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ZEOLITIC IMIDAZOLE FRAMEWORK 8 DECORATED GRAPHENE OXIDE (ZIF-8/GO) MIXED MATRIX MEMBRANE (MMM) FOR CO_2/CH_4 SEPARATION

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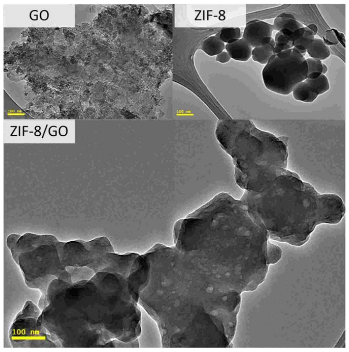
Graphical abstract



Abstract

Recently, metal-organic framework composited with graphene oxide (MOF/GO) has been explored and has shown superior properties compared to both of the parent materials. Thus, this study aims to utilize zeolitic imidazole framework 8 (ZIF-8), a subclass of MOF, decorated graphene oxide (ZIF-8/GO) as filler in mixed matrix membrane (MMM) for CO_2 separation. ZIF-8/GO has been successfully synthesized using aqueous room temperature method. Distortion of ZIF-8 structure after GO incorporate was observed from TEM and decreasing pore properties, while their crystal structure are intact. The role of the composite on gas permeation is also evaluated using pure N_2, CH_4 and CO_2. The presence of ZIF-8/GO into membrane has increase CO2 permeance from 59.03 ± 13.87 GPU to 79.92 ± 18.26 GPU with insignificant changes in the gas pair selectivities even only 0.5wt% (total solids) of ZIF-8/GO incorporated.

Keywords: Graphene oxide, ZIF-8, ZIF-8/GO, Gas separation, Mixed Matrix Membrane (MMM)

1.0 INTRODUCTION

Recent membrane development has focusing on integrating inorganic particles (dispersed phase) into polymeric membrane (continuous phase) known as mixed matrix membrane (MMM). Significant improvement offered by MMM compared to its polymeric counterpart is expected with superiority of inorganic particle while offering ease processability and maintaining moderate processing cost. Gas separation performance of MMM are the main driving force in the development of membrane. Compared to polymeric membrane, the embodiment of filler would introduce additional separation mechanism to improve the membrane performances. First attempt in MMM development by Zimmerman *et al.* [1] has highlighted significant contribution of inorganic particles towards properties of resulting MMMs surpassing Robeson Upperbound.

The advancement of material sciences has concurrently encourages the advancement of

MMM. Different filler utilized offers different new separation mechanism (i.e. molecular sieving, permeation path tortuosity) and functional group, hence, resulting in different membrane properties and performances. To date, various potential MMMs have been explored by utilizing zeolites [2], silica [3], carbon nanotubes (CNT) [4], metal-organic framework (MOF) [5-7], graphene oxide (GO) [8] and clay particles [9] as dispersed phase.

Recently, utilizing composite of MOF and GO has been reported. MOF was synthesized on the surface of exfoliated GO sheet. The carboxyl group presence in GO reacted with MOF to create a porous interface, which provide active sites for various applications. For example, Kumar *et al*. [10] has reported MOF/GO using zeolitic imidazole framework 8 (ZIF-8, subclasses of MOF) for CO_2 adsorption. It was observed that the CO_2 uptake increase dramatically from 27wt% to 72.4wt% when 20wt% of GO composited with ZIF-8.

Research on MOF/GO is relatively new strategies in material development. Therefore, this study aims to investigate the influence of the composite materials as filler in MMM for CO_2 separation. ZIF-8 is selected as our parent MOF since it is among matured MOF to date.

2.0 METHODOLOGY

2.1 Materials

Zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$), 2-methylimidazole (2-MeIM), triethylamine (TEA) and graphene oxide sheets (GO) were purchased from Sigma Aldrich. All chemicals were used without further purification.

2.2 ZIF-8/GO Composite Synthesis

The ZIF-8/GO composite was prepared by modifying ZIF-8 synthesis procedure described in literature [11]. Briefly, $Zn(NO_3)_2$ (2g, 6.72 mmol) was dissolved in 12g of deionized water. Separately, ligand solution was prepared by dissolving 2-MeIM (3.312 g, 40.34 mmol) into deionized water (48.56g), followed by 3.0 mL of TEA. 5wt% of GO (based on $Zn(NO_3)_2$ mass) was dispersed into the ligand solution and sonicated for 30 minutes. The Zn solution was slowly added to the ligand solution with continuous stir for 30 minutes where greyish mixture form instantaneously. The precipitate was collected by centrifuge and washed with deionized water three times before drying in oven at 120°C for minimum 12 hours. Pure ZIF-8 was prepared using similar procedure without GO inclusion step.

2.3 Asymmetric fat sheet MMM preparation

ZIF-8/GO (0.5wt% from total solids) was dispersed into NMP:THF (4:1) via sonication. Approximately 10% of the PSf (total 12.5g) was added under stirring for the purpose of priming. The remaining PSf was gradually added and the mixture was kept stirring until the solution became homogeneous. The casting dope was then hand-cast using a casting bar to a thickness of 120–190 μm before immersed into coagulation bath (tap water at room temperature) where the membrane was solidified. After immersion for 1 day, the membrane was post-treated in methanol and n-hexane, each for 2 h, before being air-dried for 24 hours in the ambient atmosphere. The pristine PSf membrane was prepared by the same process without filler inclusion. The surface of the membrane was then brought into contact with 3 wt% PDMS/n-hexane solution for 10 min to seal possible pinholes before it was “cured” at 60°C for 12 hours.

2.3 Characterizations

A differential scanning calorimeter (DSC) of membranes was characterized using a Mettler Toledo DSC 822e with heating-cooling-heating from 50 to 400 °C at 10 °C min^{-1}. The T_g of the sample was determined as the midpoint temperature of the transition region in the second heating cycle.

Thermogravimetric analysis (TGA) (Mettler Toledo thermogravimetric analyser) records the weight changes of the sample when heated continuously from 50 to 900 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere (flow rate of 20 mL min^{-1}).

X-Ray Diffraction (XRD) analysis using a Siemens D5000 Diffractometer. The X-rays emitted towards the sample and diffracted at different angles (2θ) and intensities by CuKa radiation with a wavelength λ=1.54 Å at room temperature.

The specific surface area and pore volume of the crystals were measured using a Micromeritics gas adsorption analyzer ASAP2010 instrument equipped with commercial software for calculation and analysis. The BET surface area was calculated from the adsorption isotherms using the standard Brunauer–Emmett–Teller (BET) equation. The mesopore volume was obtained using a BJH plot while the micropore volume was obtained using the t-plot method of Lippens and de Boer with the adsorption data.

Scanning electron microscopy (SEM) was used to observe the membrane structure and morphology using TM3000, Hitachi. Membrane samples were fractured cryogenically in liquid nitrogen and coated with gold before they were imaged.

Transmission electron microscope (TEM) (JEOL, JSM-6701FJEOL 1230) was applied to observe the nanostructures of the samples. Samples were prepared by dispersing the powder in methanol and their drip was used for the dispersion of ZIF-8 on carbon-coated copper grids operating at 300 kV.

Gas permeation tests were performed using a constant pressure–variable volume system. The membranes were placed into the permeation cell with an effective permeation area of 12.5 cm^2 and exposed to pure N_2, CH_4 or CO_2 gas at 4 bar and the temperature was 27 °C. The pressure-normalized flux (permeance) of gas i was calculated as follows:

$$(P/l)_i = \frac{Q_i}{\Delta p.A} = \frac{dV/dt}{\Delta p.\pi r^2} \qquad (1)$$

where i represents the gas penetrant, *Vi* is the volume of gas permeated through the membrane (cm^3, STP), *A* is the effective membrane area (cm^2), *t* is the permeation time (s) and *Δp* is the transmembrane pressure drop (cmHg). The permeance is expressed in gas permeation units, GPU, as 1 GPU = 1 × 10^{-6} cm^3 (STP) cm^{-2} s^{-1} cmHg^{-1}.

The selectivity was obtained using eqn (2):

$$\alpha_{i/j} = \frac{(P/l)_i}{(P/l)_j} \qquad (2)$$

where $\alpha_{i/j}$ is the selectivity of gas penetrant *i* over gas penetrant *j*, $(P/l)_i$ and $(P/l)_j$ are the permeance of gas penetrants *i* and *j*, respectively.

3.0 RESULTS AND DISCUSSION

The XRD analysis was done to identify crystal phase of prepared samples. The presence of strong peaks implies a high crystallinity of the prepared ZIF-8 showing good agreement with our previous work [11] where the peaks at 2θ = 7.30, 10.35, 12.70, 14.80, 16.40 and 18.00° correspond to planes (110), (200), (211), (220), (310), and (222), respectively (Figure 1). The prepared ZIF-8/GO also showing similar peaks indicates the ZIF-8 successfully prepared within GO. The area under graph of ZIF-8/GO, calculated using software OriginPro®, is slightly diminished compared to pure ZIF-8. This is due to the presence of secondary species (GO) that commonly cause peaks interference. However, only minimal amount of GO was used to cause any notable changes in the peaks.

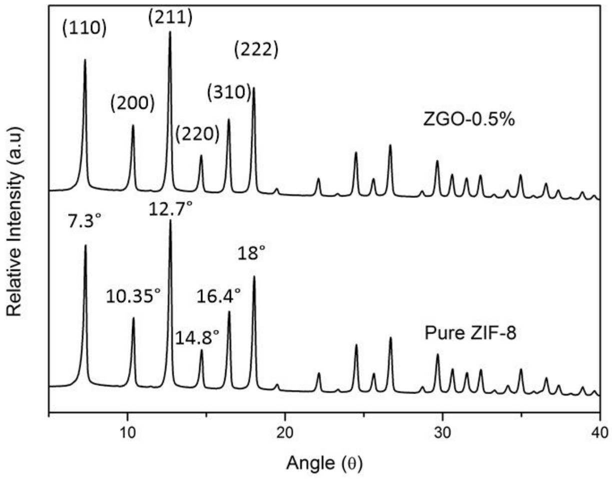


Figure 1 XRD peaks of pure ZIF-8 and ZIF-8/GO composite

The TEM analysis of GO, ZIF-8 and ZIF-8/GO are presented in Figure 2 with scale bar of 100nm. The synthesized ZIF-8 shows clear dodecahedron structure similar to previous work [11-12]. The GO sheets shows non-exfoliated likely due to no sonication procedure was introduce in the sample preparation stages. The ZIF-8/GO morphology is closely resembles ZIF-8 structure while no GO was observed. Compared to pure ZIF-8, ZIF-8/GO closely packed together and behaves as agglomeration. Kumar *et al.* [10] has highlighted that GO acted as template for ZIF-8 formation on the GO layer. Since only minimal GO was used in this study, ZIF-8 formed surrounds the GO sheets and closely packed to shadow GO layers from visible through TEM analysis. Moreover, the ZIF-8/GO hardly resembles ZIF-8 structure although XRD analysis has confirmed that the composite possess similar crystal structure as their parent MOF. This is likely due to distortion of ZIF-8 crystal when competing for active sites on GO [13].

The surface properties of prepared ZIF-8 and ZIF-8/GO are presented in Table 1. The surface area of pure ZIF-8 is comparable with literatures using aqueous room temperature synthesis method. After GO was introduced as template, the all surface properties of the ZIF-8/GO diminished compared to the parent ZIF-8. This is likely due to distortion of ZIF-8 structure embedded on the GO layer, thus diminished in pore structure [13].

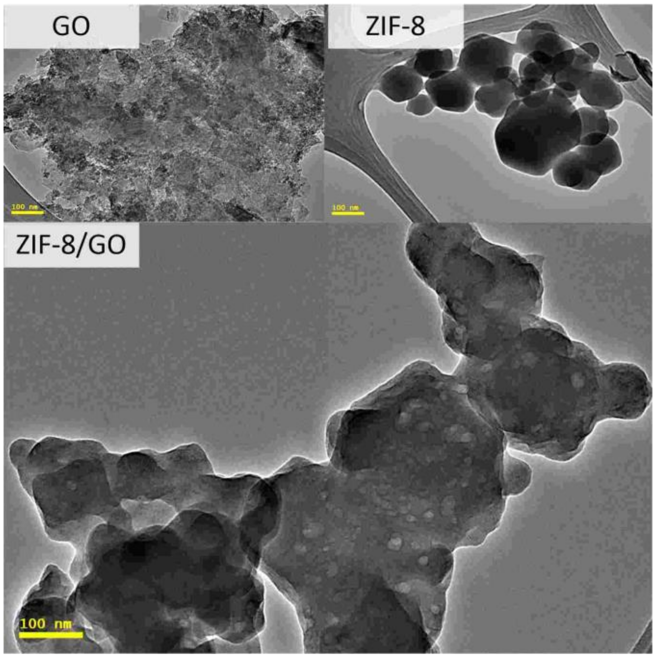


Figure 2 TEM analysis of GO, pure ZIF-8 and ZIF-8/GO

Table 1 Surface properties of ZIF-8 and ZIF-8/GO

Sample	BET surface area (m^2/g)	Mesopore volume (cm^3/g)	Micropore volume (cm^3/g)	Total Pore volume (cm^3/g)
ZIF-8	918.57	0.1976	0.2566	0.4542
ZIF-8/GO	698.02	0.1852	0.2327	0.4179

The T_g of the prepared membranes is presented in Table 2. The T_g of neat PSf membrane was comparable with the value previously reported [7] indicates high rigidity of the polymer. Upon ZIF-8/GO incorporation, slight increase in the MMM's T_g indicates increased rigidity due to good interaction between PSf and ZIF-8/GO.

The influence of ZIF/GO on gas permeation properties is presented in Table 2. The performance of neat PSf membrane is comparable with other reported flat sheet PSf membrane [14]. From T_g analysis, the membrane shows increased in rigidity should decreased the CO2 permeance while increased the gas pair selectivities. Interestingly, upon incorporation of ZIF-8/GO into PSf matrix, the CO_2 permeance shows dramatically increased (35%) while minor changes in gas pair selectivities. This is likely contributed by the porosity of ZIF-8/GO that provides permeation channels for all gases. Moreover, the intrinsic CO_2/CH_4 selectivity of pure ZIF-8 is normally less than 7 [15] and only minimal amount of GO incorporated to provides notable changes in the selectivity. Nevertheless, the inclusion of ZIF-8/GO into PSf matrix has beneficial towards the CO_2 permeance without compromising their selectivity.

Table 2 The glass transitional temperature and gas permeation properties of neat PSf and PSf/ZIF-8/GO

Sample	T_g (°C)	CO_2 Permeance (GPU)	$\alpha_{CO2/CH4}$	$\alpha_{CO2/N2}$
Pure PSf	180.1	59.0 ± 13.9	18 ± 3.9	23± 4.2
PSf/ZIF-8/GO	181.3	79.9 ± 18.3	18 ± 3.6	24± 4.6

4.0 CONCLUSION

The ZIF-8/GO composite has been successfully synthesized using aqueous room temperature system. The distortion of ZIF-8 crystal was observed through TEM due to competition on the active site as only minimal amount of GO was incorporated. The presence of ZIF-8/GO into PSf matrix has shown positive remarks on membrane performance. The porosity of ZIF-8/GO provides channel for gas permeation has resulting 35% increment of CO2 permeance without diminishing the gas pair selectivities. Thus, further studies of ZIF-8/GO as filler in MMM for gas separation, especially CO_2 separation, is warranted.

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