipitate was separated by centrifugation and washed several times with deionized water and acetone. For amine-functionalized TiO₂, dopamine and PEI were subsequently used as modification reagents [44,47]. A facile chelation procedure was conducted. 0.5 g TiO₂ powders were suspended in 100 ml deionized water under ultrasonic treatment for 2 h. 0.25 g dopamine and 0.25 g PEI were successively dissolved in 100 ml solution (adding Tris-HCl, pH = 8.5) used as modification reagent solution via Michael addition or Schiff base reaction at room temperature for 5 h. The obtained modified TiO₂ was designed as DA-PEI-TiO₂. A color change from white (TiO₂) to brown (DA-PEI-TiO₂) was observed during the functionalization procedure. During the modification procedure,
the effect of mass ratio of DA and PEI was studied by adjusting from 2:1 to 1:1 and then to 1:2. In addition, the effect of molecular weight of PEI was investigated by changing from 600 to 1800 and then to 10,000. The remaining steps are the same as above.

2.3. Membranes fabrication

A certain amount of fillers (TiO₂ or DA-PEI-TiO₂) were dispersed into 7/3 (wt) ethanol/water mixed solution followed by sonication for 30 min in an ice bath. Then, dried PEBA polymers were added into the mixtures and heated with stirring and refluxing under 80 °C for 12 h.
2.4. Characterizations

The neat PEBA was prepared following the similar procedure. The membrane was pretreated by being immersed in water for 24 h. The free-standing membranes for characterization and analysis were prepared by casting the bubble free solution on PVDF supports, which were prepared by casting the bubble free polymer solution on the glass plate. The membrane was made by using DA and PEI, no obvious change in particle size was observed by using DA and PEI, no obvious change in particle size was observed. To observe the morphologies of the mesoporous TiO₂ and the top surfaces and cross sections of the membranes, scanning electron microscope (SEM, S-4800, Hitachi, Japan) was used together with energy-dispersive X-ray spectroscopy (EDXS). Surface area and pore size distribution of the unmodified and modified TiO₂ were measured by ASAP 2460 with N₂ adsorption–desorption isotherms (77 K) and CO₂ adsorption isotherm (298 K). The crystalline structure of unmodified and modified TiO₂ were analyzed through X-ray Diffraction (XRD, Bruker, DB Advance) using Cu Kα radiation (λ = 1.54 Å) at 40 kV and 15 mA at room temperature. The functional groups of synthesized unmodified and modified TiO₂ were characterized by Fourier transform infrared (FTIR, AVATAR-FT-IR-360, Thermo Nicolet, USA) spectra in the range of 600–4000 cm⁻¹. The surface chemical composition of the particles (TiO₂, DA-PEI-TiO₂) was investigated by X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250, USA).

2.5. Gas separation experiments

Gas permeation test were conducted to investigate the gas transport behavior of the as-prepared membranes using the method reported in our previous work [48,49]. For pure gas permeation tests of CO₂ and N₂, the temperature and pressure were set at 20 °C and 0.3 MPa respectively. After reaching the steady state, flow rate of permeation was calculated by utilizing a bubble flow meter. For mixed-gas permeation test, CO₂/N₂ mixtures (volume ratio 50:50) were used as feed gas and Ar was chosen as sweep gas. All the gas permeation experiments were performed more than four times.

The gas permeability can be calculated using the following equation:

\[
P = \frac{QL}{\Delta pA}
\]

where \(P\) is the gas permeability \([1 \text{ Barrer} = 10^{-10} \text{ cm}^2(\text{STP})\text{cm}^2/(\text{s} \cdot \text{cmHg})]\), \(Q\) is the volume permeate rate of gas \((\text{cm}^3/\text{s})\), \(L\) is selective layer thickness \((\text{cm})\), \(\Delta p\) is the transmembrane pressure \((\text{cmHg})\) and \(A\) is the effective membrane area \((\text{cm}^2)\) for gas permeation.

The selectivity of CO₂/N₂ can be calculated by the ratio of permeability of the individual gas, can be expressed as follow:

\[
\alpha = \frac{P_A}{P_B}
\]

where \(P_A\) and \(P_B\) are the permeability of pure gas \(A\) and \(B\), respectively.

3. Results and discussion

3.1. Characterization of the fillers and membranes

The morphologies of the unmodified and modified TiO₂ was characterized by SEM as shown in Fig. 2, showing the TiO₂ with average particle size of ∼700 nm (Fig. 2a, b) [46]. After grafting amine groups by using DA and PEI, no obvious change in particle size was observed (Fig. 2c, d).

FTIR was used to further confirm the chemical groups and the spectra are shown in Fig. 3. There are some characteristic peaks in TiO₂ spectra. The broad peak at 500–600 cm⁻¹ is due to the vibration of the Ti-O bonds. The peaks appearing at 1630 and 3300 cm⁻¹ are due to the vibration of the C=H and N−H bonds and appears at 1370 and 1500 cm⁻¹ [44,50]. These characteristic bands suggest that by the facile one-step amine modification, the DA and PEI can be grafted onto the TiO₂ in the 3 samples modified with different PEI molecular weights.

XPS is utilized to further analyze the elemental compositions of the mesoporous TiO₂ and DA-PEI-TiO₂ (M(PEI) = 1800) fillers (Fig. 4). TiO₂, which was synthesized by anhydrous acetone, was not roasted, therefore, carbon and oxygen element on the outer surface of TiO₂ were checked by XPS. The Ti2p spectra reveal the Ti2p3/2 and Ti2p1/2 spin-orbital splitting photoelectrons of Ti⁴⁺, identical to those of pure TiO₂.
at binding energies of 458.9 and 464.6 eV. The characteristic signal of N1s at 400 eV is observed in the modified TiO₂. As shown in Table 1, the present of N1s, along with the increased C1s after DA and PEI modification also indicate the successful introduction of DA and PEI in TiO₂.

XRD analysis was used to study the crystal structure of the synthesized TiO₂ and its modifications by various DA/PEI mass ratios and PEI molecular weights. The patterns in Fig. 5 showed that the synthesized TiO₂ has highly crystalline structure, matching well with the reported literature [46]. The peaks at 25.4°, 37.8°, 48.3°, 54.2°, 55.3°, and 62.8° could be assigned to the diffractions of the (1 0 1), (0 0 4), (2 0 0), (1 0 5), (2 1 1), and (2 0 4) crystal planes of the anatase phase in TiO₂ (JCPDS file No. 21-1272) [51]. The significant broadening of the different peaks is owing to the relatively small size of the TiO₂ crystallites that make up the TiO₂ microspheres. As shown in Fig. 5, both unmodified and modified TiO₂ possess highly crystalline structure.

Fig. 6 shows CO₂ adsorption isotherms for the unmodified and DA/PEI modified TiO₂ at 298 K. As expected, high CO₂ sorption capacity was obtained in the porous TiO₂ nanoparticles. After introducing amine groups, the modified TiO₂ particles show higher affinity toward CO₂.

Fig. 7. (a) and (b) are the N₂ adsorption and desorption isotherms at 77 K for TiO₂ and DA-PEI-TiO₂ microspheres, respectively. (c) and (d) are the BJH pore size distribution curves of TiO₂ and DA-PEI-TiO₂.

Fig. 8. Surface (a–e) and cross-section (f–j) SEM images of unmodified TiO₂/PEBA mixed matrix membranes with various TiO₂ loading. (a, f) 0 wt%, (b, g) 1 wt%, (c, h) 2 wt%, (d, i) 3 wt %, (e, j) 3.5 wt%.
which would enhance the CO2 sorption in the resulting TiO2 mixed matrix membranes [52]. We speculated that the synergy effect between the porosity and N-doped sites can account for the observed higher CO2 adsorption on amine functionalized TiO2 [53].

The N2 adsorption–desorption isotherms of the unmodified and modified TiO2 particles at 77 K and the corresponding pore-size distribution of the particles are shown in Fig. 7. BET surface areas of TiO2 and DA-PEI-TiO2 (M(PEI) = 1800) are 143.85 and 134.64 m²/g, respectively. In both isotherms as type IV isotherm, capillary condensation is accompanied by hysteresis [52]. In addition, these particles are categorized in mesoporous (pore size 2–50 nm) materials. Therefore, the adsorption in the particles is determined by the adsorptive interactions and interactions between the molecules in the condensed state [54]. The hysteresis loop shape of amine-functionalized TiO2 particles might be associated with partially pore blocking; the pore volume decreased to 0.19 cm³/g.

The morphologies of the as-prepared membranes were characterized by SEM, including the pure PEBA, unmodified TiO2 filled PEBA MMMs, and modified TiO2 filled PEBA MMMs. As shown in Fig. 8, incorporating TiO2 fillers into the PEBA matrix leads to morphological

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**Fig. 9.** Cross-section SEM images of modified TiO2/PEBA mixed matrix membranes with various DA/PEI ratios and PEI molecular weights.

**Fig. 10.** Effect of unmodified TiO2 loading on the CO2/N2 separation performances of TiO2/PEBA mixed matrix membranes. Pure gas permeation test was at 0.3 MPa and 20 °C.

**Fig. 11.** Compared with pure PEBA membrane, effects of DA/PEI mass ratio and PEI molecular weight on CO2 permeability and CO2/N2 selectivity of 3 wt% DA-PEI-TiO2/PEBA MMMs. (a) M(PEI) = 600, (b) M(PEI) = 1800, and (c) M(PEI) = 10,000. Pure gas permeation was measured at 0.3 MPa and 20 °C.
changes while the distribution of fillers in polymer is uniform with TiO₂ loading no more than 3 wt%. Agglomeration occurs as increasing the TiO₂ loading to 3.5 wt%, leading to some defects observed in the cross-section SEM images of 3.5 wt% TiO₂/PEBA MMM (Fig. 8j). Combined with the morphology and separation performance discussed later, we chose 3 wt% as the optimized TiO₂ loading for development of the following modified TiO₂/PEBA MMMs.

The SEM images of PEBAX MMMs filled with TiO₂ nanoparticles modified by various DA/PEI mass ratios and PEI molecular weights are shown in Fig. 8. The amine-functionalized TiO₂/PEBA MMMs. It was found that when the optimized DA/PEI ratio and PEI molecular weight for fabricating the PEBAX MMMs is the best for CO₂/N₂ separation with CO₂ permeability of 63 Barrer and CO₂/N₂ selectivity of 104.

3.2. Gas separation performance

3.2.1. Effect of unmodified TiO₂ loading

The effect of unmodified TiO₂ loading on the CO₂/N₂ separation performance of TiO₂/PEBA MMMs was investigated. As shown in Fig. 10, when unmodified TiO₂ loading was increased to 3 wt%, both the CO₂ permeability and CO₂/N₂ selectivity are gradually increased in the MMMs. The CO₂ permeability kept increasing while the CO₂/N₂ selectivity decreased by further increasing the TiO₂ loading more than 3 wt%. As the unmodified TiO₂ loading rose to 4 wt%, the CO₂/N₂ selectivity dropped to 45, which is close to the intrinsic selectivity of pure PEBAX membrane, indicating the present of non-selective defects probably caused by nanoparticles agglomeration in the matrix [36,50]. Compared to pure PEBAX membrane, CO₂ permeability was increased by 193% and CO₂/N₂ selectivity was increased by 47% in the TiO₂/PEBA with optimized loading of 3 wt%. This can be due to the constructed CO₂-facilitated transport pathways by incorporating mesoporous TiO₂ fillers to enhance the CO₂ separation over N₂ [55-57].

3.2.2. Effect of fillers type

The effects of DA/PEI mass ratio and the molecular weight of PEI on the CO₂/N₂ separation performance were studied, as shown in Fig. 11. Overall, compared to the unmodified TiO₂/PEBA MMM with 3 wt% loading, the incorporation of amine-functionalized TiO₂ exhibited a substantial enhancement in CO₂/N₂ selectivity while a decrease in CO₂ permeability at the same TiO₂ loading. The higher selectivity is primarily attributed to the enhanced CO₂ sorption in the MMMs. Furthermore, there is a general trade-off between permeability and selectivity by varying the DA/PEI ratio, while length of the grafted PEI chain affected the CO₂/N₂ separation performance remarkably. In particular, as the molecular weight of PEI is 10,000, the long polymer chain on the outer surface of TiO₂ might increase the CO₂ diffusion resistance, leading to decrease CO₂ permeability and CO₂/N₂ selectivity [58]. There is an optimized DA/PEI ratio and PEI molecular weight for fabricating the amine-functionalized TiO₂/PEBA MMMs. It was found that when the molecular weight of PEI is 1800 and the mass ratio of DA and PEI is 1:1, the gas separation performance of the resulting DA-PEI-TiO₂/PEBA MMMs is the best for CO₂/N₂ separation with CO₂ permeability of 63 Barrer and CO₂/N₂ selectivity of 104.

3.2.3. Comparison with upper-bound and other studies

As shown in Fig. 12, unmodified TiO₂/PEBA (3 wt%) and DA-PEI-TiO₂/PEBA (3 wt%) MMMs with 2008 Robeson upper-bound surpassed the Robeson upper-bound reported in 2008. We also compared our results with those reported in the literature summarized in Table 2. Although it is difficult to make a direct comparison of gas separation performance for PEBAX-based MMMs with the literature values because of the difficult experimental conditions and calculation techniques employed to evaluate the gas separation performance of the membrane. We can still make a general comparison and note that it can be apparently seen that mixed matrix membranes showed overall higher performance than the pure polymeric membrane. Among these membranes, this work indicated that the as-prepared DA-PEI-TiO₂/PEBA MMM (3 wt%, M(PEI) = 1800) could be a potential candidate for an efficient CO₂ capture process.

3.2.4. Effect of operation temperature

The effect of operation temperature was studied, as showed in

![Fig. 12. Comparison of CO₂/N₂ gas separation performances of pure PEBAX, TiO₂/PEBA MMM (3 wt%) and DA-PEI-TiO₂/PEBA (3 wt%) MMMs with 2008 Robeson upper-bound. The symbols in the dash cycle are 3 wt% DA-PEI-TiO₂/PEBA MMMs, e.g., “1/1, 1800” represents DA/PEI mass ratio of 1/1 and PEI molecular weight of 1800.](Image)

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<th>Membrane</th>
<th>Permeability CO₂ (Barrer)</th>
<th>Selectivity</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
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<td>Pebax-UO-66 (10 wt%)</td>
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<td>56.6</td>
<td>3</td>
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<td>42.6</td>
<td>4</td>
<td>25</td>
<td>[61]</td>
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<td>25</td>
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<td>121.5</td>
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<td>25</td>
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<tr>
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<td>3</td>
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<td>10</td>
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<td>101</td>
<td>3</td>
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Table 2: Comparison of membrane performance of PEBAX 1657-based membrane.
Fig. 13. Effect of operation temperature on CO2 permeability and CO2/N2 selectivity of pure PEBA and DA-PEI-TiO2/PEBA (3 wt%, M(PEI) = 1800) membranes. Pure gas permeation test was measured at 0.3 MPa and 20 °C.

Fig. 14. Long-term operation test on DA-PEI-TiO2/PEBA MMM (3 wt%, M(PEI) = 1800). Mixed gas permeation was measured at 0.1 MPa and 20 °C.

3.2.5. Long-term operation stability

Long term operation test of mixed-gas permeation was carried out to further investigate the structural stability of DA-PEI-TiO2/PEBA MMM (3 wt%, M(PEI) = 1800). The data were recorded after the whole permeation system was steady. As shown in Fig. 14, during the entire test period of over 100 h, the membrane exhibited stable separation performance with average CO2 permeability of 52 Barrer and CO2/N2 selectivity of 82.

4. Conclusion

Mixed-matrix membranes composed of PEBA and dopamine (DA)/polyethyleneimine (PEI) grafted TiO2 were prepared and their CO2/N2 separation performances were investigated. TiO2 particles were functionalized with dopamine and polyethyleneimine by a one-step method. The incorporation of TiO2 nanoparticles simultaneously enhanced the CO2 permeability and CO2/N2 selectivity of the pure PEBA membrane. The CO2/N2 selectivity was further increased by the DA/PEI functionalization on the TiO2 fillers, owing to the higher CO2 sorption capacity from the grafted amine groups. The DA/PEI modified TiO2/PEBA MMM with optimized DA/PEI mass ratio of 1:1, PEI molecular weight of 1800, and TiO2 loading of 3 wt% exhibited the highest CO2/N2 selectivity up to 101, with CO2 permeability of 67.7 Barrer at 0.3 bar and 25 °C, which transcends the 2008 Robeson upper-bound.

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