Supplementary Information - Extrinsic Cation Selectivity of 2D Membranes

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I. SELECTIVITY CONTROLS

Figure S1 shows the control measurements we took to demonstrate that our technique can measure selectivity. Fig S1(a) shows that a bare capillary does not show any selectivity, this confirms that the voltage offsets we observe in the Fig 1 (main text) are not due to electrode potentials. Fig S1(b) demonstrates the results with the commercially available membrane Nafion.[1]
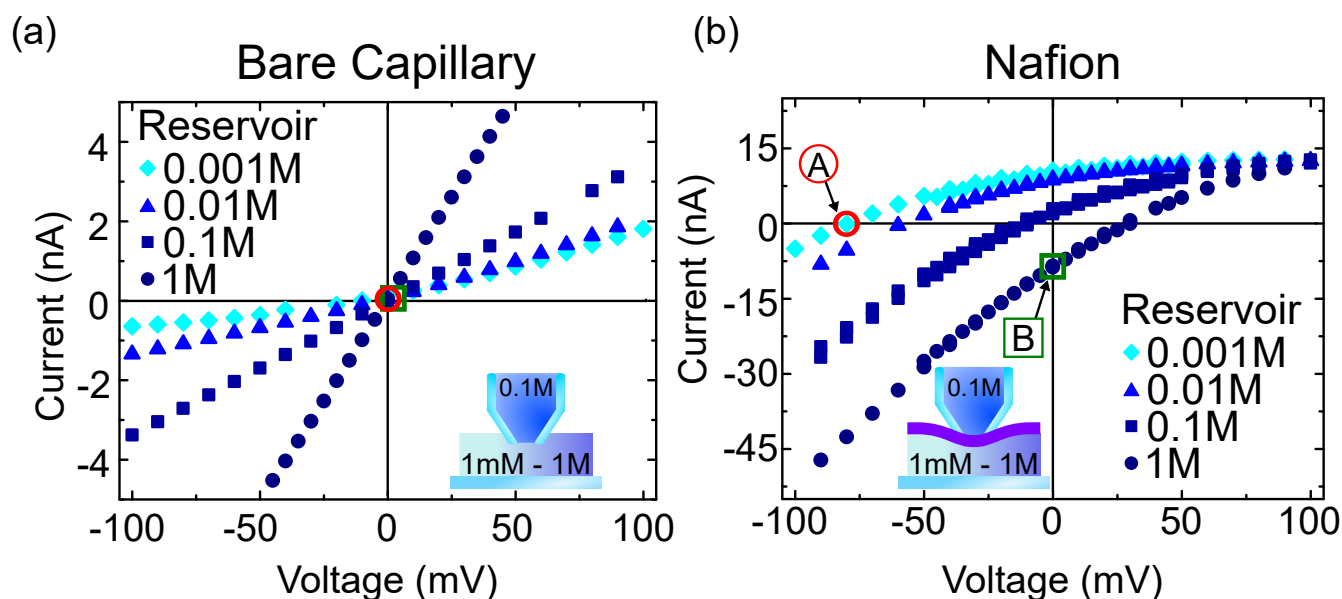

Figure S1. (a) Typical I-V curves for a bare capillary (180 nm). The solution in the capillary is 0.1M KCl and the reservoir solution is varied from 0.001M to 1M (all solutions pH 6). All the curves pass close to (0, 0) indicating no selectivity. (b) Typical I-V curves for a 2μm capillary sealed with Nafion. When the solution in the reservoir is higher diffusion causes a positive current to flow indicating that the K^+ ions cross the membrane more easily than Cl^- (green square). The voltage to stop this current is indicated by a red circle.

II. KCl CURRENT SELECTIVITY

In Fig S2 we show the currents displayed in Fig 2 (main text) un-normalised and on separate plots. All have a negative gradient indicating selectivity.
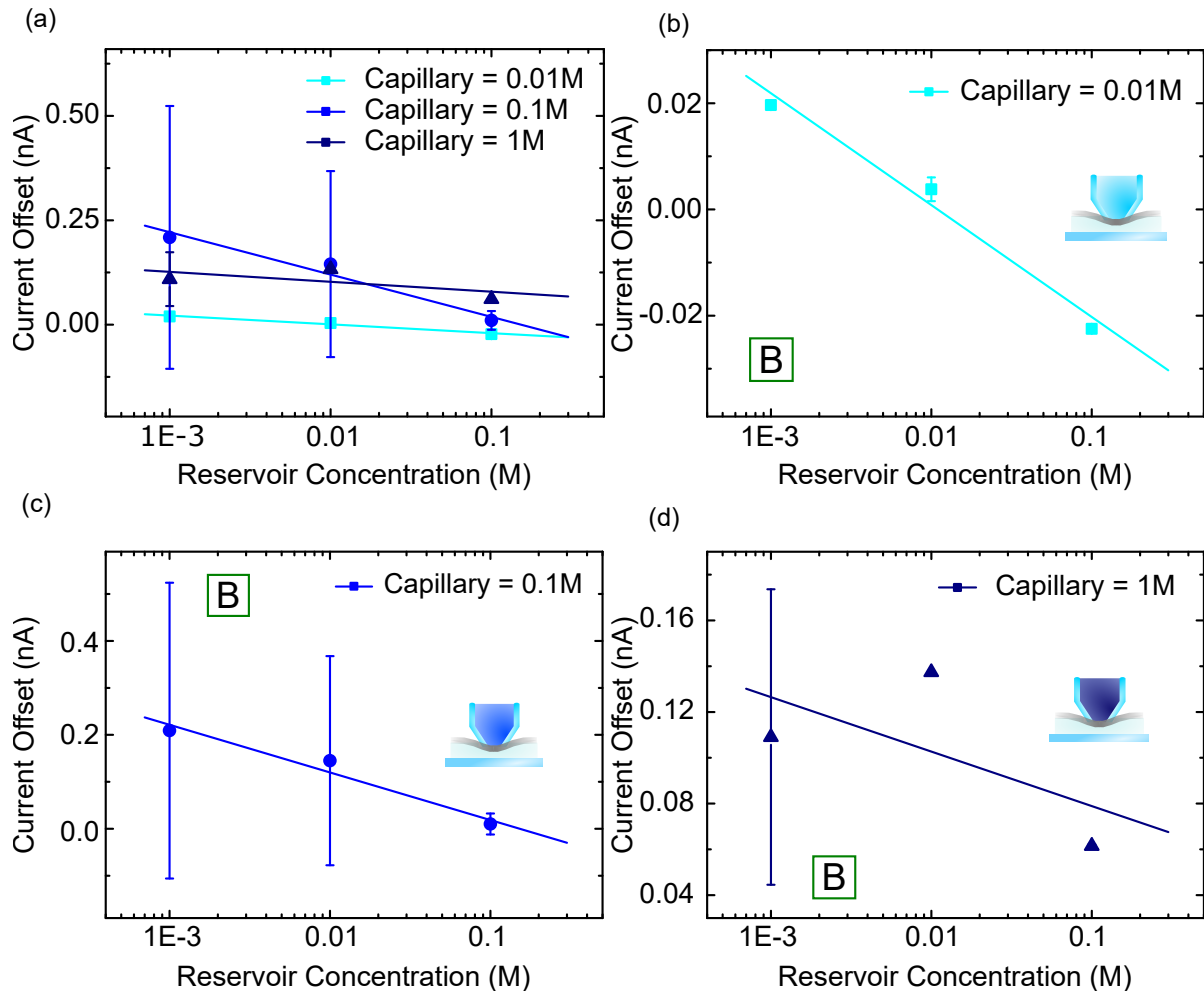

Figure S2. Un-normalised current offsets from measurements to determine the selectivity of monolayer CVD graphene to KCl (as per Fig 2 main text). The current offsets extracted from the I-V curves as the reservoir concentration is varied from 1 mM to 100 MM KCl for experiments with 0.01 M, 0.1 M and 1 M KCl in the capillary (all solutions unbuffered pH 7). (a) All shown on the same plot. (b) For 0.01 M in the capillary, from the gradient of the fitted line current offset is -0.02 nA/log(M). (c) For 0.1 M in the capillary the gradient is -0.102 nA/log(M). (d) For 1 M in the capillary the gradient is -0.024 nA/log(M)

III. DEBYE LAYER COMPARISON

There are three parameters that could influence the selectivity; the combined depth of the screening layers on both sides of the membrane, the longer screening length on the low concentration side or the shorter screening length on the high concentration side (inset Fig S3). We compared these Debye lengths with the selectivity relative to a perfectly selective membrane (%). The selectivity depends on the screening lengths and the strongest correlation is with the shorter Debye length. This Debye length is the higher concentration side of the membrane.
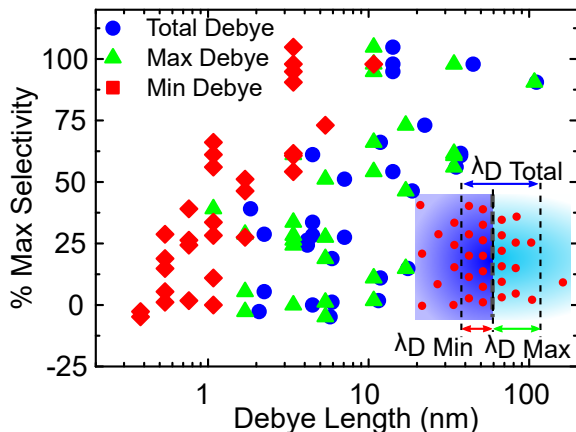

Figure S3. The % of the maximum selectivity for each combination of solutions on each side of the membrane as plotted in Fig 3 (main text) plotted against the Debye lengths on the high concentration side, low concentration side of the membrane and the total concentration. This indicates that selectivity is due to charge and is controlled by the highest concentration solution.

IV. EFFECT OF PH

By changing the pH inside the reservoir and the capillary we were able to study the affect of surface charge on the selectivity. The effect of pH change on the selective of graphene and h-BN is discussed in the main text. In Fig S4 we plot the selectivity observed for graphene and h-BN alongside positive and negative controls. A bare capillary (black line Fig S4) shows no selective across the pH range as expected. The commercial available membrane Nafion (grey line Fig S4) is none selective at low pH (pH<2) and increases to near perfect selectivity for pH>6.
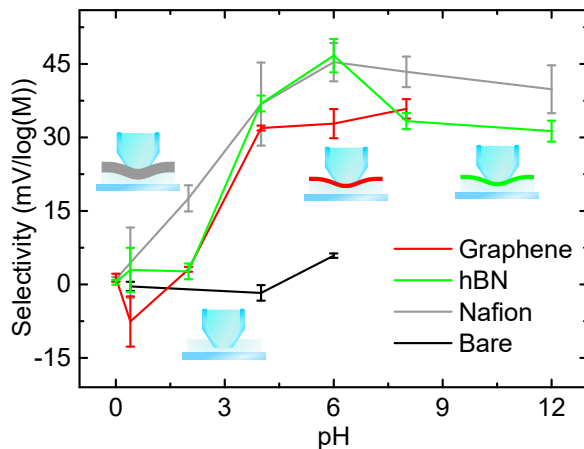

Figure S4. Effect of pH on selectivity of K+ over Cl- for different membranes. The capillary concentration was 0.1 M and the reservoir was varied from 1 mM to 100 mM. The pH of the reservoir and the capillary was set using HCl and KOH. A bare capillary used as a control shows no selectivity. The graphene membrane and the h-BN both demonstrate increasing selectivity as pH increases to pH 6. As a positive control Nafion measurements were made using a 2 μm capillary

V. OZONE TREATED GRAPHENE CURRENTS

Figure S5 plots the current offsets as in Fig 5(b) (main text) for each of the different reservoir concentrations on separate axis so that the scale of the diffusion current difference can be observed.
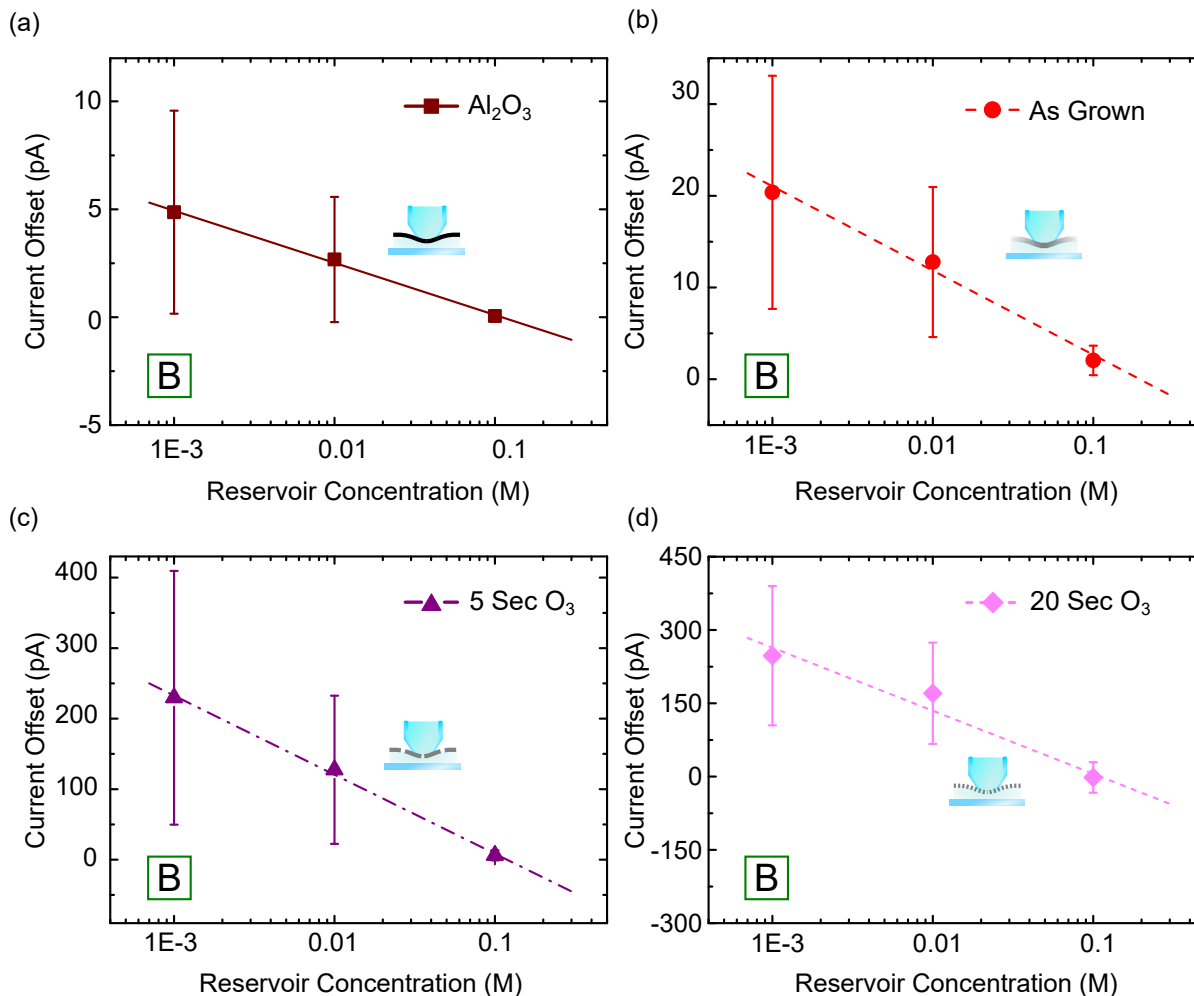

Figure S5. The effect on current offsets of blocking and creating defects (extension of Fig 5b main text). The defects in a graphene sample were blocked by depositing 2 nm of Al_2O_3 and created by exposing the graphene to ozone. The capillary (180 nm) is at 0.1 M KCl and the reservoir varied between 0.001 M and 0.1 M (all solutions unbuffered pH 7). The gradients fitted to the data are: (a) 2.41 pA/Log(M). (b) 9.18 pA/Log(M). (c) 112 pA/Log(M). (d) 129 pA/Log(M).

VI. GRAPHENE CHARACTERISATION

An example of a Raman map of the D/G ratio for our samples is shown in Fig S6. It demonstrates that the graphene is of uniform quality with a low defect density. The Raman map was measured before transfer onto NaCl.

VII. RAMAN EVIDENCE OF CHARGING

The selectivity results we presented in Fig. 4 of the main text indicate that the 2D membranes are negatively charged in aqueous solution. To complement the selectivity measurements we used our in-situ Raman capability to corroborate the charge on the membrane.[2] It has been demonstrated that doping graphene membranes electronically will cause subtle changes to their Raman spectra.[3] In particular the G peak and 2D peaks shift slightly. We compared the Raman spectra from a graphene sample which was split and part transferred on to SiO_2 and part on to salt to
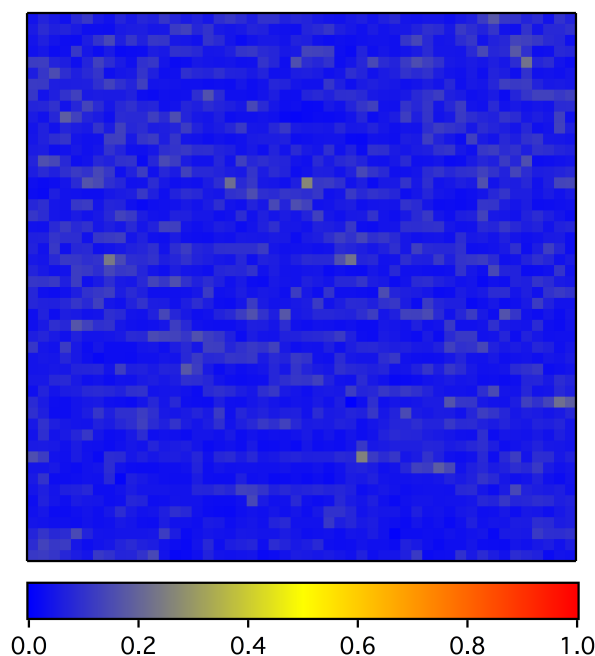
Figure S6. Raman map of the D/G ratio of the as grown graphene indicating uniform low defect density.
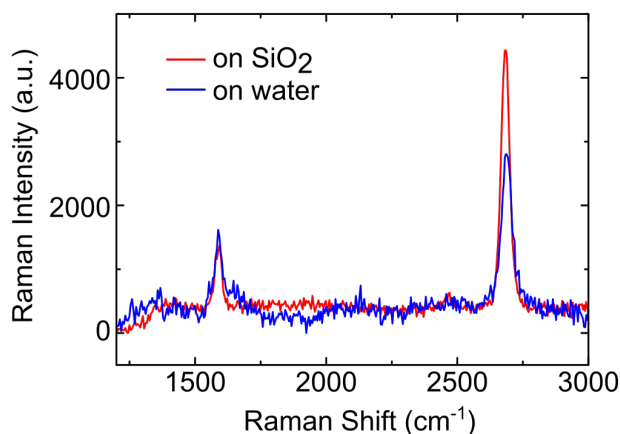

Figure S7. Raman spectra acquired from the same graphene sample split and transferred on to SiO_2 and floated on the surface of an aqueous reservoir

be floated on water. Figure S7 shows the Raman spectra from the graphene on SiO_2 and the graphene floating on an aqueous reservoir. The peak positions from 20 spectra for each sample were found by fitting a Lorentzian, Table S1, and from these we observed a significant shift in the peak positions. Compared to the spectra acquired from graphene on SiO_2 the sample floating on water has a G peak shifted by 4.8 cm^{-1} and the 2D peak is shifted by 5.9 cm^{-1}. This corresponds with the shifts reported in literature for graphene becoming negatively charged. We also observed changes in the 2D to G ratio and the FWHM of the peaks.

[1] Kenneth A. Mauritz and Robert B. Moore, "State of Understanding of Nafion," Chem. Rev. **104**, 4535–4585 (2004).

[2] Michael I. Walker, Robert S. Weatherup, Nicholas A. W. Bell, Stephan Hofmann, and Ulrich F. Keyser, "Free-Standing Graphene Membranes on Glass Nanopores for Ionic Current Measurements," Appl. Phys. Lett. **106**, 23119 (2015).

	G Peak Position	G peak FWHM	2D Peak Position	2D FWHM	2D to G ratio
Graphene on SiO$_2$	1588.7 $\pm$ 0.32 cm^{-1}	13.9 $\pm$ 0.39 cm^{-1}	2683.5 $\pm$ 0.2 cm^{-1}	17.4 $\pm$ 0.19 cm^{-1}	3.22 $\pm$ 0.14
Graphene floating on Water	1593.5 $\pm$ 3.4 cm^{-1}	17.3 $\pm$ 1.3 cm^{-1}	2689.4 $\pm$ 0.4 cm^{-1}	20.5 $\pm$ 1.57 cm^{-1}	1.97 $\pm$ 0.01

Table S1. Average G and 2D peak positions and FWHM for a graphene sample transferred onto SiO$_2$ (32 measurements) and floating on water (19 measurements).

[3] A Das, S Pisana, B Chakraborty, S Piscanec, S K Saha, U V Waghmare, K S Novoselov, H R Krishnamurthy, A K Geim, A C Ferrari, and A K Sood, "Monitoring Dopants by Raman Scattering in an Electrochemically Top-Gated Graphene Transistor." Nat. Nanotechnol. **3**, 210–5 (2008).