Supporting Information

Two-step fabrication of COF membranes for efficient carbon capture

Yuhan Wang⁺, Junyi Zhao⁺, Sui Zhang, Zhiming Zhang, Ziting Zhu, Meidi Wang, Bohui Lyu, Guangwei He, Fusheng Pan^{*}, Zhongyi Jiang^{*}

Experimental Sections

Materials

2,3,6,7,10,11-Hexahydroxytriphenylene (HHTP; 95%), tetrafluorophthalonitrile (TFPN; 99%), N,N-dimethylformamide (DMF; 99.8%), 1,4-dioxane (99.7%), NH₂OH solution (50 wt.% in H₂O) were purchased from Meryer. Triethylamine (99.0%), tetrahydrofuran (THF; 99.9%) were purchased from Aladdin. Polyacrylonitrile (PAN) substrates were supplied by Shandong Megavision Membrane Engineering and Technology Co., Ltd. (Shandong, China). All chemicals were purchased through commercial suppliers and used without further purification.

Synthesis of COF-316 powder

COF-316 powder was synthesized following the previously reported methods.¹ Briefly, 2,3,6,7,10,11-Hexahydroxytriphenylene (HHTP, 0.1856 mmol, 60 mg) and tetrafluorophthalonitrile (TFPN, 0.276 mmol, 55.2 mg) were dissolved in 4 mL 1,4-dioxane and 156 μ L triethylamine. The mixture was charged into a Pyrex tube and sonicated for 3min. Then the mixture was sealed under vacuum after degassed by two freeze-pump-thaw cycles. Subsequently, the sealed Pyrex tube was kept at 120°C for 3 days. The resulting brown powder was washed thoroughly by Soxhlet extraction with THF and acetone, and further dried under evacuation to obtain purified COF-316 powder.

Synthesis of COF-316 nanosheets

Carboxyl group modified PAN membranes were first cut into coupons with a diameter of 3.2 cm and placed between a homemade diffusion cell with an inner diameter of 3 cm. 2,3,6,7,10,11-Hexahydroxytriphenylene (HHTP, 0.046 mmol) and triethylamine catalyst (3.0 eq.) were dissolved in the aqueous phase and tetrafluorophthalonitrile (TFPN, 0.069 mmol) was dissolved in the organic phase. Subsequently, the diffusion cell was fixed at 80°C. After reaction for 3 days, COF nanosheets were synthesized in the aqueous phase which could be easily removed using a dropper. The resulting nanosheets colloidal dispersion were dialyzed in DI water for 3 days.

Synthesis of COF-316-COOH nanosheets

A 50-mL round bottom flask equipped with a condenser was charged with as-prepared COF-316 nanosheets (20.0 ml, 0.7 mg/ml), 20% NaOH solution (H₂O:ethanol = 1:1, 15.0 ml). The mixture was stirred and heated to 120°C reflux for 3 days. Then the mixture was cooled to room temperature for dialysis in 1M HCl for 2 hours.

Synthesis of COF-316-AO nanosheets

A 50-mL round bottom flask equipped with a condenser was charged with as-prepared COF-316 nanosheets (20.0 ml, 0.7 mg/ml), Anhydrous THF (10.0 mL), NH₂OH solution (50 wt.% in H₂O) (5.0 mL). The mixture was stirred and heated to 90°C reflux for 3 days. Then the mixture was cooled to room temperature for dialysis in DI water for 1 day.

Preparation of the COF membranes

The PAN substrates were immersed in DI water to remove residues in the pores. The aqueous COF nanosheet suspension was sonicated for 15 min and then vacuum-filtered onto PAN substrates with the pressure of 0.4 bar. The thickness of COF membrane could be tuned by varying the volume of filtrate. The membranes were dried at room temperature for 12 h. COF membranes were also prepared on alumina or AAO flat substrates via hot-drop coating method.

Characterization

Morphologies of the synthesized COF nanosheets and COF membranes were carried out by a Regulus 8100 instrument. TEM, HR TEM, and electron diffraction were examined by JEOL JEM-F200 electron microscope. XRD curves were collected by a Smartlab instrument with Cu Kα radiation. AFM images were acquired on a Bruker Dimension Icon atomic force microscopy. Zeta potentials were taken from a Nano ZS instrument with a 4 mW He-Ne laser. FT-IR patterns were token from Thermo Scientific Nicolet iS50. WACs were measured by POWEREACH JC2000D2M static contact angle goniometer. TGA curves were recorded on a Netzsch TG209 from 40 to 800 °C with a heating rate of 10 °C min⁻¹ in N₂ atmosphere. as sorption isotherms were measured at gas adsorption instrument (Belsorp-Max apparatus). The surface area and pore size distribution were calculated by GCMC method. Qartz crystal microbalance (QCM, Q-sense E1, Biolin Scientific) was used to record the water-capture ability which was calculated by the modified Sauerbrey Equation (1):

$$\Delta m = -\Delta f \frac{\sqrt{\rho_q \mu_q}}{2f_0^2} \quad (1)$$

where Δm is the mass change on sensor surface ($\mu g \text{ cm}^{-2}$); Δf is the frequency change (Hz); f_0 is the resonant frequency of the sensor (Hz); ρ_q and μ_q is intrinsic parameters of quartz crystal: density ($\mu g \text{ cm}^{-3}$) and shear modulus ($\mu g \text{ cm}^{-1} \text{ s}^{-2}$).

Simulation analysis

Atomic models

Atomic models of COFs with AA stacking were constructed and optimized using Materials Studio, with the adoption of Dreiding force field² to mimic dispersive interactions and the utilization of the charge equilibration (Qeq) method³ to approximate atomic charges. The subsequent optimization of the unit cell of each COF was carried out using the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional implemented in Vienna Ab initio Simulation Package (VASP).⁴ The atomic charges were estimated by the Density Derived Electrostatic and Chemical (DDEC) method, based on the electrostatic potentials obtained from the VASP calculations.⁵

Electrostatic potential maps (EPM)

The sequence of charge distribution of COFs was revealed by EPM. EPM illustrated the electrostatic potential energy according to distributions of nucleus and electrons. Electron density maps with electrostatic potentials were calculated at the same level for the three optimized structures.

Gas adsorption

GCMC simulations were carried out to compute the adsorption of CO₂ for 3 COFs. A Lennard-Jones (LJ) plus Coulomb potential was used to describe the nonbonded interactions between atoms in the framework and the adsorbates. LJ parameters for the framework atoms were taken from the Dreiding force field.² The TraPPE force field⁶ was used to model CO₂. LJ parameters between different atom types were calculated using the Lorentz-Berthelot mixing rules. LJ interactions were cutoff at 12 Å, and each simulation cell was replicated in all directions to obey the minimum image convection with respect to this cutoff value. The long-range electrostatic interactions arising from the presence of atomic partial charges were summed using the method of Ewald⁷. All atoms in the COFs were held fixed during the simulations. Ten thousand Monte Carlo cycles were performed to compute the adsorption properties of both binary and ternary mixtures. The first 50% of the cycles were spent on the equilibration, and the remaining cycles were used to compute the ensemble averages of properties of the system. For a cycle, N Monte Carlo moves were performed, selected from insertion, deletion, translation, rotation, and identity change of molecules with equal probability, where N is the number of adsorbates in the simulation box at the beginning of the cycle. If the system contains less than 20 adsorbates, 20 Monte Carlo moves were carried out for that cycle. All GCMC simulations were carried out using the RASPA simulation code.⁸

Gas diffusion

MD simulations were used to gain theoretical insights into the CO₂ molecules' permeation through COF channels. In each simulation, 32 CO₂ molecules at a density of 0.002 g/cm3 were placed in feed box. Dynamic task with an NPT (constant particle number, pressure and temperature) simulation was performed with temperature at 298.0 K, pressure at 0.4 bar and time step of 1.0 fs. The simulated feed box was placed on the left side of COF membranes along the z direction. And the vacuum

chamber was placed at the other side of the COF membranes as the permeate side. The dimensions of boxs in the x-y direction were 74.31×74.31 Å², 74.06×74.06 Å², 74.06×74.06 Å², for COF 316-CN, COF 316-COOH, COF 316-AO, respectively. And the z length of simulation box was around 520 Å. Periodic boundary conditions were applied. The COF nanosheets were modelled by the Universal force field with Use current charge. In the diffusion simulations, the system was subjected to an energy minimization using the smart minimizer method which switched from steepest descent to conjugated gradient and then to the Newton method as the energy derivatives decreased to accelerate the computation. Then, a NVT (constant particle number, volume and temperature) simulation was performed with a time step of 1 fs. The Berendsen thermostat was used to maintain a temperature of 298.0 K with decay constant at 0.1 ps. The atoms of the COF nanosheet skeletons (C atoms) were frozen in the simulations. During the simulations, CO₂ molecules would pass through the channels of the COF membrane to the permeate chamber along the z direction, driven by the concentration gradient.

Gas separation performance test

The permeation experiments were conducted based on the Wicke–Kallenbach method, with CO_2/N_2 (20 vol%:80 vol%) as the binary mixed gas. The gas composition determined by gas chromatography (Agilent 7820B). The feed and sweep gas were humidified by the humidification tanks at 40 °C. During the performance test, the pressure on the upstream side was 2 bar and the sweep gas pressure on the downstream side was 1 bar.

The gas permeance (P, 1 GPU = 10^{-6} cm³ (STP) cm⁻² s⁻¹ cmHg⁻¹) and selectivity (S) were calculated using equation (1) and (2):

$$\mathbf{P} = \frac{Q}{\Delta \mathbf{p}^* \mathbf{A}} \tag{1}$$

$$S_{i/j} = P_i/P_j \tag{2}$$

where Q is the volumetric flow rate of gas i, L is the membrane thickness (cm), Δp is the partial pressure difference of gas across the membrane (bar), A is the effective membrane area (cm²).



Figure S1. SEM images of COF powders synthesized by solvothermal methods. a) COF-316-CN, b) COF-316-AO and c) COF-316-COOH.



Figure S2. Homemade diffusion cell used for the preparation of COF-316 nanosheets.



Figure S3. XRD patterns of supported COF-316@HPAN membrane.



Figure S4. AFM images with height profiles alone the white lines of a) COF-316-CN nanosheets, b) COF-316-COOH nanosheets, and c) COF-316-AO nanosheets.



Figure S5. (a) XRD pattern of multi-layer stacking and (b) TGA curves.



Figure S6. Simulation snapshots of CO₂ molecules adsorption within a) COF-316-CN pores, b) COF-316-COOH pores, and c) COF-316-AO pores.



Figure S7. ATR-IR of PAN membranes (black line), COF-316-CN membranes (red line), COF-316-COOH membranes (yellow line), and COF-316-AO membranes (indigo line).



Figure S8. Simulation snapshots of CO₂ molecules transporting through the a) COF-316 channels, b) COF-316-COOH, and c) COF-316-AO channels at 0 ps and 500 ps.



Figure S9. FT-IR of COF-316-AO membrane before and after test.



Figure S10. XPS spectra of COF-316-AO membrane before and after test



Figure S11. FT-IR spectra of a) COF-318 with starting materials, b) COF-318 before and after conversion. The new N–H and N-O stretching appeared in COF-318-AO.



Figure S12. FT-IR spectra of a) COF-TpDb with starting materials, b) COF-TpDb before and after conversion. The new N–H and N-O stretching appeared in COF-TpDb-AO.



Figure S13. a) XRD patterns of the COF-318 and COF-318-AO powders, b)XRD patterns of the TpDb and TpDb-AO powders, the peak disappeared owing to the destroy of framework structures.



Figure S14. Optical images and surface SEM images of the membranes for depositing nanosheets on different substrates. a) α -Al₂O₃, b) AAO substrate, and c) ITO substrate.

Membrane materials		CO ₂ permeance (GPU)	CO ₂ /N ₂ selectivity	Reference
Representative polymers	pebax	287	34	9
	pebax	916	33	10
	pebax	417	22	11
	cap-ufc	1210	22	12
	PDMS	1200	53	13
	PVAm	483	65	14
MOF	ZIF-69	308.8	6.3	15
	PDA/UiO-66	1115	51.6	16
	ZIF-8	22	52	17
	ZIF-8@CA	24.2	168.8	18
	CAU-1	4000	22.8	19
	CAU-1	2388	14.8	20
	MIL-125	372	38.7	21
	HKUST-1	270	14.32	22
	Ni ₃ (HITP) ₂	4770	10.2	23
	Cu(dhbc) ₂ (bpy)	1143.9	28.6	24
COF	PEI-COF	1300	35	25
	COF	558.7	69.5	26
		370.7	79.8	
		242	107.1	
2D materials	MoS ₂ SILM	47.88	131.42	27
	WS ₂ SILM	47.3	153.21	28
	M SILM	80	87	29
	BN SMILM	20.3	90	30

Table S1. Summary of CO₂/N₂ separation performance

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