Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Experimental methods

Preparation of GO membranes: GO solution was synthesized from the natural graphite flakes using the modified Hummer method. 6 g of graphite (Alfa Aesar, 325 mesh, 99.8 %), 5 g of $NaNO_3$, and 370 g of H_2SO_4 (purity 95 %) were successively added to a beaker containing a stirrer. After 1 h cooling in an ice water bath, 24 g of $KMnO_4$ was slowly added into the mixture. The mixture was stirred at room temperature until it became a highly viscous liquid. 600 ml of 5 wt% H_2SO_4 aqueous solution was added to the above solution and stirred for 1 h. Then, 30 wt% H_2O_2 aqueous solution was slowly added until it became yellow and stirred for 1 h. The products were washed 15 times using mixture of 3 wt% H_2SO_4 and 5 wt% H_2O_2, and finally washed using deionized (DI) water until those yielded aqueous dispersions of GO sheets. GO papers were fabricated by vacuum-assisted filtration of GO dispersions through Anodisc membrane filters (Whatman®, 0.2 μm pore size) followed by air drying and peeling from the filters. In this study, 4 – 10 μm thick GO membranes were fabricated for characterizations.

ZnO-ALD: GO membranes and SiO_2/Si pieces as reference samples were loaded into an atomic layer deposition (ALD) reactor (S200, Savannah, Cambridge NanoTech Inc.). The deposition was implemented at the temperature of 70 ^{o}C and the pressure of ~ 10^{-1} torr using diethylzinc ($Zn(C_2H_5)_2$, DEZ, Aldrich) and H_2O as precursors. The employed carrier gas was N_2 (20 sccm). The ALD process was set in exposure mode to ensure infiltration of Zn into micrometer-thick GO membranes. For each ALD cycle, water pulse was 0.1 s in duration, followed by a 40 s exposure, and 60 s purging time; 0.02 s in duration, 40 s exposure, and 60 s purging time for DEZ pulse. The growth cycle was repeated 50 times.

Characterization of mechanical properties: Pure GO (pGO) and ZnGO membranes of 30-mm in diameter were laser-cut into rectangular strips of 2-mm wide and 20- to 30-mm long. The laser cutting method has advantages of precisely controlling sample width and effectively minimizing mechanical damage compared to the common razor blade cutting. A microtester (Deben, N200) with a constant displacement rate of 1.7 μm/s was used to study mechanical

properties of these specimens. A FESEM (JSM-700F, JEOL) was exploited to measure sample thickness at the fracture position. Uniaxial tensile measurements were carried out at room conditions with a gap between clamps of 12 mm. Tensile strength was recorded as the highest stress obtained and stiffness was calculated from the slope of the stress-strain curve after initial strain hardening for all samples.

Characterization of electrical properties: The experiments of ZnGO and pGO strips were carried out under ambient conditions using a 2-point Au probe which is free from contact resistance. Silver-filled conductive epoxy was pasted onto GO strips as electrodes with 3 mm inter-spacing. An Agilent B1500A semiconductor device parameter analyzer was used to measure IV characteristics of these specimens. ZnO ALD on Si was also characterized as reference specimen. For evaluation of electrical conductivities, the sample thickness was ~ 5 μm.

Permeation tests: A 1-cm^2-aperture glass container for permeation tests was sealed by two rubber gaskets that clamped a GO membrane from both sides. The container was placed inside a desiccator filled with silica gels to stabilize testing conditions and the experiments were carried out at room conditions (24 ^oC, 1 atm, 30 % humidity). A thick PET sheet was used instead of GO membranes for leak testing. A precision balance (CPA225D, Sartorius) with minimum resolution of 0.01 mg was used to measure weight loss after certain time. In case of open aperture, GO membranes were removed and evaporation rates for some liquids such as water, methanol, ethanol, and acetone were tested. For each liquid, using identical membranes (open, pGO and ZnGO), the permeation tests were repeated consecutively at least three times. Moreover, to further ensure no vapor leaking in cycling tests, we used fast curing epoxy to seal the 1-cm^2-aperture container cover with the membrane instead of using the rubber gaskets. The same tests were performed again, yet the changes of the vapor permeation rate with each cycle are minor. Then the measured permeation rate values were averaged.

Other characterizations: X-ray photoelectron spectroscopy (XPS) was performed using an Al Kα X-ray source (Multilab 2000, Thermo). The spot size for each measurement is 0.5 μm^2.

The XPS depth profile was performed on the ZnGO samples by Ar sputtering. The etch time step was 100 s.

EDX mapping (JSM-700F, JEOL) was implemented at the cross-section of ZnGO and pGO membranes to study the distribution of chemical elements.

A Raman spectrometer (inVia Raman microscope, Renishaw) equipped with 514 nm laser line and an objective (x100) was adopted in this study. The backscattered Raman light was diffracted by an 1800 $gr.mm^{-1}$ grating. To avoid local heating effects, the laser power density was kept below 100 $\mu W.\mu m^{-2}$.

XRD (D8 Discover, Bruker) was used to study the crystallinity and structure change in GO membranes after different treatments.

For contact angle measurement (DSA 100, Krüss®), water droplets (3 µl) were manually dropped onto the surface of these specimens at various locations. The data was collected from at least 4 different locations for each sample.

For TEM study (ARM200F, JEOL), GO pieces were attached on Cu substrate and a focused ion beamed (JIB-4601F, JEOL) was used to mill the cross-section of GO pieces before TEM characterization at 200 kV.

Supporting figures

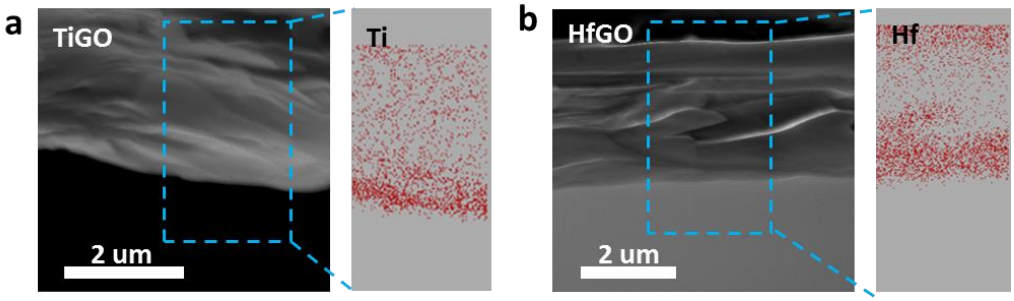

Figure S1. (a, b) Left side is the SEM images of Ti-impregnated GO (TiGO) and Hf-impregnated GO (HfGO); **(a, b)** Right side is its corresponding EDX mapping of Ti and Hf, respectively.

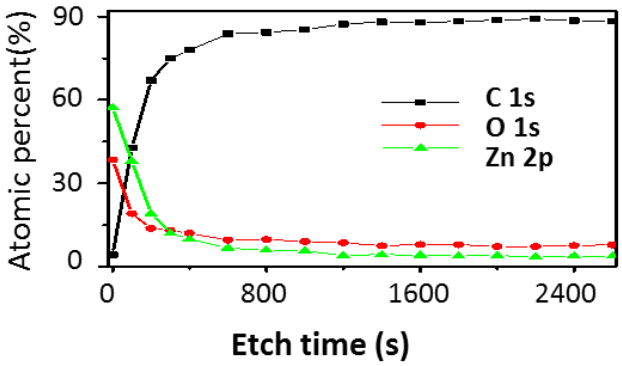

Figure S2. XPS etch profile for C 1s, O 1s, and Zn 2p orbitals in the ZnGO specimen.

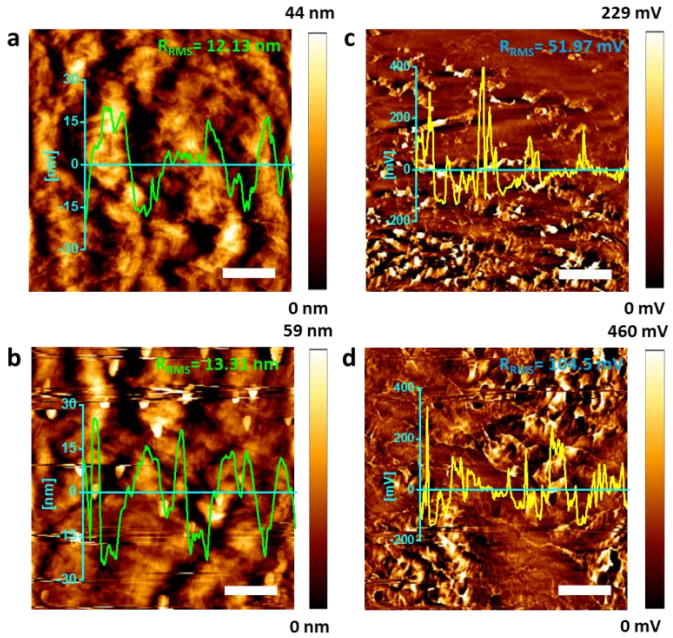

Figure S3 (**a**-**b**) AFM topographic images and height profiles of pGO and ZnGO; (**c**-**d**) The corresponding AFM lateral force images and voltage profiles of pGO and ZnGO, respectively. Scale bar = 1 µm.

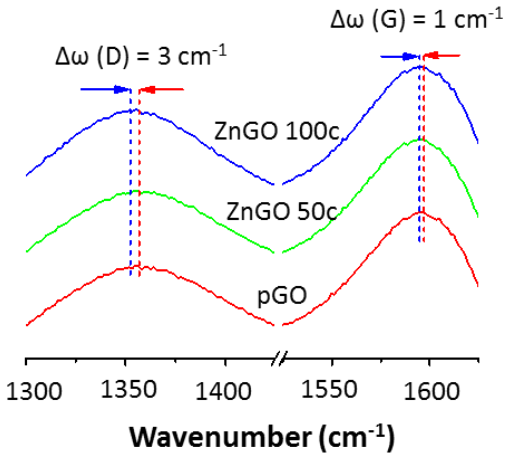

Figure S4. Raman spectra of diverse GO membranes upon different ALD cycles.

Table S1 Kinetic diameter and relative polarity of various polar vapors at 298 K

Vapor	**Kinetic diameter [1] [Å]**	**Relative polarity [2]**
H_2O	2.6	1.000
Methanol	3.6	0.762
Ethanol	4.5	0.654

Acetone	4.6	0.355
Toluene	6.1	0.099

Table S2. Comparison of permeation rates of H_2O and some common organic solvents through various GO papers from literature

#	Experimental conditions	Permeability				[Unit]
		H_2O	Methanol	Ethanol	Acetone	
[3]	1-μm-thick free standing GO, argon atmosphere, humidity 0%	10	--	10^{-5}	10^{-5}	10^{-6}mm.g/cm^2.s.bar
[4]	5-μm-thick PTFE-supported GO, air pressure of 1 bar	11.6	2.5	0.2	--	10^{-6}mm.g/cm^2.s.bar
[5]	53-nm-thick AAO-supported base-refluxing reduced GO, pressurized at 5 bar	3.3	--	0.2	--	l/m^2.h.bar
[6]	1.85-μm-thick 10 %-porous-PC-supported GO, pressurized	71	--	--	--	l/m^2.h.bar
[7]	2-μm-thick free-standing GO, pressurized at 2 bar.	16	--	0.37	--	10^3 Barrer
-	Our 10-μm-thick free standing Zn impregnated GO, solvent-vapor pressure at room condition, control humidity at 30%	5.8	2.2	0.4	1.3	mg/h. cm^2

References

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