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COF membranes with uniform and exchangeable facilitated transport carriers for efficient carbon capture

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Materials

Natural graphite flake (10000 mesh) was purchased from Qingdao Tianhe Graphite Co. Ltd. (Shandong, China). Potassium permanganate (KMnO₄), concentrated sulfuric acid (H₂SO₄, 98 wt%), and hydrochloric acid (HCl) were obtained from Tianjin Jiangtian Chemical Technology Co., Ltd. (Tianjin, China). Sodium nitrate (NaNO₃), acetone, N, N-dimethylacetamide and hydrogen peroxide aqueous solution (H₂O₂, 30 wt%), were received from Tianjin Jiangtian Chemical Technology Co., Ltd. (Tianjin, China). 1,3,5-Triformylphloroglucinol (Tp) and triaminoguanidinium chloride (TG_{Cl}) were purchased from Yanshen Technology Co., Ltd (Jilin, China). Polyacrylonitrile (PAN) substrates with a molecular weight cut-off of 100,000 were bought from Shandong Megavision Membrane Engineering and Technology Co., Ltd (Shandong, China). All the chemical reagents were of analytical grade and used as received.

Synthesis procedures

Synthesis of GO nanosheets

Graphene oxide (GO) nanosheets were synthesized according to the modified Hummers' method, and the procedure refers to our previous reported.^{1, 2} A certain amount of graphite powder and NaNO₃ was added to 115 mL 98 wt% H₂SO₄ and cooled in an ice bath. Afterwards, 15 g KMnO₄ was slowly added to the mixture. After being stirred for 2 h, the mixture was further stirred for 2 h at 35 °C. Then, 230 mL deionized water was slowly added to the flask, ensuring the temperature was below 100 °C. Then maintain it at 98 °C for 3 h to ensure the graphite was highly oxidized. The mixture was then diluted by slowly adding it to 1 L deionized water. After that, H_2O_2 was added to remove the residual KMnO₄ and MnO₂. The mixture was then filtered and washed with 500 mL HCl (0.5 M). Finally, a yellow–brown GO aqueous dispersion was obtained by centrifuging at 8000 rpm to remove incompletely exfoliated graphite.

Synthesis of cationic COF TpTG_{Cl}

TpTG_{Cl} was synthesized via Schiff-base condensation between 0.2 mmol Tp (42 mg) and 0.2 mmol TG_{Cl} (28 mg) in a sealed Pyrex tube.³ The mixtures (dioxane: water=2: 0.6 mL) were charged into the Pyrex tube and sonicated for 20 min. The mixtures were degassed under liquid N₂ (77 K) by three freeze-pump-thaw cycles. The Pyrex tube was then vacuum-sealed and kept at room temperature until the reaction mixtures attended the room temperature. The sealed Pyrex tube containing the reaction mixture was kept at 120 °C for 3 days. The bulk TpTG_{Cl} was obtained as a brown-colored precipitate. The product was washed thoroughly with N, N-dimethylacetamide, water, and acetone respectively and dried at 90 °C for 24 h under vacuum to obtain the final TpTG_{Cl}. The products were then dispersed into deionized water to obtain a suspension of TpTG_{Cl} nanosheets

Preparation of cationic COF TpTG_B

 $TpTG_B$ was synthesized via a two-step ion-exchange process. Firstly, 30 mg prepared $TpTGc_1$ powder was dispersed in 60 mL 2% dilute ammonia solution and stirred vigorously at room temperature for 8 h. Then, the suspension was centrifuged

at 10000 rpm for 10 min to obtain the TpTG_{OH} nanosheets solution. Secondly, the obtained TpTG_{OH} was dispersed in 60 mL boric acid solution of 0.1 mol/L and stirred vigorously at room temperature for 12h. Then, the suspension was centrifuged at 5000 rpm for 10 min and the supernatant was collected for further centrifuged at 10000 rpm to obtain the precipitation of TpTG_B nanosheets. The obtained TpTG_B nanosheets were washed several times by deionized water after dispersing in water to obtain TpTG_B nanosheets dispersion with a concentration of about 0.015 mg/mL.

Preparation of COF membranes

COF membranes were synthesized by vacuum-assisted self-assembly method with a TpTG_B/GO nanosheets mass ratio of 15:0, 15:0.5 15:1, 15:2, 15:5 on a polyacrylonitrile (PAN) substrate. Then, the fresh membranes were treated in a vacuum oven at 45 °C for 12 h before testing. The control membranes were also prepared according to the above method. To eliminate the influence of thickness on the performance of the control experiment, the control membranes and other test membranes were kept with similar solid content.

Characterization of materials and membranes

The surface charge properties and dispersibility of $TpTG_B$ and GO nanosheets were measured by Malvern zetasizer Nano-ZS instrument with a 4 mW He-Ne laser. The morphology of $TpTG_B$ and GO nanosheets were obtained by a transmission electron microscope (TEM, JEM-2100F). The atomic force microscopy (AFM) images of $TpTG_B$ and GO nanosheets were obtained by a multifunctional scanning probe microscope (NTEGRA Spectra). The N₂ adsorption-desorption isotherms at 77 K were measured by BELsorp-Max apparatus, the surface area, and the distribution of pore size of COFs powder were calculated by Brunauer-Emmett-Teller (BET) and Nonlocal-Density-Functional-Theory (NLDFT) methods. Before measurement, the sample was degassed at 423 K overnight and tested at 303 K. The chemical analyses of samples were performed by Fourier transform infrared spectroscopy (FT-IR, BRUKER Vertex 70) with a range of 4000-400 cm⁻¹. The morphologies of membranes were characterized by a field emission scanning electron microscope (SEM Nanosem 430). The X-ray diffraction (XRD) was employed to characterize the interlayer d-spacing of stacked nanosheets by a MiniFlex600 X-ray diffractometer (CuK α) at a speed of 5°/min. The gas permeation experiments were carried out at humidified state. In order to better exhibit the interlayer d-spacing during the test, we conducted the XRD tests at humidified state. The membranes were first put in a relative humidified state of 85% for 2 h to ensure sufficient hydration, and then were placed in the apparatus for subsequent measurements.

Gas permeation experiments

The gas separation performances of COF membranes were evaluated by homemade apparatus with a constant pressure/variable volume method.^{4, 5} Mixed CO₂/CH₄ (30/70 vol%) was employed as the testing gas and N₂ as the sweep gas. The permeation experiments were conducted under a humidified state (the relative humidity is about 85%), at 30 °C and a feed pressure of 2 bar. The sweep gas flow rate was controlled by a mass flowmeter and fixed at 30 mL (STP) min⁻¹. The

compositions of the feed and permeate gas were analyzed by an in-line gas chromatograph (Agilent 6820). The gas permeance is obtained using the following equation:

$$\left(\frac{P}{l}\right)_{i} = \frac{Q_{i}}{\Delta p_{i}A} \tag{1}$$

$$\alpha_{ij} = \frac{\left(\frac{P}{l}\right)_i}{\left(\frac{P}{l}\right)_j} \tag{2}$$

Where (P/l) refers to the gas permeance (GPU, 1 GPU=10⁻⁶ cm³ (STP)/(cm²·s·cmHg), Q_i (cm³/s, STP) is the volume flow rate of "*i*", ΔP_i (cmHg) is the partial pressure difference across the membrane, A (cm²) represents the membrane area (3.1 cm² in this study). The subscript "*i*" and "*j*" refers to different gases. The gas separation performances of membranes were calculated from the average value of at least three separate tests for different membranes.



Fig. S1. The XPS pattern of $TpTG_B$ powder (a) and (b).

Table 1. The XPS results of the $TpTG_B$ powder.

Samula	Elements (at. %)					
Sample	С	0	Ν	В	Cl	
TpTG _B	57.97	18.27	23.55	0.16	0.05	



Fig. S2. Solid-state ¹³C NMR of TpTG_{Cl}.

The sharp peak at ~100 ppm signified the exocyclic C=C carbon adjacent to the C=O carbon. The peak at 150 ppm, representing C=C carbon attached to the N. Carbon signal of guanidinium C=N appeared at ~162 ppm, and a small keto (-C=O) carbon signal was noted in between 180 and 182 ppm. The sharp signal of exocyclic double is the strong evidence of irreversible enol to keto tautomerism in TpTG_{CI}.



Fig. S3. The top-view SEM of (a) TpTG_B-GO (2)/PAN, (b) TpTG_B-GO (5)/PAN.



Fig. S4. The cross-section SEM of TpTGB-GO (1)/PAN.



Fig. S5. Digital photographs of (a) AAO, (b) AAO@ PDA, (c) AAO@PDA.

AAO substrates were modified before preparing membranes using dopamine according to the literature.⁶ Dopamine (2 mg/mL) was dissolved in 10 mM Tris–HCl (pH, 8.5) in a glass garden (diameter, 60 mm). Then the AAO substrate membrane

(Fig. S5(a)) was placed at the bottom of the dish and treated with dopamine at 20 °C for 20 h, leading to the PDA layer deposited on the support surface (AAO@PDA, Fig. S5(b)). When a certain amount of nanosheets were deposited on AAO@PDA substrate, the $TpTG_B$ -GO membranes (Fig. S5(c)) were successfully prepared.



Fig. S6. Comparison of the thickness of COF membranes with literatures. Detailed data are

listed in Table S2.

Table S2. The detailed comparison of the thickness, methods, factors for different COF

membranes.

Membrane	Thickness(nm)	Method	Ref.	
ACOF-1	8000	8000 Solvothermal		
LDH-COF	2000	Solvothermal	8	
COE I 7U1 - ACOE 1	450	Temperature-swing	0	
COP-LZUT-ACOP-1	430	Solvothermal	9	
TpPa-1-GO	300	Vacuum-filtration	10	
CTF-1-GO	100	Vacuum-filtration	11	
TpEBr@TpPa-SO3Na	21	Layer-by-Layer	12	
TpTG _B -GO	20	Vacuum-filtration	This work	

Sample	B (at.%)	(P/l) _{CO2} (GPU)	$\alpha_{\rm CO2/CH4}$	The enhancement of selectivity	Ref
GO		105	16	1 69	4
B-GO	8.20	650	75	4.08	
$TpTG_{cl}$ -GO (1)		131.8	9.3	2 80	This work
$TpTG_{B}-GO(1)$	0.16	164.2	26.9	2.89	

 Table S3. The relationship between membrane performance improvement and element B

 content.



Fig. S7. The gas separation performance of TpTG_B-GO (1) membrane at humidified and dry

state.



Fig. S8. The influence of temperature on TpTG_B-GO (1) membrane performance for mixed gas

under humidified state.



Fig. S9. Single gases permeance of TpTGB-GO membranes at humidified.

framework membranes						
Membrane	P(atm)	T(°C)	$(P/l)_{CO2}(GPU)$	$\alpha_{\rm CO2/CH4}$	Ref	
HKUST-1	2	35	18100	1.2	13	
ZIF-90	4.4	35	325	1.44	14	
ZIF-7 ₂₂ -8	2	25	45.5	25	15	
Uio-66-NH ₂ /PIM-1	5	25	37.5	37	16	
GO-Borate	2	30	650	75	4	
GO-Borate(dry)	2	30	92.4	25.1	4	
GO	2	35	110	10	17	
GO-[BMIM][AC]	2	25	37	39	18	
GO-[BMIM][BF ₄]	2	25	60	30	18	
MXene-Borate/PEI	2.5	25	350	15.3	19	
ACOF-1	2	120	3.66	86.3	7	
COF-LZU1-ACOF-1	1	25	60	4.14	9	
$TpTG_B-GO(1)$	2	30	164.2	26.9	This	
$TpTG_{B}$ -GO (2)	2	30	80.1	30.54	1 MIS	
$TpTG_B$ -GO (5)	2	30	59.05	35.7	WUIK	

Table S4. Performance comparison of membranes in this work with some representative 2D,

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