Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Dielectric response and proton transport in water confined in graphene oxide

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SI

Thickness measurement

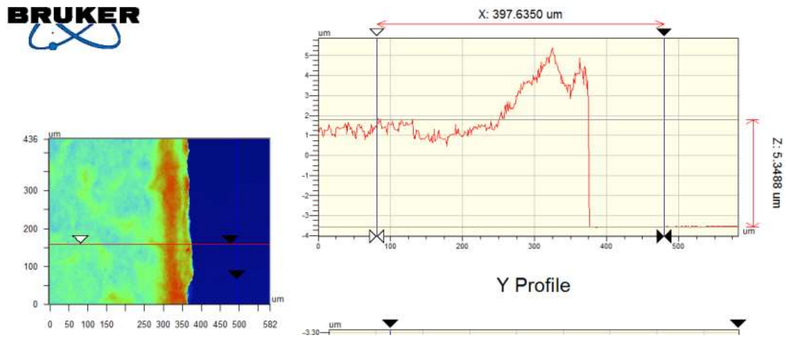

Fig. S1 Thickness measurement of graphene oxide membrane using optical profilometry.

The thickness of GO membranes supported on substrates was measured using optical profilometry. The presence of wrinkles caused the measured thickness to be a little larger than the actual one. Here the smallest step size was taken as the thickness of the membrane which matches very well with the thickness obtained through the cross-sectional FESEM image.

SII

Custom-made set-up for impedance measurements under variable relative humidity

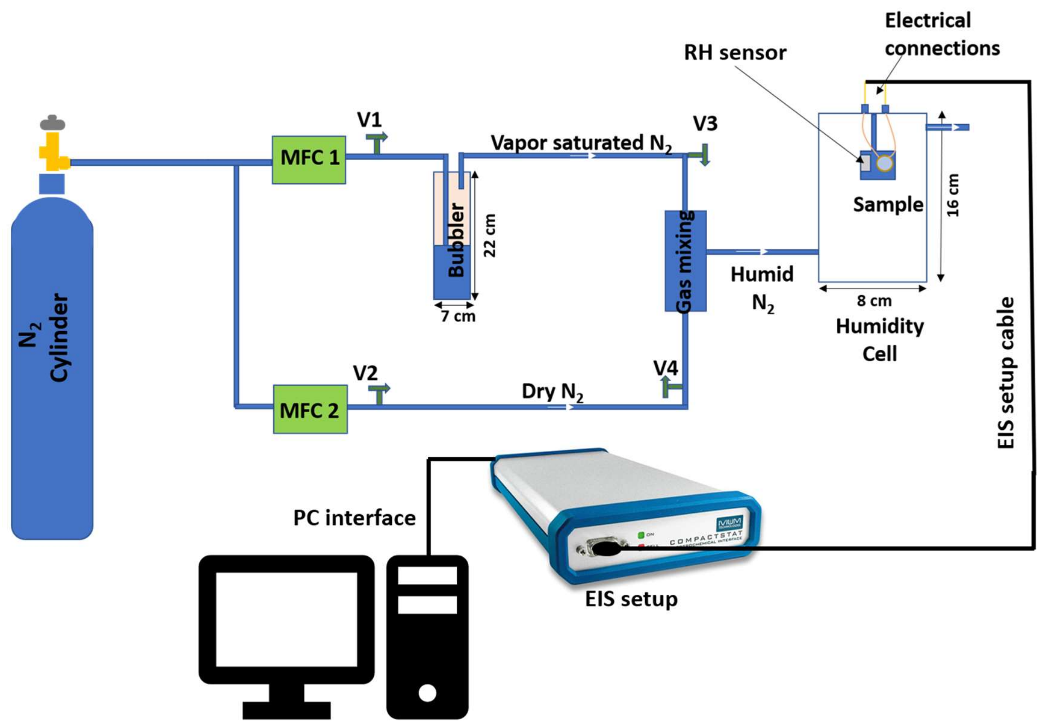

Fig. S2 Schematic of the setup for measuring impedance at variable humidity conditions. Here V1-V4 are ball valves. MFC denotes Mass Flow Controller.

SIII
Flake size measurement

(a) (b)

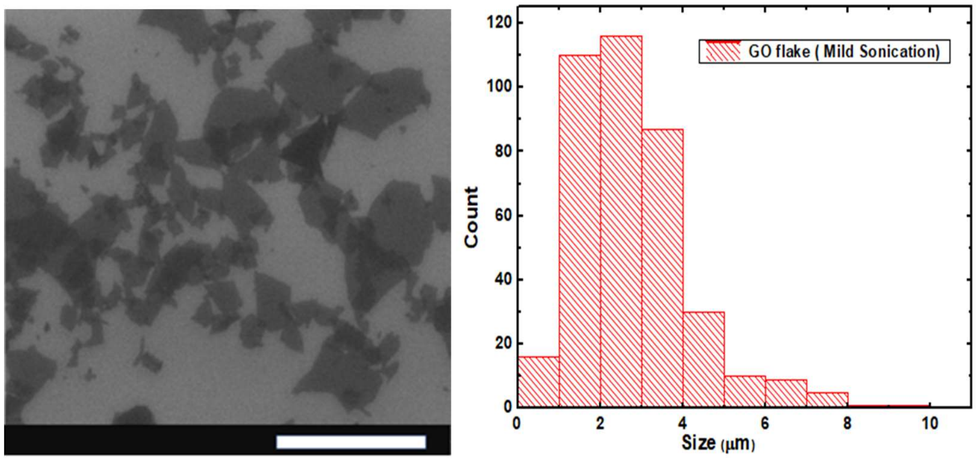

Fig. S3 (a) SEM image of a graphene oxide flakes on SiO_2/Si substrate cast from a highly diluted solution (scale bar is 10 μm). (b) Flake size distribution obtained from the FESEM image of flakes (Here the counts are based on numbers, not on the area).

SIV

Raman Spectrum

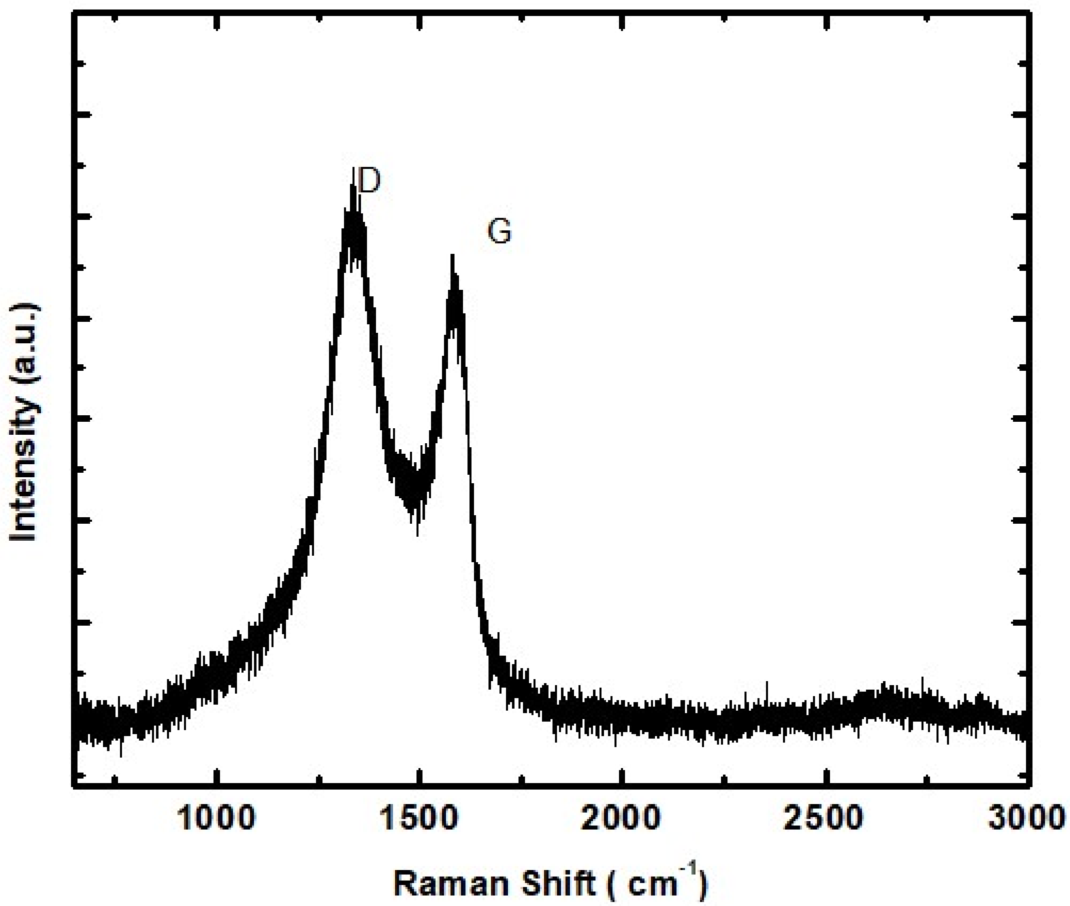

Fig. S4 Raman spectrum of graphene oxide.

The Raman spectrum of graphene oxide was taken with a 632.81 nm He-Ne laser. The position of the D peak and G peak were found to be at 1339.8 cm^{-1} and 1580.7 cm^{-1} respectively with the area integrated ratio I_D/I_G = 2.48.

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XPS survey spectra

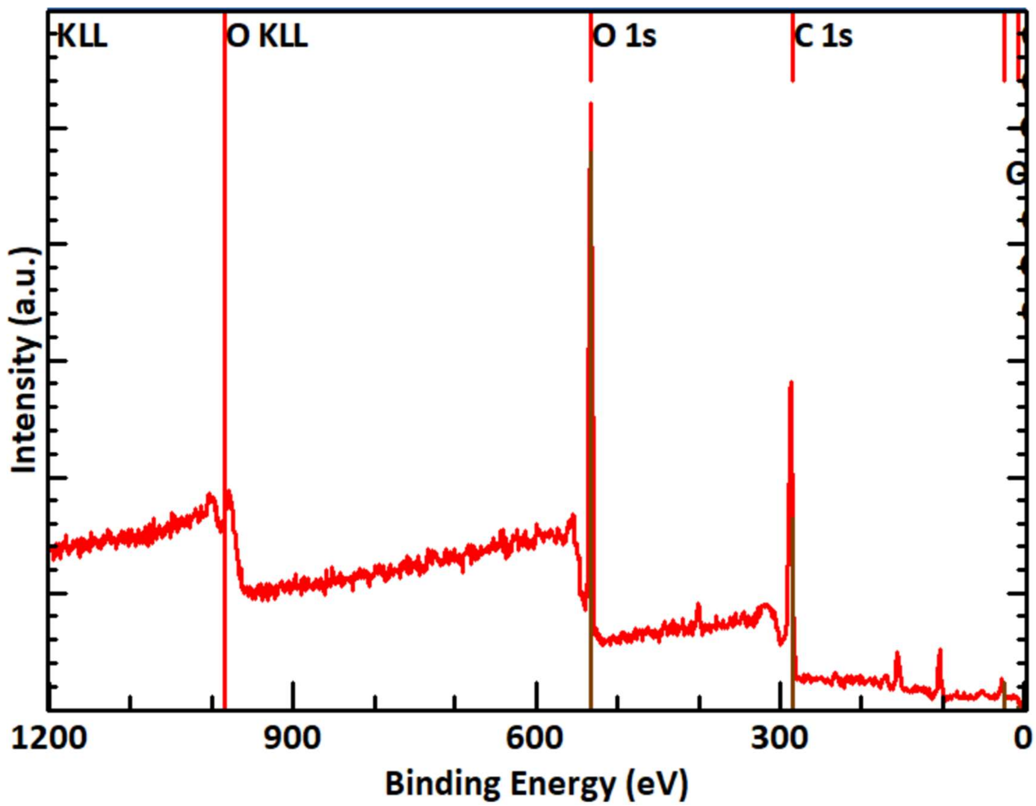


Fig. S5 XPS survey spectrum of graphene oxide showing Os1 and Cs1 peaks.

The total area under O1s curve is 13437 units, while the total area under the C1s curve is 10390 units. The sensitivity factor ratio of oxygen and carbon is 2.93:1. From this, it follows that the C:O elemental ratio is 2.27:1.

SVI

Water adsorption by graphene oxide membrane

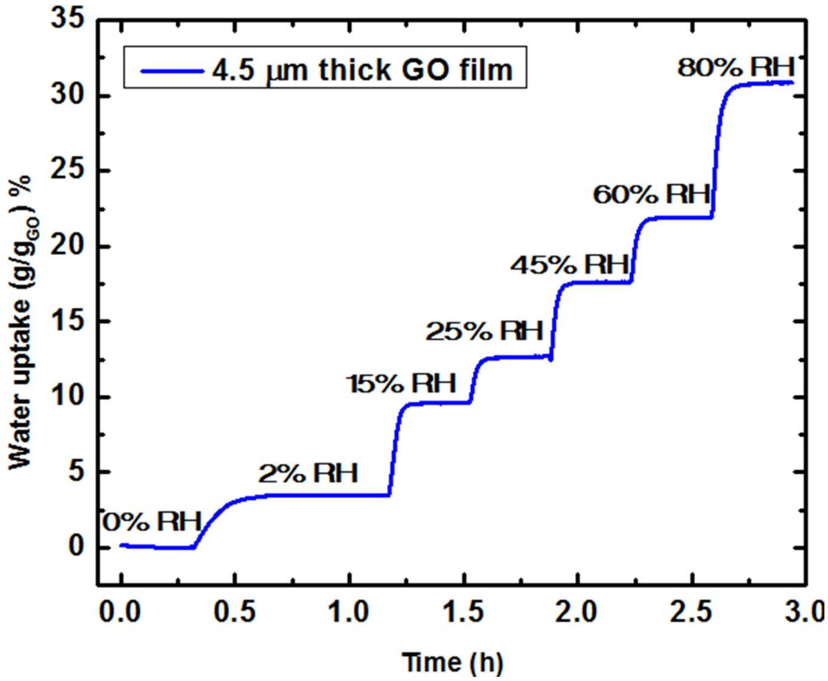


Fig. S6 Dynamic vapor sorption data of water uptake by a GO membrane at different RH%.

SVII

Increase in the interlayer spacing with RH

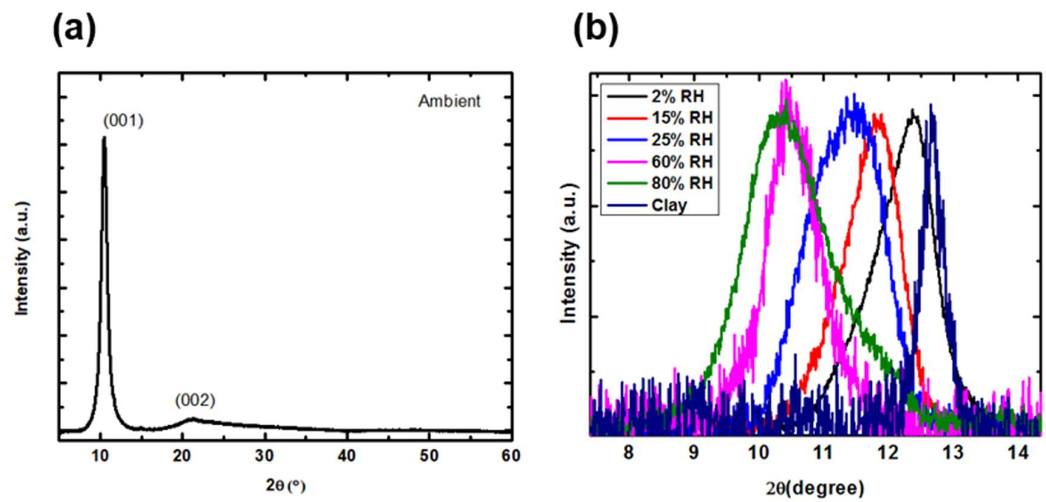


Fig. S7 (a) XRD of graphene oxide in the ambient environment (~ 50% RH) (b) Change in position of (001) peak with RH%.

The calculated interlayer spacing of GO in the ambient environment is 8.4 Angstroms. The estimated mean crystallite size based on the Scherrer equation was 10 nm.

SVIII

Impedance of graphene oxide at different humidities

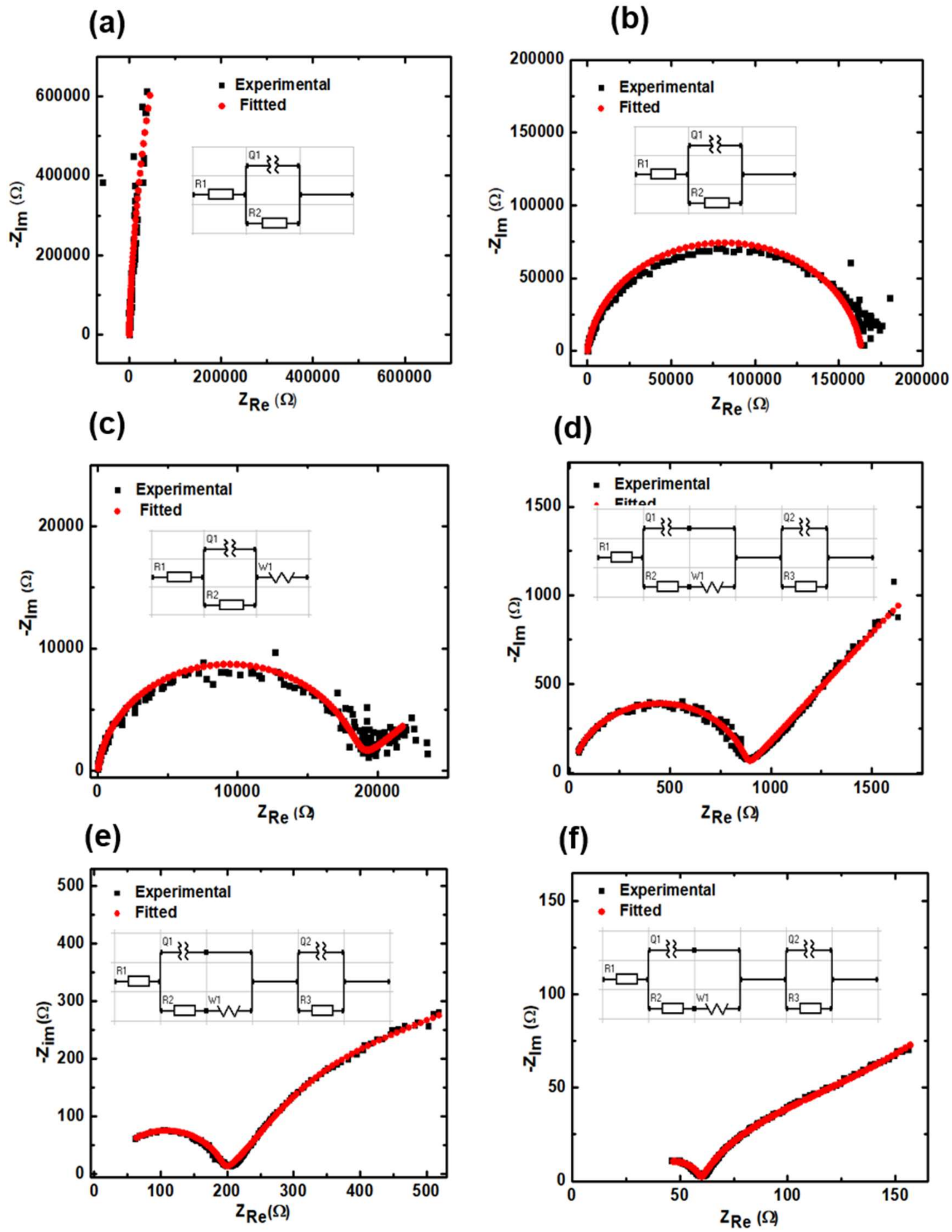


Fig. S8 Nyquist plot of graphene oxide at (a) 2% RH, (b) 15% RH, (c) 25% RH, (d) 45% RH, (e) 60% RH and (f) 80% RH in the frequency range 10 Hz to 500 kHz.

Fitting parameters

Sample 1 RH%	R1 Ω	R2 Ω	R3 Ω	Q1 S^{n1}/Ω	n1	Q2 S^{n2}/Ω	n2	W $S^{0.5}/\Omega$
2	18	`>10^{7}	__	1.386×10^{-9}	0.9830	__	__	__
15	*	165500	__	2.999×10^{-9}	0.9398	__	__	__
25	*	19850	__	2.729×10^{-9}	0.9610	__	__	1.677×10^{-5}
45	17	1110	4133*	4.137×10^{-9}	0.9454	4.294×10^{-5}	0.822	9.321×10^{-5}
60	24	223	737	7.398×10^{-9}	0.9303	6.564×10^{-5}	0.8741	2.753×10^{-4}
80	33	38	109	17.23×10^{-9}	0.9423	1.431×10^{-4}	0.8405	9.004×10^{-3}

Sample 2 RH%	R1 Ω	R2 Ω	R3 Ω	Q1 S^{n1}/Ω	n1	Q2 S^{n2}/Ω	n2	W $S^{0.5}/\Omega$
2	18	>10^{7}	__	1.436×10^{-9}	0.9811	__	__	__
15	*	241600	__	3.479×10^{-9}	0.9285	__	__	__
25	*	26230	__	3.073×10^{-9}	0.9539	__	__	1.522×10^{-5}
45	20	1273	1861*	3.893×10^{-9}	0.9521	3.039×10^{-5}	0.8578	7.78×10^{-5}
60	23	274	222	5.922×10^{-9}	0.9430	5.514×10^{-5}	0.9621	1.855×10^{-4}
80	33	47	115	21.98×10^{-9}	0.9207	1.811×10^{-4}	0.7303	1.157×10^{-3}

Sample 3 RH%	R1 Ω	R2 Ω	R3 Ω	Q1 S^{n1}/Ω	n1	Q2 S^{n2}/Ω	n2	W $S^{0.5}/\Omega$
2	19	$>10^7$	__	1.383×10^{-9}	0.9851	__	__	__
15	*	163500	__	3.155×10^{-9}	0.9393	__	__	__
25	*	18170	__	2.913×10^{-9}	0.9593	__	__	2.213×10^{-5}
45	19	828	695*	4.255×10^{-9}	0.9499	4.082×10^{-5}	1.098	1.223×10^{-4}
60	22	171	141	10.23×10^{-9}	0.9149	6.369×10^{-5}	0.9904	4.11×10^{-4}
80	33	47	116	138.7×10^{-9}	0.8324	1.307×10^{-4}	0.9123	1.411×10^{-3}

* Large error in the fitted value

Calculating the bulk resistance and capacitance of GO at different RH%.

The value of resistance and capacitance of graphene oxide at different RH% can be calculated from R2 and Q1. The bulk resistance equals R2, and the capacitance is calculated from constant phase element (CPE) Q1.

The impedance of CPE is given by

$$Z(\mathrm{CPE}) = Y_0^{-1}(j\omega)^{-n}$$

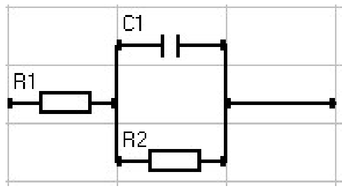
Here $Y_0 = 1/Q$. The value of capacitance is calculated from the formula [1].

$$C = Y_0(\omega''_m)^{n-1}$$

Here, ω_m'' is the frequency where the semicircle portion has the maximum value for the imaginary part of Z.

SIX

Dispersion in R and C values



In the above circuit, R1 varies from 17 Ω to 33 Ω for the samples studied in this work.

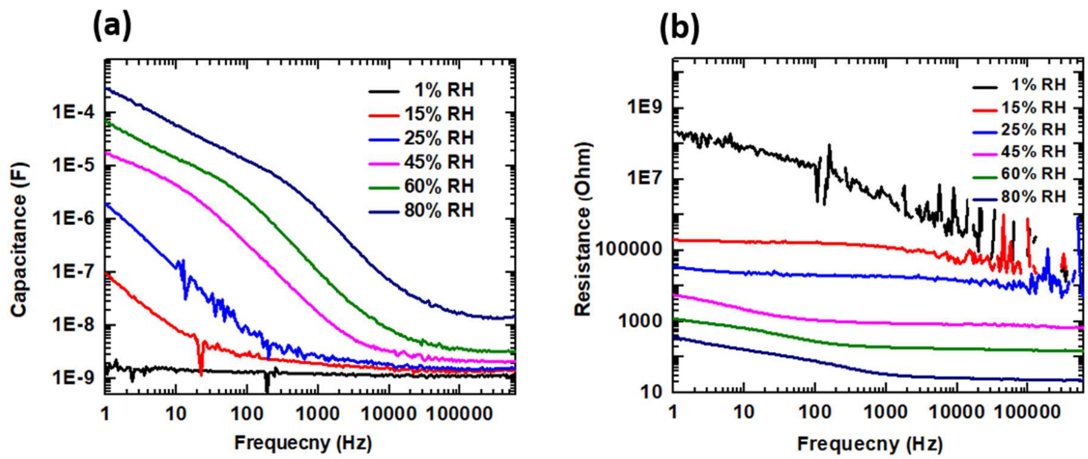


Fig. S9 (a) Dispersion of capacitance value of graphene oxide with the frequency of the applied bias frequency. (b) Dispersion in resistance values with the frequency of applied voltage bias.

SX

Comparison: Capacitance and loss: full frequency versus high-frequency fit

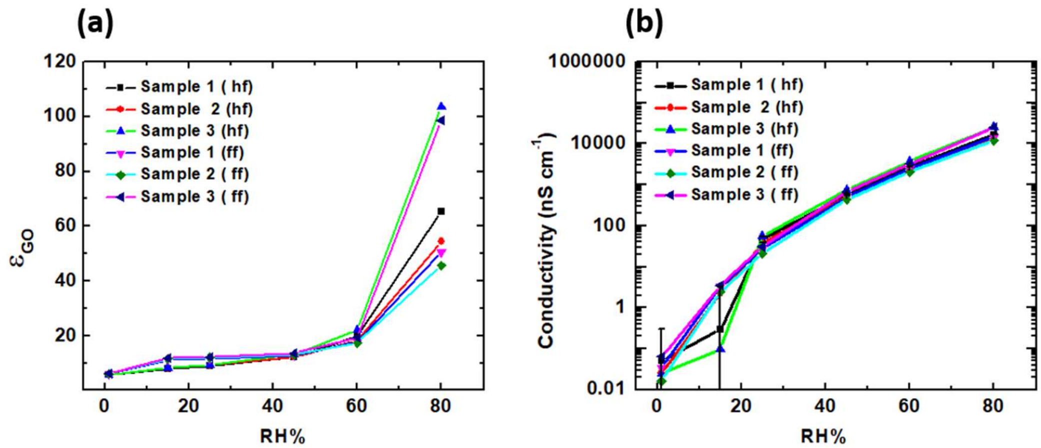


Fig. S10 (a) Comparison of the dielectric value of GO calculated from high-frequency fit (hf) and full-frequency fit (ff) (10 Hz to 500 kHz). (b) Comparison of the conductivity of GO calculated from high-frequency fit and full frequency fit (10 Hz to 500 kHz).

SXI

Calculation of lower bound of water dielectric

From the effective-medium approach [2], the dielectric constant of a composite ($\varepsilon_{\mathrm{eff}}$) will be in the limits

$$1/[(\theta/\varepsilon_1) + (1-\theta)/\varepsilon_2)] \leq \varepsilon_{\mathrm{eff}} \leq \theta\varepsilon_1 + (1-\theta)\varepsilon_1$$

θ is the vol. fraction of the inclusion
ε_1 is the dielectric constant of the inclusion (water)
ε_2 is the dielectric constant of the host matrix (Unhydrated GO)

$\varepsilon_{\mathrm{eff}}$ is known from the experimental data (Fig. 3(b) of main text). The value of θ can be obtained from the water weight, the density of GO (1.8 g/cc) and the density of water inside GO (taken to be 1 g/cc). The dielectric value of unhydrated GO is taken from Yoshio et al. [3].

References

1. C. H. Hsu and F. Mansfeld, Technical Note: Concerning the Conversion of the Constant Phase Element Parameter Y_0 into a Capacitance, *Corrosion*, 2001, **57** (9), 747–748.

2. P. S. Neelakanta, Handbook of electromagnetic materials, *CRC*, 1995, pg. 109

3. K. Yoshio, O. Seiji and S. Koichiro, Conductive Atomic Force Microscopy of Chemically Synthesized Graphene Oxide and Interlayer Conduction, *Chem. Lett.*, 2011, **40**, 255-257.