

# Metal-Organic Frameworks Grown on Porous Planar Template with Exceptionally High Surface Area: Promising Nanofiller Platforms for CO<sub>2</sub> Separation

Hyun Hee Lee<sup>†</sup>, Seul Chan Park<sup>†</sup>, Ji Soo Roh, Gi Hyeon Moon, Jae Eun Shin, Yong Soo Kang\*, and Ho Bum Park\*

Department of Energy Engineering, Hanyang University,

Seoul 04763, Republic of Korea

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## 1. Experimental procedures

**Materials.** Fine grade synthetic graphite powder (SP-1) was supplied by Bay Carbon Inc. (Bay City, MI, USA) and used as received. Sulphuric acid ( $\text{H}_2\text{SO}_4$ , 97%), hydrochloric acid (HCl, 35 % in water) and acetone ( $\text{CH}_3\text{COCH}_3$ , 99.5%) from Daejung Chemicals & Metals Co. (Siheung, Korea), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 50 % in water) and potassium permanganate ( $\text{KMnO}_4$ ) from Junsei Chemical Co. (Tokyo, Japan) were also used as received. Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ , 99.8%), methanol ( $\text{CH}_3\text{OH}$ , 99.8%), n-decane anhydrous ( $\text{CH}_3(\text{CH}_2)_8\text{CH}_3$ , > 99%) zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and 2-methylimidazole were purchased from Sigma-Aldrich and used without further purification. PEBAX<sup>®</sup>1657 (comprise 60 wt.% of PEO and 40 wt.% PA-6) were provided by Arkema Inc., and used as received.

**GO synthesis.** GO suspension was synthesized using the modified Hummers method.<sup>1, 2</sup> Sulphuric acid (450 mL) was added to graphite powder (10 g). The temperature of the solution was maintained at 5 °C and stirred for 60 minutes. A small amount (1.5 g) of potassium permanganate was added to the mixture and stirred for another 60 minutes. Then, a large amount of potassium permanganate (30 g) was added to the mixture and stirred for 30 minutes. In this step, the solution changed in color from black to dark green. The solution was heated to 40 °C and stirred for an hour. Deionized water (450 mL) was poured dropwise into the solution slowly to prevent a thermal explosion. In this step, the solution turned to dark brown. The solution was isothermed at 90 °C for 30 minutes, and diluted hydrogen peroxide solution (10 wt.%, 300 mL) was poured into the solution and stirred for 15 minutes. The color of the solution changed to light brown. Synthesized graphene oxide was purified with hydrochloric acid and acetone. The GO solution was filtered with glass micro fiber (Whatman<sup>™</sup>, UK) and washed with hydrochloric acid (10 wt.%, 3000 mL) for three times then with acetone (3000 mL) for three times. Filtered GO cakes were dried at 40 °C for 24 h under vacuum. After drying, synthesized GO powder was dispersed in deionized water at the concentration of 1.0 mg/mL (adjusted to pH 10.0 with 1 M NaOH 3.5 mL for 1 L solution) and bath sonicated for 1 hour followed by heavily sonicated with a tip sonicator (Sonics & Materials Inc., VC505, 500 W, 20 kHz) for 3 hours for better dispersion and reduced flake size.

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**Synthesis of porous graphene oxide (PGO).** PGO solution was readily prepared as follows. Diluted H<sub>2</sub>O<sub>2</sub> aqueous solution (3 wt.%) was added into the GO solution with 7.5:1 volume ratio. The mixture was vigorously stirred for 5 minutes and bath sonicated for 10 min. After that, the mixture was hydrothermally treated inside of an autoclave at 180 °C for 6 h and cooled down to room temperature at ambient conditions.

**Synthesis of the ZIF-8/PGO, ZIF-8/GO nanosheet and neat ZIF-8.** Synthesized PGO solution (0.882 mg/mL) was further diluted to 0.176 mg/mL by methanol, followed by 10 minutes of vigorous agitation. Two precursors of ZIF-8, Zn (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.366 g) and 2-methylimidazole (0.811 g) were dissolved in 15 and 20 mL of methanol, respectively. After mixing of two solutions, 5 mL of diluted PGO solution was immediately added into the mixture, followed by stirred for 5 hours to generate the complete ZIF-8 nanocrystals on the PGO planes. Finally, the mixture was washed by methanol 3 times by centrifuge and re-dispersed in the methanol solvent. ZIF-8/GO was synthesized through the same process with GO solution instead of PGO solution. Neat ZIF-8 nanocrystal was synthesized via the same process without PGO solution.

**Preparation of the mixed-matrix membrane.** PEBAX<sup>®</sup>1657 pellet was dissolved in mixed solvent (ethanol and DI water, 7:3 wt.) with 3 wt.% and stirred at 353 K for 5 hours. After cooling of the solution to room temperature, prepared-fillers (ZIF-8, ZGO, ZPGO) were added, then vigorously stirred for 10 minutes. After that, polymer/filler solutions were degassed for 30 minutes by bath sonication. The obtained solutions were poured into Teflon dishes and slowly dried at 298 K in the temperature-controlled oven for 2 days. After that, the samples were placed in the vacuum oven at 298 K for another 2 days to entirely evaporate the residual solvent.

**Characterization.** The morphologies of ZIF-8, ZIF-8/GO and ZIF-8/PGO were observed by tunneling electron microscope, TEM (JEM 2100F, JEOL, Japan). A drop of the methanol-diluted ZIF-8/PGO solution was dried on the holey carbon grid prior to the observation. Growth of ZIF-8 on GO and PGO was confirmed by Brunauer–Emmett–Teller (BET) pore size distribution and pore volume analyses performed at 77 K with nitrogen using 3Flex from micromeritics, USA and X-ray diffraction (XRD) patterns recorded on a spectrometer (D8

Advance, Bruker, Germany) fitted with a monochromated Al K $\alpha$ 1 X-ray source ( $\lambda = 1.5406$  Å) at 40 kV and 40mA (1.6 kW) at the scan rate of 1 degree/min. The chemical bonding and coordination of the additives (GO, PGO, ZIF-8, ZGO and ZPGO) were investigated with X-ray photoelectron spectroscopy, XPS. The analyses were performed using a ESCA system (XPS-theta probe, Thermo Fisher Scientific Co., USA) equipped with a monochromatic Al K $\alpha$  source (C correction: 284.5 eV). Concentration of prepared solutions and composition of each solute were calculated with the thermogravimetric analysis, TGA (Q500, TA instruments, USA), results. 5 drops of each solution was measured under the condition of a ramp of 5 °C/min to 800 °C after drying solvent at 70 °C isotherm for 30 minutes with N<sub>2</sub> flow. BET surface area was fit from nitrogen adsorption-desorption isotherms collected in the same condition while analysing pore size distribution. Dispersive property of each additive was confirmed by ultraviolet-visible spectroscopy, UV-vis (Specord 200, Analytik Jena, Germany), data measured at different solution concentration (5-50 µg/mL) and Beer's law.<sup>3</sup> Further dispersive property within the membrane and how additives affect membrane characteristic were analysed by differential scanning calorimetry, DSC (Q20, TA instruments, USA), from -80 °C to 300 °C at the heating rate of 10 °C/min. The density values of the fillers were determined by pycnometer method with the solvent of n-decane. The density values of the MMMs were determined by ASTM D792 method also with the solvent of n-decane. Specific affinity of prepared fillers for CO<sub>2</sub> at room temperature was also measured by BET test of CO<sub>2</sub> and N<sub>2</sub> at 298 K.

**Calculation of ZIF-8 and PGO composition in the solutions via TGA results.** Before measuring ZIF-8/GO and ZIF-8/PGO solution, powder state of each component, ZIF-8, GO and PGO, was measured with the same procedure. At 800 °C, after calcination, GO and PGO had been all burnt out and ZIF-8 crystals were turned into ZnO lost certain ratio of weight, which accords with previous works.<sup>4, 5</sup> For ZIF-8/GO and ZIF-8/PGO nanocomposite dispersion, firstly, as boiling point of the solvent, methanol, is 64.7 °C, filler's weight percentage in the solution was measure at 70 °C after drying. And the composition of ZIF-8 and PGO in the composite was calculated by the following equations.

$$M_{800^{\circ}C} = M_{ZnO} = M_{ZIF-8} \times \frac{MW_{ZnO}}{MW_{ZIF-8}}$$

$$M_{70^{\circ}C} - M_{ZIF-8} = M_{PGO(GO)}$$

$$Weight_{ZIF-8} \% + Weight_{PGO(GO)} \% = 100$$

Where  $M_{70^{\circ}\text{C}}$ ,  $M_{80^{\circ}\text{C}}$  are the weight of the sample at  $70^{\circ}\text{C}$  and  $80^{\circ}\text{C}$  respectively,  $M_{\text{ZnO}}$ ,  $M_{\text{PGO}}$  (or  $M_{\text{GO}}$ ) and  $M_{\text{ZIF-8}}$  are the weight of each species in the composite respectively.  $MW_{\text{ZIF-8}}$  and  $MW_{\text{ZnO}}$  are molecular weight of ZIF-8 ( $\text{C}_8\text{H}_{10}\text{N}_4\text{Zn}$ ) and ZnO (81.4 g/mol, 227.6 g/mol respectively) of the species, and  $\text{Weight}_{\text{ZIF-8}}\%$  and  $\text{Weight}_{\text{PGO}}\%$  are the weight percentages of ZIF-8 and PGO in the composites, respectively.

**Calculation of crystallinity of MMMs via DSC results.** Crystallinity was calculated by equation,

$$X_c = \frac{\Delta H_m}{\Delta H_m^0}$$

where  $\Delta H_m$  is the melting enthalpy calculated from the area of DSC melting peak and  $\Delta H_m^0$  is the melting enthalpy of the pure crystalline phase of PA, 230 J/g<sup>6</sup>. Crystallinity of polyethylene oxide (PEO) regions was omitted as the peak appeared below room temperature so that the value is not likely to represent membrane properties and peak showing  $T_g$  of PEO blocks too weak to be trusted. Glass transition temperature ( $T_g$ ) of PA segment was not shown.

**Calculation of fractional free volume (FFV) of MMMs.** FFV of MMMs was calculated by equation,<sup>7</sup>

$$FFV_{\text{MMM}} = FFV_{\text{polymer}} \cdot \varphi_{\text{polymer}} + FFV_{\text{filler}} \cdot \varphi_{\text{filler}} + FFV_{\text{air}} \cdot \varphi_{\text{air}}$$

where  $\varphi$  is fractional volume of each component and air stands for interfacial void between polymer and filler owing to their incompatibility.  $FFV_{\text{polymer}}$  was calculated by equation,<sup>8</sup>

$$FFV_{\text{polymer}} = 1 - 1.3 \vartheta_w \rho_{\text{polymer}}$$

where  $\rho_{\text{polymer}}$  is density of PEBAX<sup>®</sup>1657 measured by the buoyancy method and  $\vartheta_w$  is van der Waal's volume of the repeat unit of the PEBAX<sup>®</sup>1657 in  $\text{cm}^3\text{g}^{-1}$  ( $0.590 \text{ cm}^3\text{g}^{-1}$ <sup>9</sup>). FFV of fillers were calculated from pore volume ( $V_{\text{pore}}$ ) in  $\text{cm}^3/\text{g}$  and density ( $\rho_{\text{filler}}$ ) measured as follows,

$$FFV_{\text{filler}} = V_{\text{pore}} \cdot \rho_{\text{filler}}$$

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Next, fractional volume ratio was calculated by two equations,

$$\varphi_{polymer} + \varphi_{filler} + \varphi_{air} = 1$$

$$\rho_{MMM} = \rho_{polymer} \cdot \varphi_{polymer} + \rho_{filler} \cdot \varphi_{filler} + \rho_{air} \cdot \varphi_{air}$$

In addition, according to the free volume theory, FFV has a relation with D as follows,

$$\log D = A - \frac{B}{FFV}$$

**Gas permeation measurement.** The CO<sub>2</sub> and N<sub>2</sub> permeability of the prepared mixed matrix membranes were measured using a high-vacuum time-lag apparatus with a calibrated downstream volume of 80.93 cm<sup>3</sup>. The pressures at the upstream and downstream were measured using Baratron 626B pressure transducers (MKS Instruments Corp., MA, USA) with a full-scale of 1000 Torr and 10 Torr, respectively. The permeation measurements were performed at 35°C. The membrane films were used as they are without masking. Effective area of the membrane was 13.8 cm<sup>2</sup> and the upstream pressure was maintained at 3 atm. The linear slope of the pressure increases at the downstream as a function of time represented the gas permeation rate. The permeability coefficient was determined by the following equation:

$$P = \frac{dp}{dt} \left( \frac{VT_0 l}{p_0 T \Delta p A} \right)$$

where  $P$  (Barrer) is the gas permeability,  $V$  (cm<sup>3</sup>) is the downstream volume,  $l$  (cm) is the membrane thickness,  $\Delta p$  (cmHg) is the pressure difference between upstream and downstream,  $T$  (K) is the measurement temperature,  $A$  (cm<sup>2</sup>) is the effective membrane area,  $p_0$  and  $T_0$  are the standard pressure and temperature, respectively, and  $dp/dt$  is the pressure increase rate at steady state. The ideal selectivity of two components is defined as the ratio of the measured gas permeability value:

$$\alpha = \frac{P_1}{P_2}$$

where  $P_1$  and  $P_2$  represent the permeability of each species, respectively.

The mixed gas permeation properties of the same MMMs were measured by constant-pressure variable-volume method using cross flow cell. The mixture of CO<sub>2</sub> and N<sub>2</sub> (50:50) was purchased from Seoul Specialty Gases Co., LTD and used as received. Conditions such

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as transmembrane pressure, temperature and effective area were the same as the single gas permeability test and stage cut was controlled below 1% by retentate flow. To study plasticization effect, the same measurement was carried out under the transmembrane pressure from 1bar to 10 bar. Retentate flow was measured by Agilent ADM 2000 flow meter and permeate flow was measured by bubble flow meter. The composition of permeate flow was detected by Agilent 7890A gas chromatography.

**Gas sorption measurement.** The gas sorption of CO<sub>2</sub> and N<sub>2</sub> was measured by a pressure decay method with a dual volume, dual transducer sorption apparatus<sup>10, 11</sup> at pressures from 1 to 10 bars. The sorption measurement apparatus was located in a temperature-controllable water bath at 35 °C. There were two chambers in the sorption apparatus, a sample container and a reference volume, which were separated by a valve. The volumes of the chambers were carefully calibrated using the Burnett method.<sup>10, 12</sup> The pressure change during the sorption measurement was monitored by a pressure transducer from Delta Metrics (Worthington, OH, USA) with a full-scale of 1000 psia and an accuracy of 0.05%. Sorption measurements were performed on films. Approximately 1.0 g to 1.5 g of membrane coupons were placed in the sample chamber, which was then sealed with a VCR gasket. The sorption apparatus was placed in a constant temperature water bath at 35 °C. The sorption system was degassed for at least 12 hours to remove any dissolved gas molecules in the polymer matrix under vacuum condition. Afterwards, the valve between the sample and charge volumes was closed, and the desired amount of gas was charged into the reference volume. From the pressure transducer attached to the charge volume, along with the known charge cell volume and temperature, the Soave-Redlich-Kwong (SRK) equation of state was used to estimate the number of moles of gas in the charge volume, using critical parameters from Smith et al.<sup>13</sup> The valve was then opened and closed, released gas was injected into the sample container, initiating sorption into the polymer matrix. Pressure decay occurred at a level equal to the gas sorption. Using the SRK equation of state, a mole balance was established between the initial and equilibrium conditions of the sample chamber so that the number of moles of gas which sorbed into the polymer film was calculated once the chamber pressure was constant.<sup>10</sup> Equilibrium was achieved in few minutes to several hours depending on the gas species and samples. Following equilibrium, the charge volume was pressurized again, gas was released into the sample chamber, and the sorption measurement was repeated. This process was continued

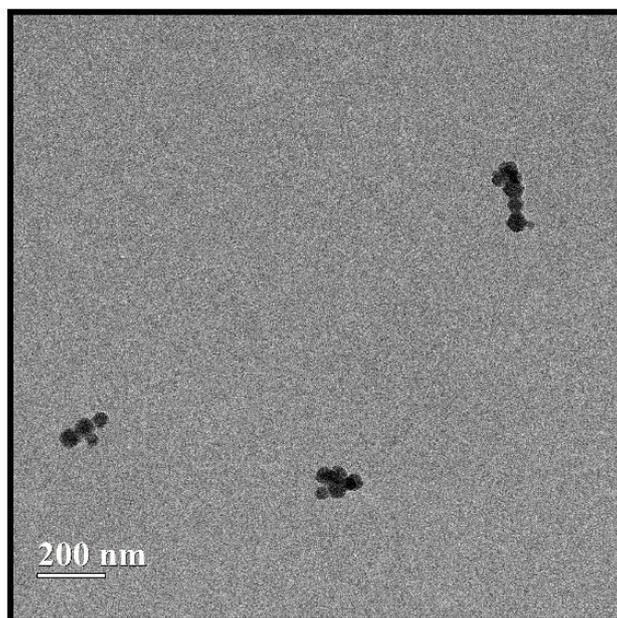
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until the pressure reached approximately 10 bars and the sorption isotherm was obtained. For each sample tested, sorption isotherms were determined as a function of increasing pressure and in the order of N<sub>2</sub> and CO<sub>2</sub>. As PEBAX<sup>®</sup>1657 is amorphous polymer, its sorption is mainly governed by Henry's law. The apparent solubility coefficient is defined as the concentration term,  $C$ , divided by pressure,  $p$ , as is shown in following equation:<sup>14, 15</sup>

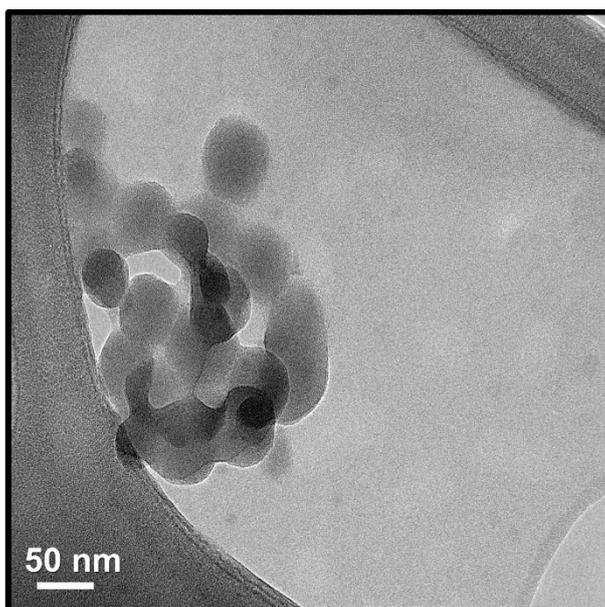
$$S(p) = \frac{C}{p}$$

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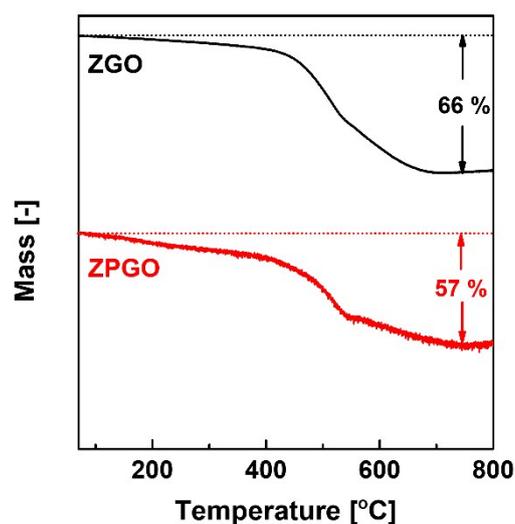
## 2. Characteristics of the composites



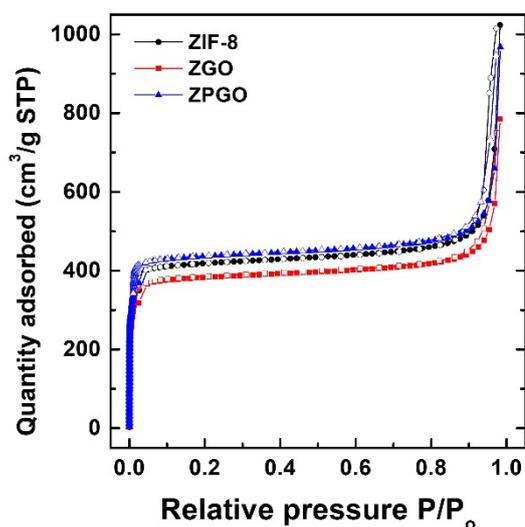
**Figure S1.** TEM image of neat ZIF-8 nanocrystals grown without a template



**Figure S2.** TEM image of ZGO



**Figure S3.** Thermal gravimetric analysis (TGA) spectra of ZGO and ZPGO. As GO is burnt off and ZIF-8 is calcinated to ZnO at 800 °C, ZIF-8 mass was calculated by multiplying residue at 800 °C and 2.796, molecular weight ratio of ZIF-8 to ZnO and GO mass was calculated by subtracting ZIF-8 mass from whole composite mass before calcination.

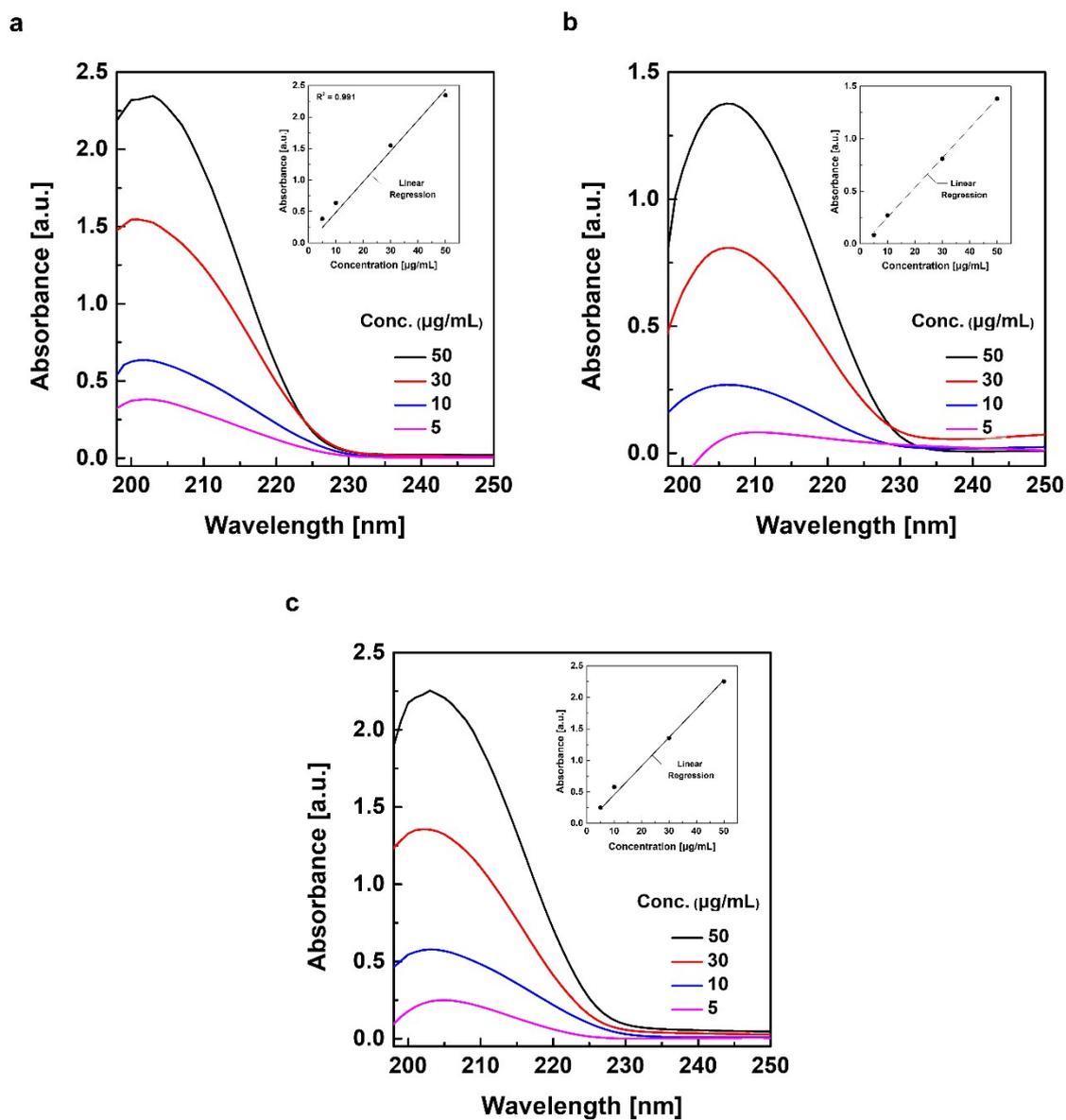


**Figure S4.** Nitrogen adsorption-desorption isotherms of neat ZIF-8, ZGO and ZPGO at 77K. Open symbol is desorption and filled symbol is adsorption data.

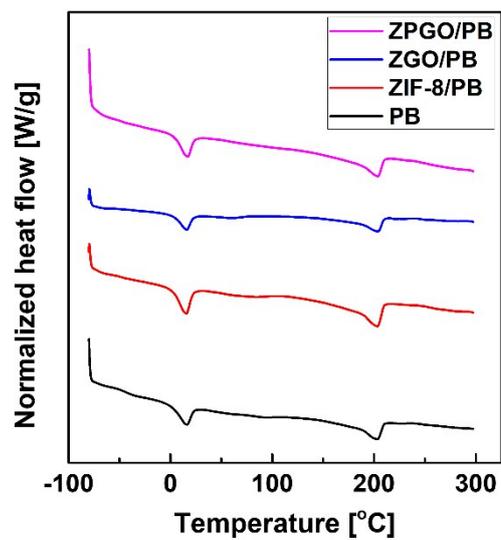
**Table S1.** Comparison of the BET surface area of ZPGO with other recent literatures

Material	BET surface area (m <sup>2</sup> /g)	Application	Reference
HFGO/ZIF-8	590	Oil-water separation	<i>Angew. Chem. Int. Ed.</i> , 2016, <b>55</b> , 1178 <sup>16</sup>
GO/ZIF-8	819	CO <sub>2</sub> capture	<i>Chem. Commun.</i> , 2013, <b>49</b> , 4947 <sup>17</sup>
rGO/ZIF-8	720	CO <sub>2</sub> capture	<i>J. Mater. Chem. A</i> , 2016, <b>4</b> , 7710 <sup>18</sup>
GO/CTF-1	791	H <sub>2</sub> /CO <sub>2</sub> separation	<i>J. Mater. Chem. A</i> , 2016, <b>4</b> , 13444 <sup>19</sup>
MgCGR-2	1474	CO <sub>2</sub> capture	<i>Angew. Chem. Int. Ed.</i> , 2016, <b>55</b> , 1 <sup>20</sup>
GO/MOF-5	806	Gas adsorption	<i>Adv. Mater.</i> 2009, <b>21</b> , 4753 <sup>21</sup>
CNT-MIL	651	CO <sub>2</sub> /N <sub>2</sub> separation	<i>ACS Appl. Mater. Interfaces</i> , 2015, <b>7</b> , 14750 <sup>22</sup>
CNT/ZIF-8	1124	C <sub>3</sub> H <sub>6</sub> /C <sub>3</sub> H <sub>8</sub> separation	<i>J. Mater. Chem. A</i> , 2016, <b>4</b> , 6084 <sup>23</sup>
PGO/ZIF-8 (ZPGO)	2170	CO <sub>2</sub> /N <sub>2</sub> separation	This work

### 3. Characteristics of the mixed matrix membranes

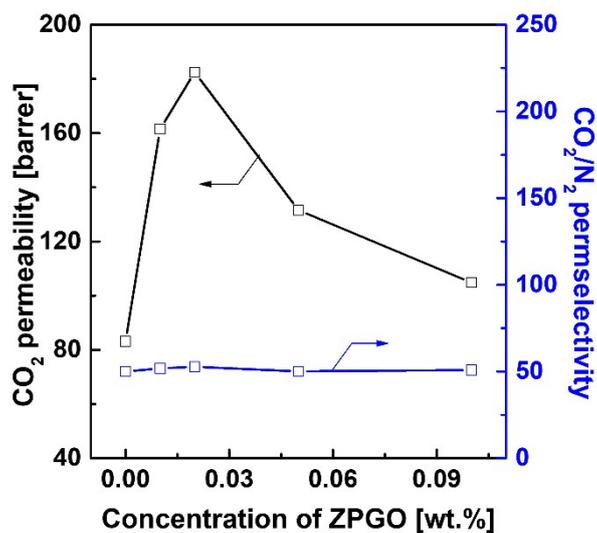


**Figure S5.** UV-vis spectra of (A) ZIF-8, (B) ZGO and (C) ZPGO dispersed in the MMM solvent (7:3 of EtOH/H<sub>2</sub>O, w/w)

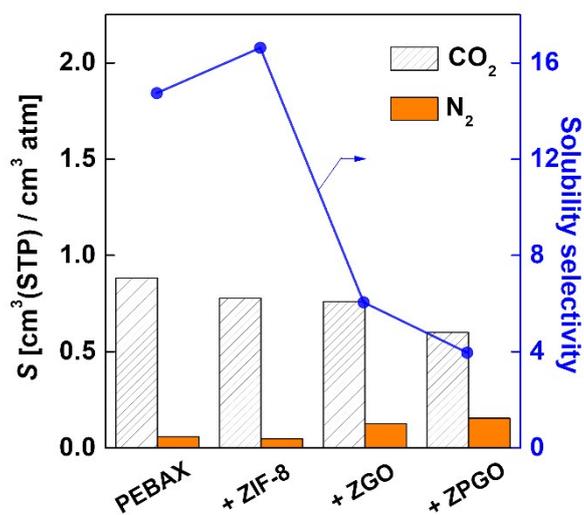


**Figure S6.** Differential scanning calorimeter (DSC) spectra of developed MMMs

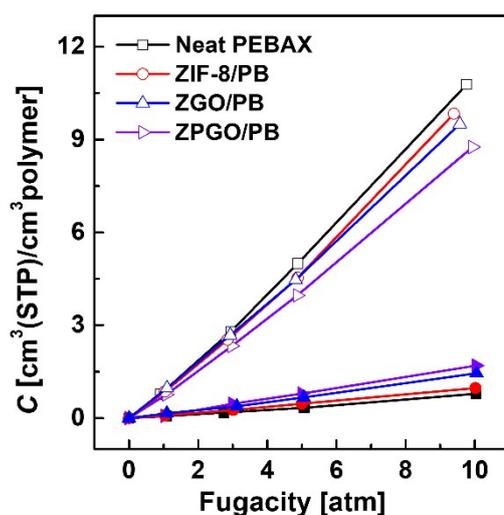
#### 4. Gas transport properties of the mixed matrix membranes



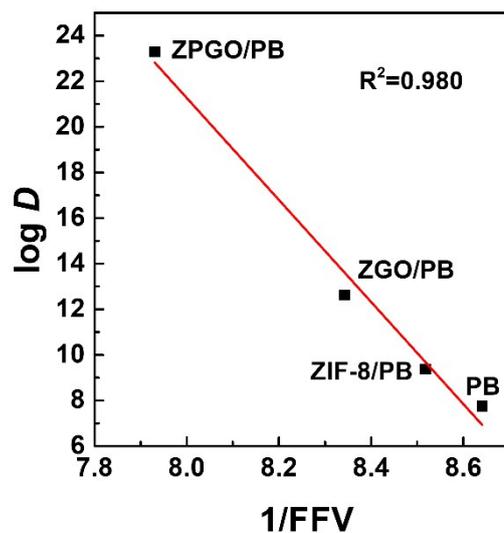
**Figure S7.** CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> permselectivity of ZPGO incorporated MMM at various concentrations



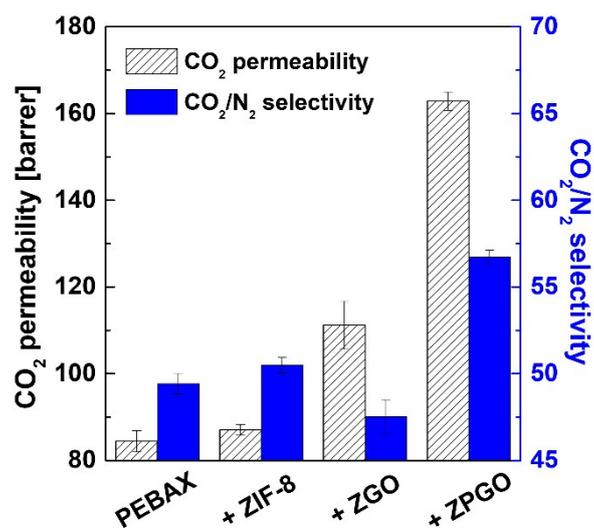
**Figure S8.** CO<sub>2</sub> and N<sub>2</sub> solubility coefficient and selectivity of prepared MMMs.



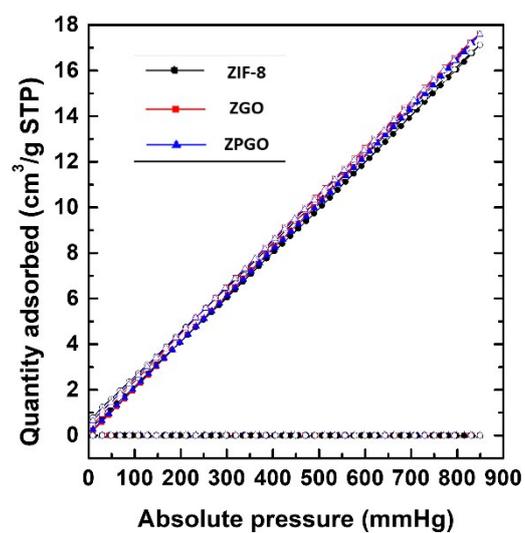
**Figure S9.** CO<sub>2</sub> and N<sub>2</sub> sorption isotherms of prepared MMMs from 1 to 10 atm. Incorporated filler concentration of MMMs was fixed at 0.02 wt.%. All sorption tests were performed at 35 °C. Open symbol is CO<sub>2</sub> and filled symbol is N<sub>2</sub>



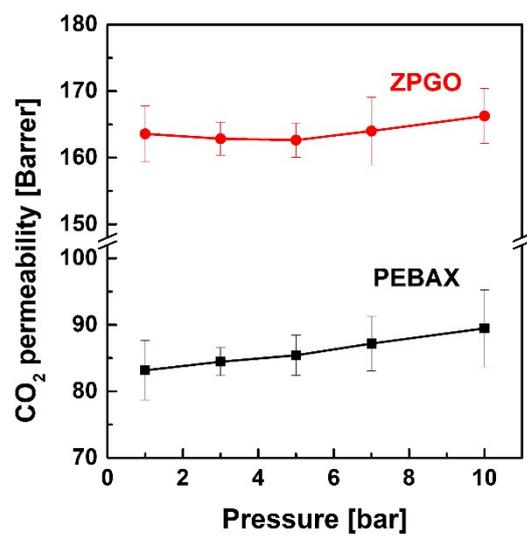
**Figure S10.** The linear relationship between logarithmic diffusivity and reversed fractional free volume of MMMs.



**Figure S11.** Mixed gas separation performance of MMMs.



**Figure S12.** BET tests of CO<sub>2</sub> (linear upwards line) and N<sub>2</sub> (~o) at 298 K. Open symbol is desorption and filled symbol is adsorption data.



**Figure S13.** CO<sub>2</sub> permeability under mixed gas condition (50:50) of ZPGO/PB and PB as a function of transmembrane pressure.

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