Supporting materials for

Enhancing CO$_2$ separation performance of composite membrane by incorporation of amino acid-functionalized graphene oxide

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1. Experimental

1.1 Preparation of amino acid-functionalized graphene oxide nanosheets

Pristine graphene oxide was prepared by Hummers method as reported.[1] In a typical reaction, 5 g of graphite powder and 2.5 g of NaNO$_3$ were added to 115 mL of 98 wt % H$_2$SO$_4$ at 0 °C. Then 15 g of KMnO$_4$ was added in batches to keep the temperature under 5 °C. After stirring for 2 h, the mixture was transferred into oil bath at 35±2 °C and stirred for 30 min. A 230 mL portion of water was added into the mixture gradually to keep the temperature below 100 °C. Afterwards the temperature was raised to 98 °C and kept for 3 h in order to improve the oxidation degree of graphite oxide product. Followed by adding 20 mL of H$_2$O$_2$, the resulting viscous mud was diluted. Then the mixture was centrifuged and washed with water several times, and the concentrate was diluted and sonicated for 1 h. Finally, the yellow-brown GO aqueous dispersion was obtained by centrifuging at 10500 rpm to remove the large and not fully exfoliated parts. For amino-acid functionalized graphene oxide nanosheets, dopamine and cysteine were subsequently used as modification reagents. Firstly, a facile chelation procedure was conducted. 0.5 g GO powders were suspended in 250 ml deionized water under ultrasonic treatment for 2 h to break aggregates, and 0.5 g dopamine was dissolved in 250 ml Tris-HCl (pH = 8.5) used as

modification reagent solution. The GO suspension was mixed with the same volume of modification reagent, followed by vigorous stirring for 24 h.[2] The polydopamine-coated GO nanosheets were collected by centrifugation, washed with distilled water until neutral and dried in a vacuum oven at 80 °C for 24 h. Secondly, 0.5 g polydopamine-coated GO nanosheets subsequently reacted with cysteine in 5 wt % aqueous solution via Michael addition or Schiff base reactions at 60 °C for 6 h.[3] The obtained polydopamine-coated GO nanosheets and the further amino-acid functionalized graphene oxide nanosheets were designated as GO-DA and GO-DA-Cys, respectively.

1.2 Characterization of the GO, GO-DA and GO-DA-Cys nanosheets

The morphology of the GO, GO-DA and GO-DA-Cys nanosheets was characterized by transmission electron microscopy (TEM, JEOL, Tecnai G2 F20).).

Fourier transform infrared spectra (FTIR, 4000–400 cm^{-1}) were recorded on a Nicolet MAGNA-IR 560 instrument.

The surface chemical composition of the nanosheets (GO, GO-DA and GO-DA-Cys) was monitored by X-ray photoelectron spectroscopy (XPS) using a PHI 1600 spectrometer with Mg K a radiation for excitation.

The thermal stability of GO, GO-DA and GO-DA-Cys nanosheets as well as the content of cysteine in GO-DA-Cys nanosheets was explored by thermal gravity analysis (TGA, NETZSCH-TG209 F3 instrument, Germany) with a heat rate of 10 °C min^{-1} and temperature range of 40-800 °C.

The powder XRD of GO, GO-DA and GO-DA-Cys nanosheets was operated on a Rigaku D/max2500v/Pc (Cu Ka) instrument at an angular range of 5-60 °, with a piecewise scanning speed 2 ° min^{-1}.

1.3 Characterization of membranes

The cross-section morphology and dispersion of nanosheets (GO, GO-DA and GO-DA-Cys) in the membrane samples were examined with a Nanosem 430 field emission scanning electron microscope operated at 10 kV. Membrane samples were cryogenically fractured in liquid nitrogen and then sputtered with a thin layer of gold.

FT-IR of membranes was used to investigate the inner interaction between

nanosheets and polymer matrix.

The XRD of membranes was operated on a Rigaku D/max2500v/Pc (Cu Ka) instrument at an angular range of 5-60 $^{\circ}$, with a piecewise scanning speed 2 $^{\circ}$ min^{-1}.

To determine the glass transition temperature (T_g) of unfilled SPEEK and the composite membranes, differential scanning calorimetry (DSC) was performed on a 204 F1 NETZSCH. At least 10 mg of each sample was collected in an aluminum sample holder. Samples were preheated under nitrogen from room temperature to 150 °C at 10 °C min^{-1}, then cooled to 90 °C and reheated to 260 °C. The thermal gravimetrical analysis (TGA) was performed on a PerkinElmer TGA 4000. At least 10 mg of each sample was placed into a small aluminum sample holder. The sample was heated to 900 °C at a heating rate of 10 °C min^{-1} under a constant nitrogen flow of 20 ml min^{-1}.

The static contact angles of water on the membranes were measured at ambient temperature using a contact angle goniometer (JC2000C Contact Angle Meter, Powereach Co., Shanghai, China). A water drop with a volume of 5 μL was dropped onto the membranes with a microsyringe. Six contact angles at different locations on each sample were recorded and three samples were measured for each membrane. The error of measurement for each sample was around ±5%.

Water uptake and area swelling of membranes were measured and calculated by the method reported in our previous study.[3] Membranes were dried at 60 °C till constant weight (W_{dry}, g) and the area (A_{dry}, cm^2) of membranes were measured. Then, the weights (W_{wet}, g) and areas (A_{wet}, cm^2) of wet membranes were measured each time after gas permeability test immediately. The water uptake and area swelling were the average of three measurements with an error within 5.0% and calculated based on the following calculations: Water uptake = (W_{wet}-W_{dry})/W_{dry} and Area swelling = (A_{wet}-A_{dry})/A_{dry}, respectively.

Mechanical property of the membranes was studied using a universal tensile and compression test systems (Yangzhou Zhongke Jiliang LTD, China). Each sample was cut into 1.0 cm × 4.0 cm and examined with an elongation rate of 10 mm min^{-1} at room temperature.

2. Results and discussion

Table S1 Elemental analysis on surface of as-prepared GO and amine acid-functionalized GO from XPS.

Samples	Element (atom %)			
	C1s	O1s	S2p	N1s
GO	74.7	25.3	-	-
GO-DA	72.3	21.2	-	6.5
GO-DA-Cys	55.2	19.4	11.0	13.6

Table S2 The mechanical properties of membranes.

Sample	Young's modulus (GPa)	Tensile (MPa)	Elongation at break (%)
SPEEK	0.55	48	10.9
SPEEK/GO-8	0.59	52	8.93
SPEEK/GO-DA-8	0.78	55	8.36
SPEEK/GO-DA-Cys-8	0.82	57	7.01

Table S3 T_g of membranes.

Membrane	T_g (°C)
SPEEK/GO-2	168.6
SPEEK/GO-4	172.5
SPEEK/GO-6	173.3
SPEEK/GO-DA-2	170.0
SPEEK/GO-DA-4	170.2
SPEEK/GO-DA-6	172.0

Water uptake and area swelling of membranes are measured. The membrane weight and area swelling become constant in 1.5 h, and the water uptake and area swelling of the membranes are shown in Fig. S1. Compared with the unfilled SPEEK membrane, both the water uptake and area swelling of the composite membranes are increased from 12.1% and 6.1% for unfilled SPEEK to 27.3% and 13.1% for SPEEK/GO-DA-

Cys-8 membrane, respectively. These increases are due to the increased free volume and decreased crystallinity of the composite membranes after incorporation of nanosheets fillers.
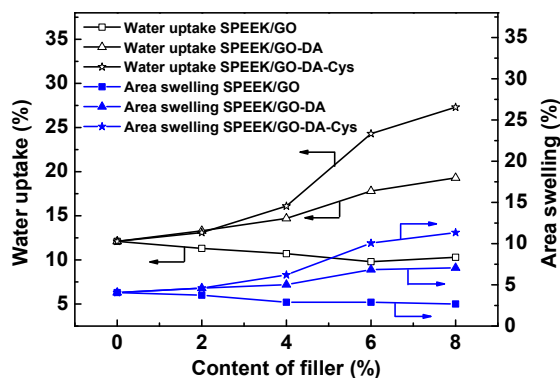

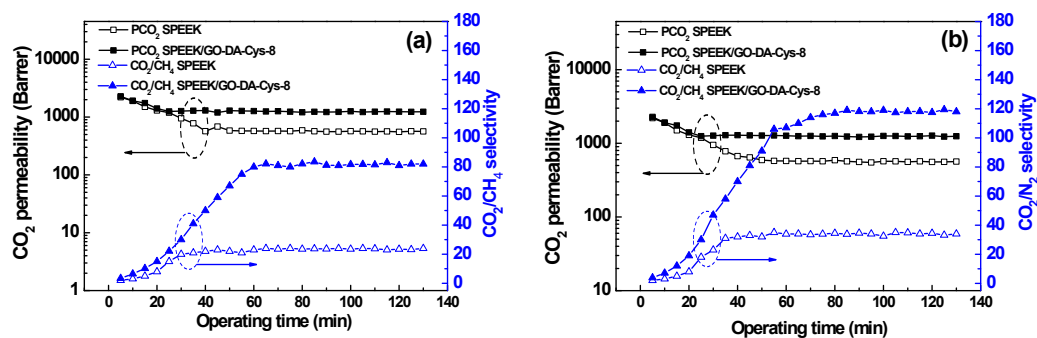**Fig. S1.** The water uptake and area swelling properties of the unfilled SPEEK membrane and composite membranes (25 $^{\circ}$C, 1 bar).

Fig. S2. Dynamic CO_2 separation properties of unfilled SPEEK membrane and SPEEK/GO-DA-Cys-8 membrane: (a) CO_2/CH_4 separation; (b) CO_2/N_2 separation. Wet membranes are test at 1 bar feed pressure and 25 °C.

3. Gas separation performance
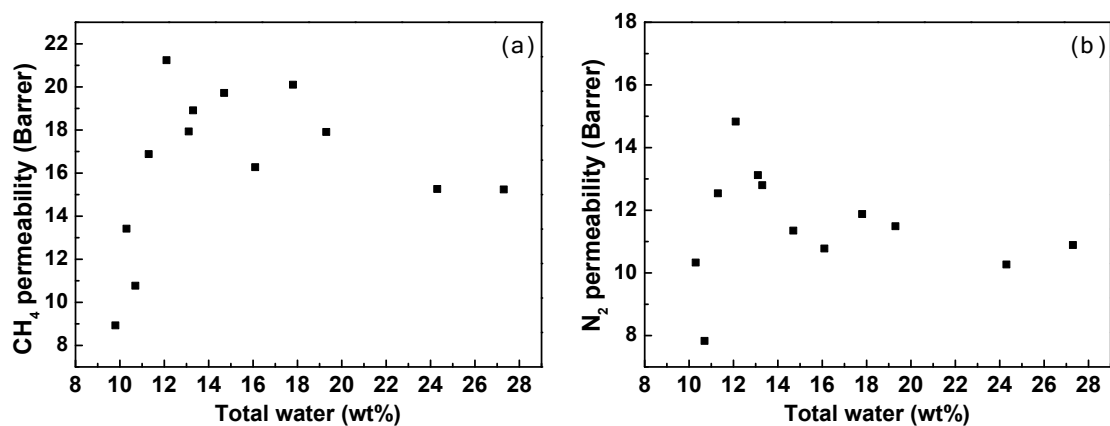
3.1 Effect of water uptake

Fig. S3. (a) Correlations between pure gas CH_4 permeability and total water and (b) Correlations between pure gas N_2 permeability and total water in membranes (1 bar, 25 ^oC).

Table S4. Total water and bound water in membranes.

Membrane	Total water (wt %)	Bound water (wt %)
SPEEK	12.1	2.5
SPEEK/GO-2	11.3	2.8
SPEEK/GO-4	10.7	3.1
SPEEK/GO-6	9.8	3.6
SPEEK/GO-8	10.3	2.7
SPEEK/GO-DA-2	13.3	3.0
SPEEK/GO-DA-4	14.7	3.4
SPEEK/GO-DA-6	17.8	3.9
SPEEK/GO-DA-8	19.3	5.1
SPEEK/GO-DA-Cys-2	13.1	3.0
SPEEK/GO-DA-Cys-4	16.1	5.1
SPEEK/GO-DA-Cys-6	24.3	5.6
SPEEK/GO-DA-Cys-8	27.3	2.5

3.2 Effect of feed gas pressure

Fig. S4 shows the effect of pressure on humidified gas permeation. Both the CO_2 permeability and CO_2/CH_4 separation factor decrease with the increase of feed pressure for the SPEEK/GO-DA-Cys membrane (Fig. S4 (a), (c), (d), (f)), which agrees with the common variation trend of facilitated transport membranes.[4,5] The carrier (primary amine) from amino acid is saturated and the complexation reaction rate is stabilized with increasing feed pressure, leading to decreased CO_2 permeability. Unlike CO_2 permeability, CH_4 and N_2 permeability are unchanged with increasing feed pressure (Fig. S4 (b) and (e)), which are well consistent with the characteristic of solution–diffusion process. If a gas permeates through the membrane following the ideal solution-diffusion mechanism, its permeability is independent of concentration driving force across the membrane.[6]
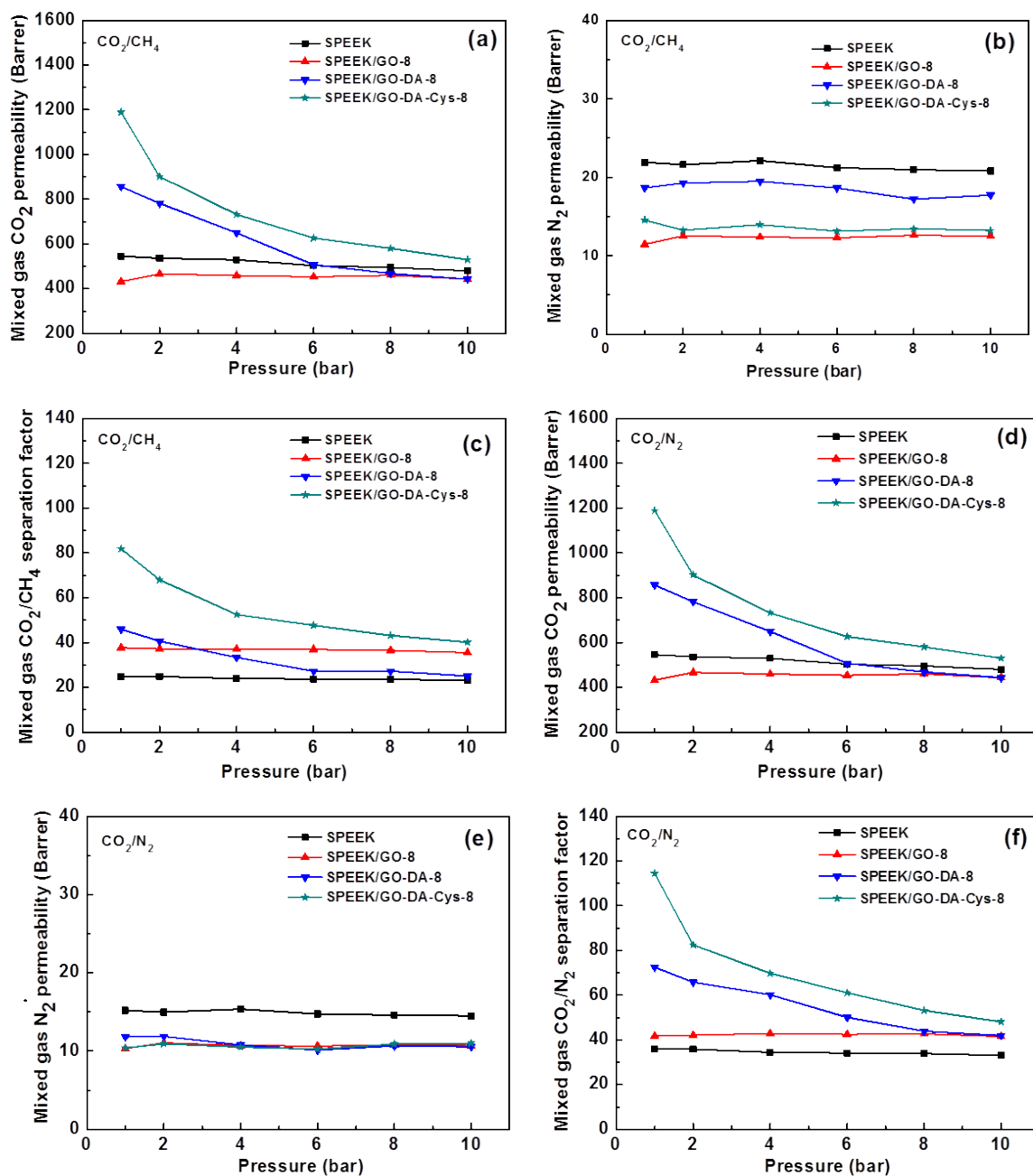
Fig. S4. Effect of pressure on (a) Mixed gas CO_2 (CO_2/CH_4 = 30/70 vol %) permeability; (b) Mixed gas CH_4 permeability (c) Mixed gas CO_2/CH_4 separation factor and (d) Mixed gas CO_2 (CO_2/N_2 = 10/90 vol %) permeability; (e) Mixed gas N_2 permeability; (f) Mixed gas CO_2/N_2 separation factor of membranes. Permeation tests were performed at 25 °C with humidified feed gas and sweep gas.

Table S5 A summary of some typical CO_2-facilitated transport fillers incorporated composite membranes reported in literatures and the current study for separation of CO_2/CH_4 and CO_2/N_2 mixtures.

Polymer	Fillers	Loading (wt%)	Operating conditions	Thickness (μm)	P_{CO2} (Barrer)	$P_{CO2/PCH4}$	P_{CO2}/P_{N2}	Ref
PES	Ag^+-Zeolite	50	mixed gas (15 % CO_2 molar fraction), 35 °C, 20 bar, dry membrane	60~70	1.02	59.6	-	7
Ultem® 1000	Ag+-HNTs	0.5	pure gas (99.97% purity), 25 °C, 15 bar, dry membrane	-	0.81	78.8	-	8
PSF	APTMS-MCM-41	40	pure gas (99.99% purity), 35 °C, 4 bar, dry membrane	-	14.8	15	14.8	9
SPEEK	TiO_2-DA-PEI	15	mixed gas (30 vol % CO_2 for CO_2/CH_4; 10 vol % CO_2 for CO_2/N_2), 25 °C, 1 bar, humidified membrane	50~60	1629	58	64	3
Pebax® 1657	PEI-MCM-41	20	mixed gas (30 vol % CO_2 for CO_2/CH_4; 10 vol % CO_2 for CO_2/N_2), 25 °C, 1 bar, humidified membrane	75~100	1521	41	102	10
Matrimid®5218	SBMA@CNT	5	mixed gas (30 vol % CO_2 for CO_2/CH_4; 10 vol % CO_2 for CO_2/N_2), 35 °C, 2 bar, humidified membrane	~50	103	36	-	11
PVAm/PS	PANI nanorods	20	mixed gas (15 vol % CO_2), 22 °C, 1.1 bar, humidified membrane	-	3080*	-	240	12

PVAm/PS	PANI nanosheets	17	mixed gas (20 vol % CO_2), 25 °C, 0.2 bar, humidified membrane	-	1200*	-	120	13
SPEEK	GO-DA-Cys	8	pure gas (99.99% purity), 25 °C, 1.5 bar, dry membrane	~65	22.26	48.8	59.8	This study
			pure gas (99.99% purity), 25 °C, 1 bar, humidified membrane	~75	1247	81.8	114.5	This study
			mixed gas (30 vol % CO_2 for CO_2/CH_4; 10 vol % CO_2 for CO_2/N_2)	~75	1227/1218	80.7	113.2	This study

*PCO_2 units GPU (asymmetric composite membrane).

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