Supplementary Material for

Ultrafast H_2-Selective Nanoporous Multilayer Graphene Membrane Prepared by Confined Thermal Annealing

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Experimental

Preparation of graphene oxide and its suspension: Graphene oxide (GO) was prepared by using the modified Hummer's method as described in our previous work.[1] Here, 3 g of GO was dispersed in 100 mL of DI water to prepare 30 mg/mL of GO solution. Then, the mixture was sonicated for 30 min and repeatedly agitated for 1 min by a shaker to form a homogenous GO suspension.

Fabrication of nanoporous GO membrane: The GO suspension was coated on a polyethersulfone (PES) membrane (GVS filter technology; pore diameter of 0.22 μm and membrane diameter of 5 cm) using a bar coater. The average thickness of the GO liquid coated on the PES membrane was 1.7 μm. The coated membrane was dried in an oven at 60°C for 24 h to remove residual DI water. To fabricate a nanoporous GO membrane, the GO membrane was hot-pressed at 150°C and 20 bar using a hot-press (Auto series compact automatic benchtop press, Carver INC.). The treatment time was varied from 30 min to 24 h for investigating the influence of the hot-pressing period on the GO structure and its gas permeation properties.

Gas permeance measurement: Single gas (H_2, N_2, CO_2, and CH_4) permeation tests of nanoporous GO membranes were conducted using a constant-volume and differential-pressure method.[2] The nanoporous GO membrane was placed on a stainless-steel mesh while the nanoporous GO layer faced the feed side and was fixed using epoxy glue. The stainless-steel mesh side was placed under vacuum. The gas flow was set at 10 sccm by using a mass-flow controller (MFC). The feed gas pressure was controlled to 1 bar at room temperature via a backpressure regulator, which was controlled using a convection oven. The permeation of gas was measured using a vacuum gauge (Teledyne Hastings Instruments, HVG-2020B). The permeance and selectivity were calculated using the following equations:

$$P\ (\text{permeance}) = V_c \cdot (dp/dt) / (R \cdot T \cdot P_a \cdot A)$$

$$S\ (\text{ideal selectivity}) = P_i / P_j$$

where V_c is the volume of the vacuum chamber(m^3), dp/dt is the pressure change in the vacuum chamber per unit of time, R is the gas constant, T is the temperature (K), P_a is the atmospheric pressure (Pa), and A is the effective area of the membrane (m^2). P_i and P_j are the permeations of pure gases i and j, respectively.

The permeability was calculated using the following equation:

$$\text{Permeability (Barrer)} = P \cdot T_m / (3.35 \cdot 10^{-16})$$

Where P is the permeance (mol / ($m^2 \cdot s \cdot Pa$)), and T_m is the thickness of the membrane(m).

Characterization: The morphology of the graphene membrane was observed using scanning electron microscopy (SEM, JSM-6701F, JEOL Ltd.). X-ray photoelectron spectroscopy (XPS) was performed using a K-alpha (Thermo U.K.) with a Cu(Kα) beam source (wavelength 1.5406 Å), and Raman spectra were obtained using a LabRAM ARAMIS (Horriba Jovin Yvon) with a 532 nm laser. X-ray diffraction (XRD) was performed using an Ultima IV (Rigaku,

wavelength: 1.54 Å) instrument, and Fourier transform-infrared spectra were measured using a Cary670 (Agilent) spectrometer. N_2 adsorption-desorption isotherms were obtained using a BELSORP-mini II instrument (BEL Japan).

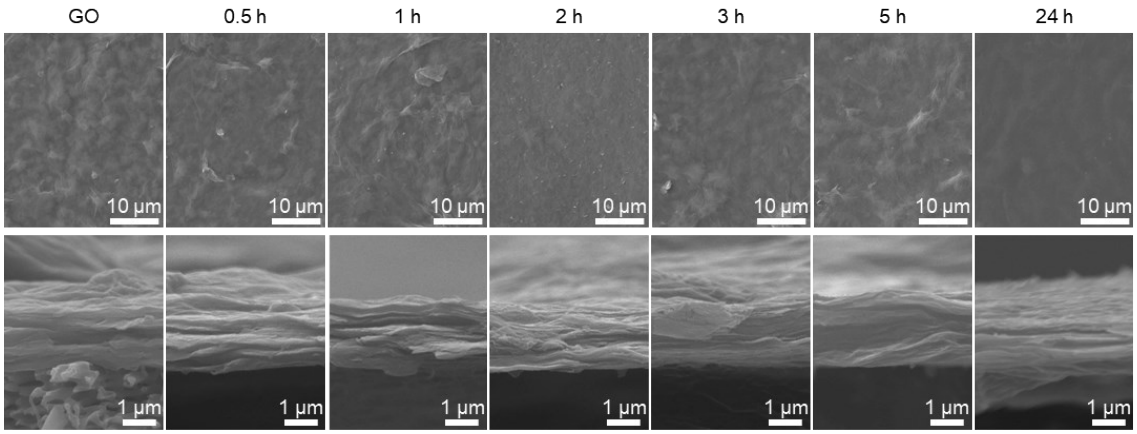

Fig. S1. Top (top) and cross-sectional SEM images (bottom) of GO membranes depending on hot-pressing time. Annealing was performed at 150℃ in air and pressure was 20 bar.

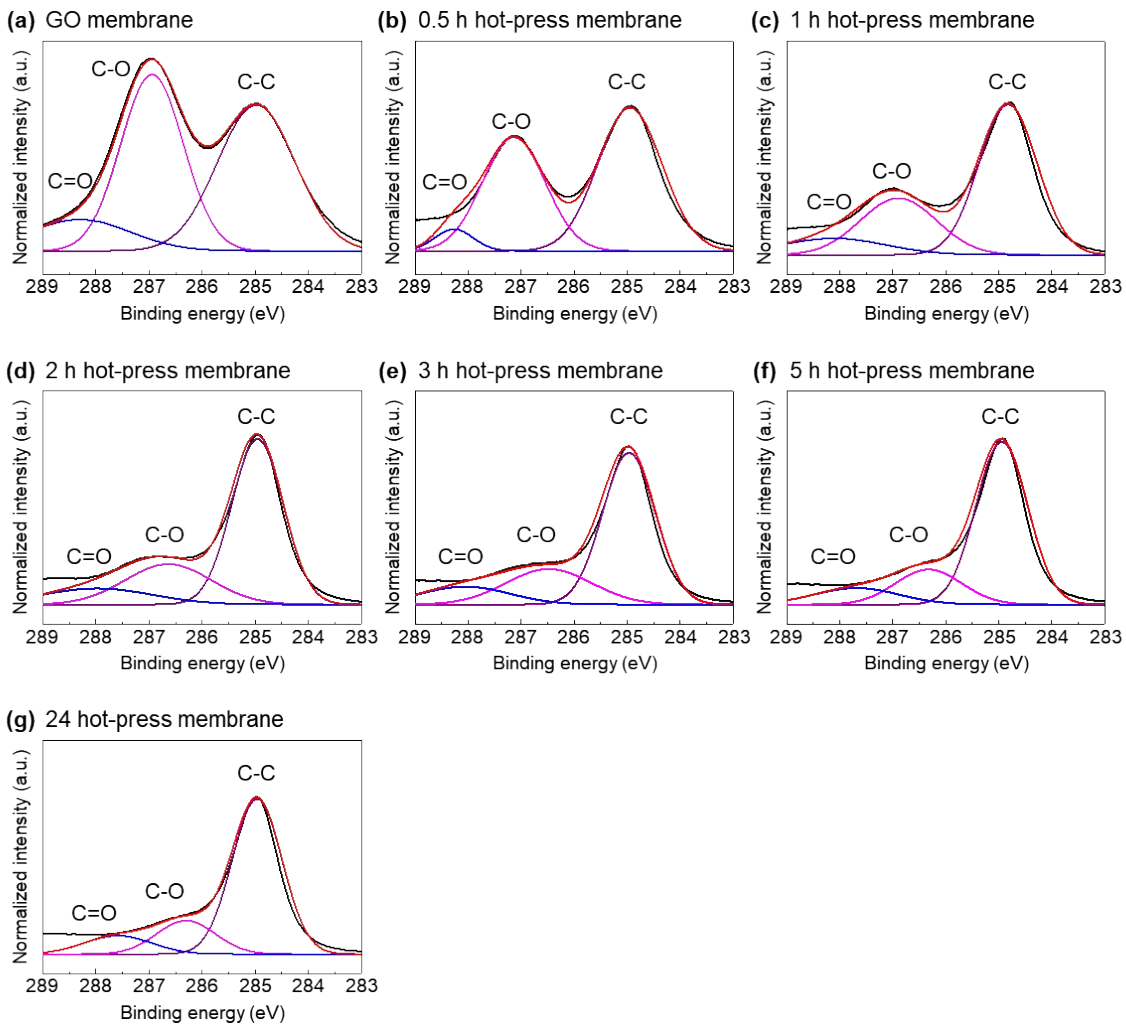

Fig. S2. XPS C1s spectra of nGO membranes depending on hot-pressing time.

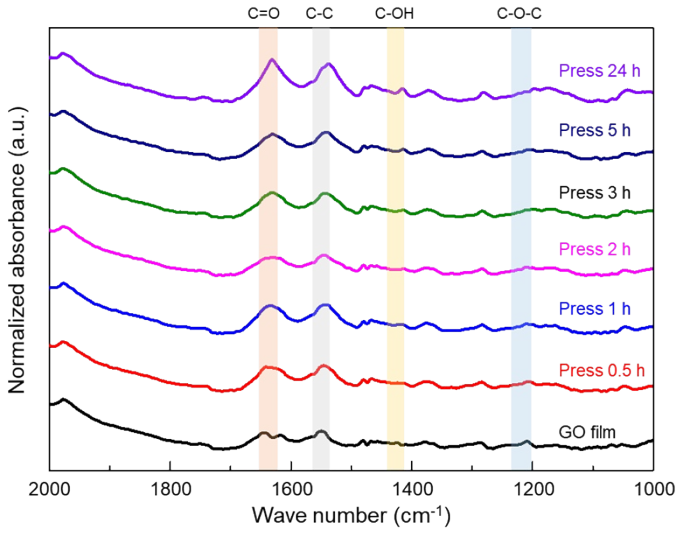

Fig. S3. FT-IR spectra of nGO membranes depending on hot-pressing time.

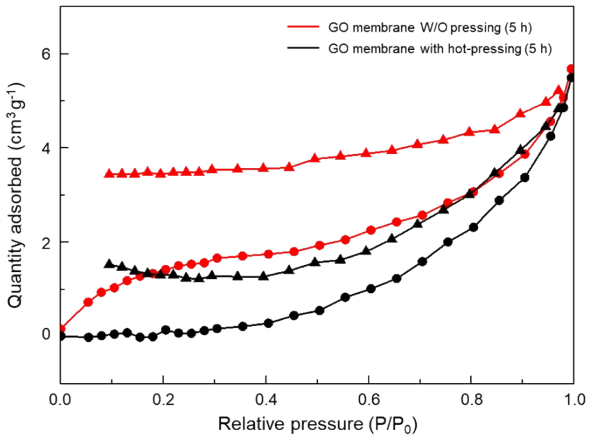

Fig. S4. N_2 adsorption-desorption isotherms of GO membrane with and without hot-pressing for 5 h. Isotherms were measured at 77 K. Significant adsorption was not observed, indicating the dense structure of the GO membrane after both annealing processes.

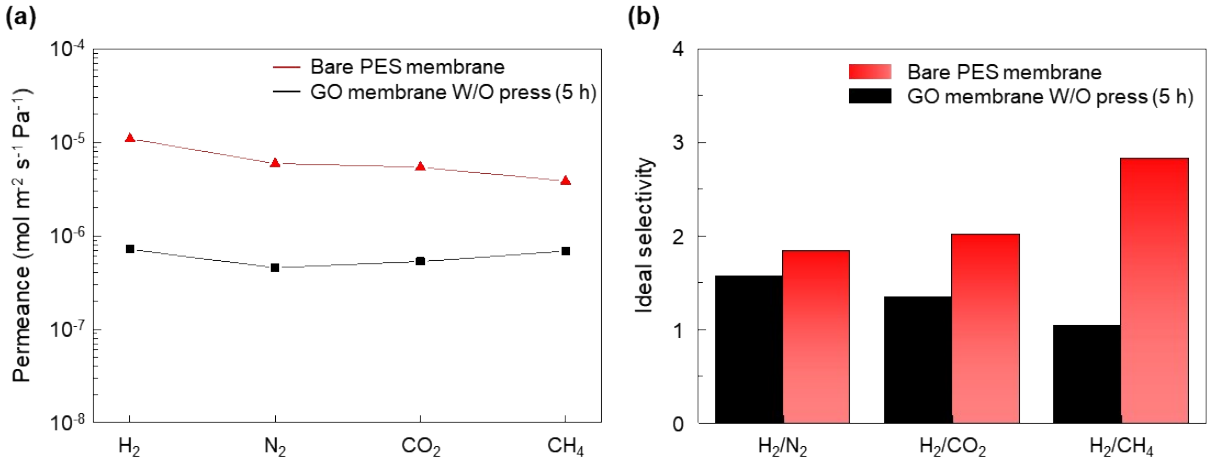

Fig. S5. (a) Single gas (H_2, N_2, CO_2, CH_4) permeance and **(b)** H_2 selectivity of GO membrane annealed at 150℃ for 5 h without hot-pressing in comparison with those of the bare PES membrane. The permeances of GO membrane after annealing tend to be rapid; however, no selectivity is observed.

Table S1. Single-gas permeation results of nGO membranes prepared with hot-pressing (5 h). The single gas permeation test was conducted at 25℃ and 1 bar pressure.

Sample		Single gas permeance (mol m^{-2} s^{-1} Pa^{-1})		H_2/CO_2 selectivity	Average permeance (mol m^{-2} s^{-1} Pa^{-1})		Average H_2/CO_2 Selectivity
		H_2	CO_2		H_2	CO_2	
Sample 1	test 1	1.41E-06	1.17E-07	12.05	1.95E-06	1.61E-07	12.12
	test 2	1.48E-06	1.16E-07	12.76			
	test 3	1.41E-06	1.15E-07	12.26			
Sample 2	test 1	2.25E-06	2.17E-07	10.37			
	test 2	2.63E-06	2.16E-07	12.18			
	test 3	2.72E-06	2.20E-07	12.36			
Sample 3	test 1	1.53E-06	1.11E-07	13.78			
	test 2	1.60E-06	1.11E-07	14.41			
	test 3	1.57E-06	1.10E-07	14.27			
Sample 4	test 1	2.73E-06	2.20E-07	12.41			
	test 2	2.36E-06	2.21E-07	10.68			
	test 3	2.36E-06	2.18E-07	10.83			
Sample 5	test 1	1.69E-06	1.40E-07	12.07			
	test 2	1.77E-06	1.39E-07	12.73			
	test 3	1.68E-06	1.37E-07	12.26			

Table S2. Comparison of H_2/CO_2 separation performance with that of the previous nanomaterial-based membranes.

Material	H_2 permeability [Barrer]	H_2/CO_2 selectivity	Thickness [nm]	Temperature [K]	Symbol	Reference
GO (Hummers)	2.7	3400	9	293	●	13
GO (Brodie's)	28.26	80.74	200	293	●	29
ZIF-8	3771	5	6000	303	▲	30
ZIF-8 modified GO	16.8	406	70	293	▼	31
ZIF-8@GO	7761	15	20000	523	▼	32
MIL-53	11971	6.8	8000	293	■	33
EFDA-GO	840	29	1000	298	◆	34
Highly oriented ZIF	89.6	106	200	303	◀	35
CMS@900	36	53	750000	423	▶	36
$Zn_2(bim)_4$	2740	60	356	298	◐	37
CTF-1	510	17	100	298	■	38
COF	105	23	41	423	●	39
GO	40	2.3	1780	298	★	This work
Without press 5 h	6400	1.4	2000	298	★	This work
With press 5 h	10360	12	1580	298	★	This work

Reference

(1) J. Kim, J.-H. Eum, J. Kang, O. Kwon, H. Kim and D. W. Kim, *Sci. Rep.*, 2021, **11**, 2063

(2) E. Choi, S. J. Hong, Y.-J. Kim, S. E. Choi, Y. Choi, J. H. Kim, J. Kang, O. Kwon, K. Eum, B. Han and D. W. Kim, *Adv. Funct. Mater.*, 2021, **17**, 2011146