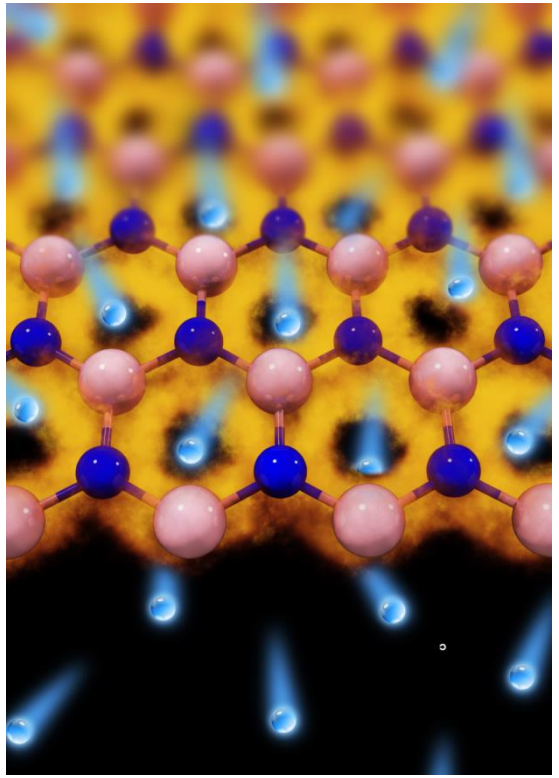
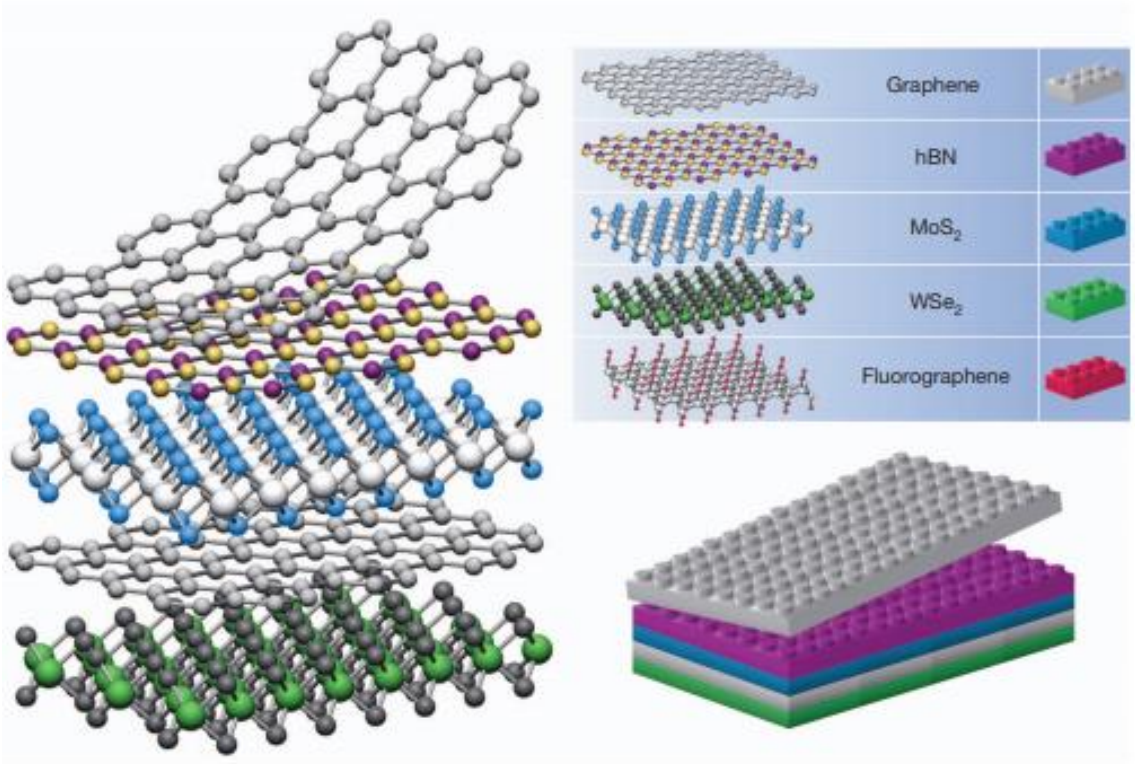
Interfacial water dissociation through proton permeable electrodes

Marcelo Lozada-Hidalgo

University of Manchester
Condensed Matter Physics Group

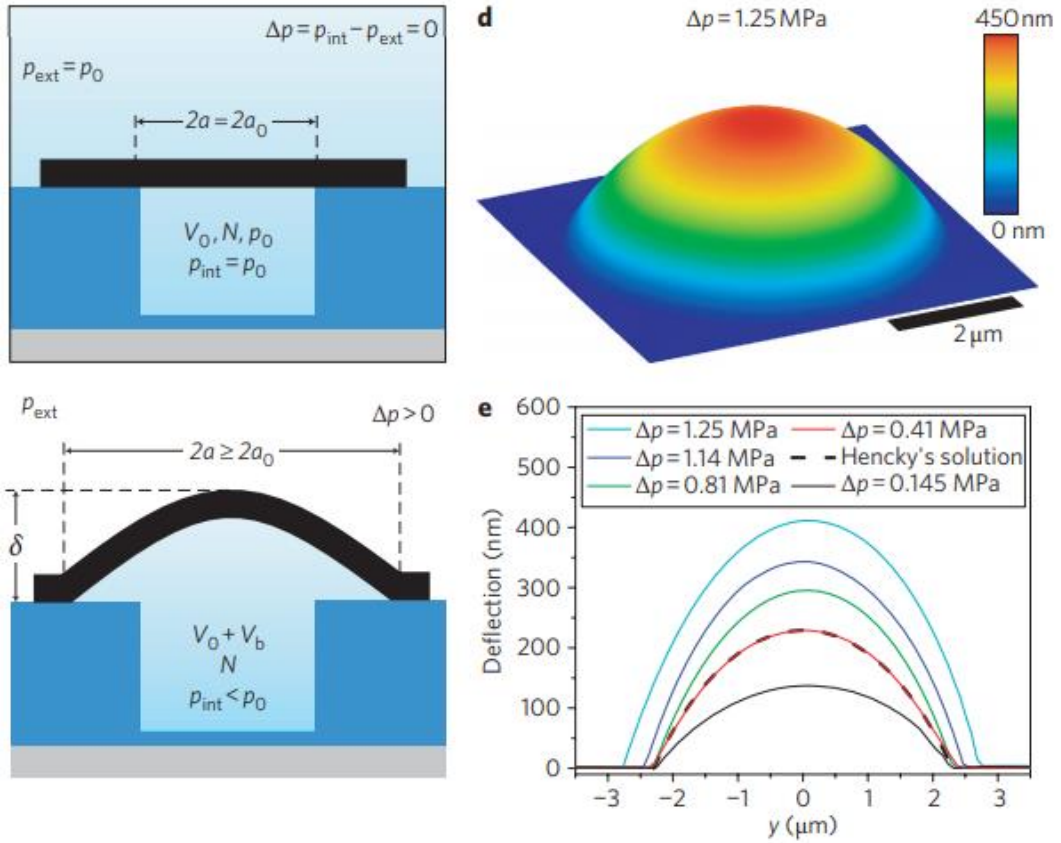


2D crystals – isolated crystallographic planes



A.K. Geim & I.V.Grigorieva, et al. *Nature* (2013)

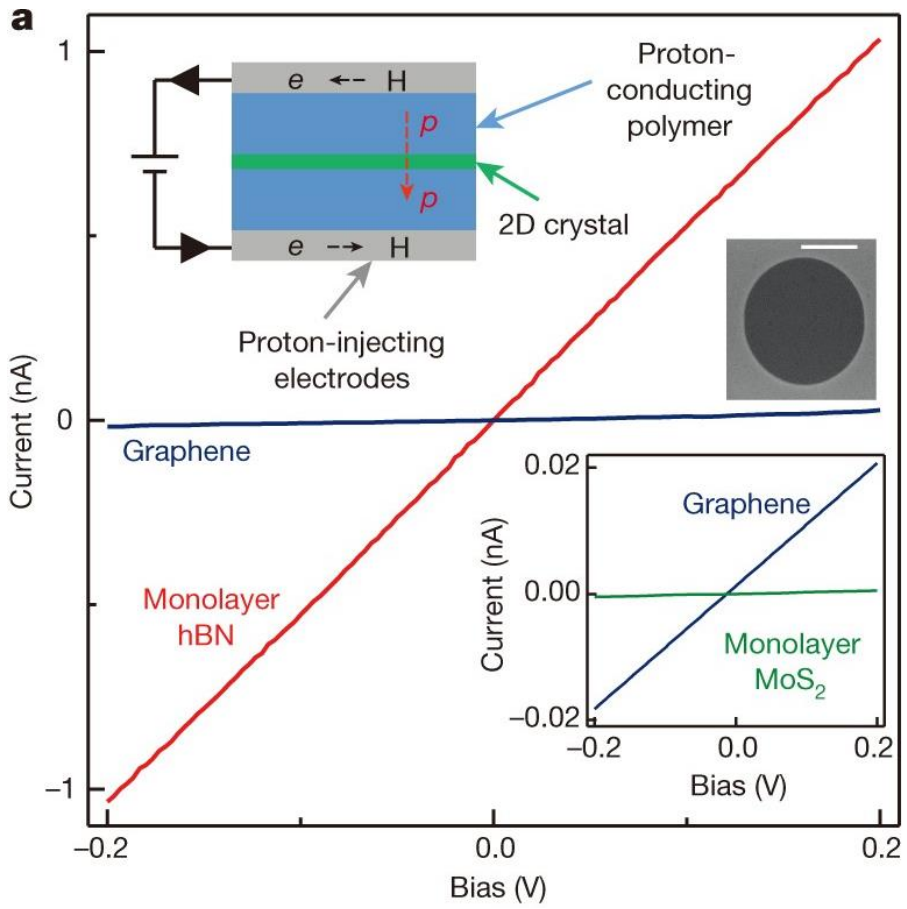
Impermeable to all atoms at ambient conditions



P. Sun, et al. *Nature* (2020)
J. S. Bunch, et al. *Nano Letters* (2008)
S. Koenig et al. *Nature Nanotechnology* (2012)
L. Wang et al. *Nature Nanotechnology* (2015)

Graphene is perfectly selective proton conductor out of plane

Excellent out-of-plane proton conductor



S. Hu, et al *Nature* (2014)

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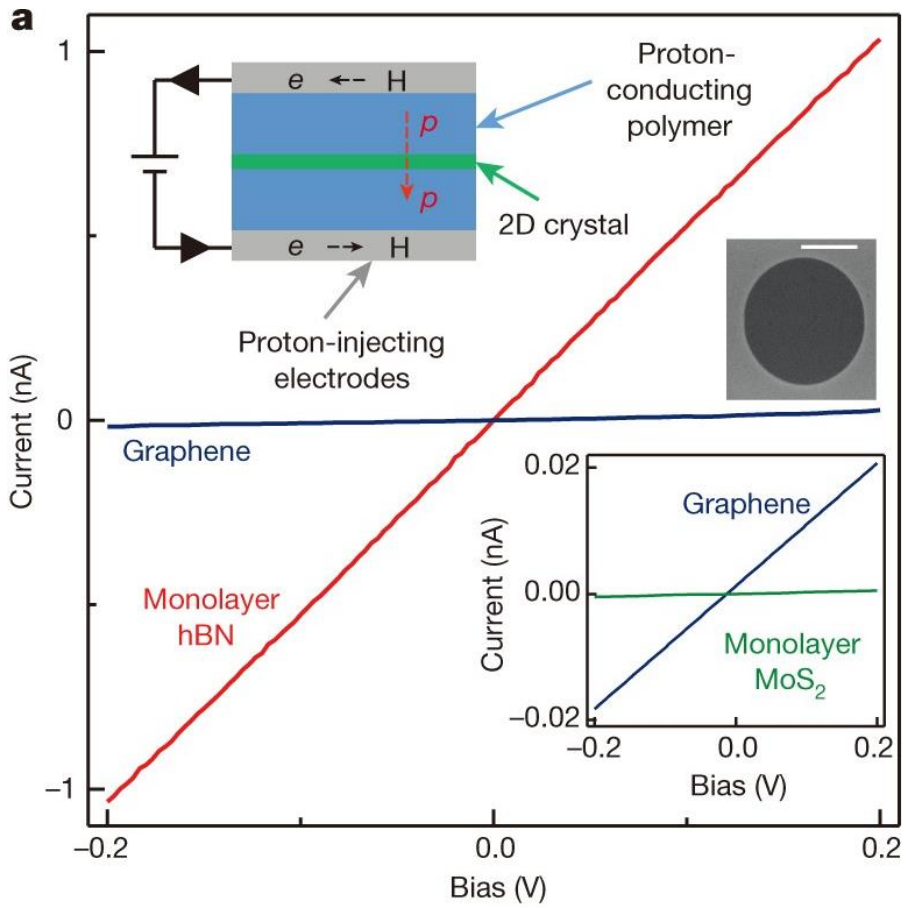
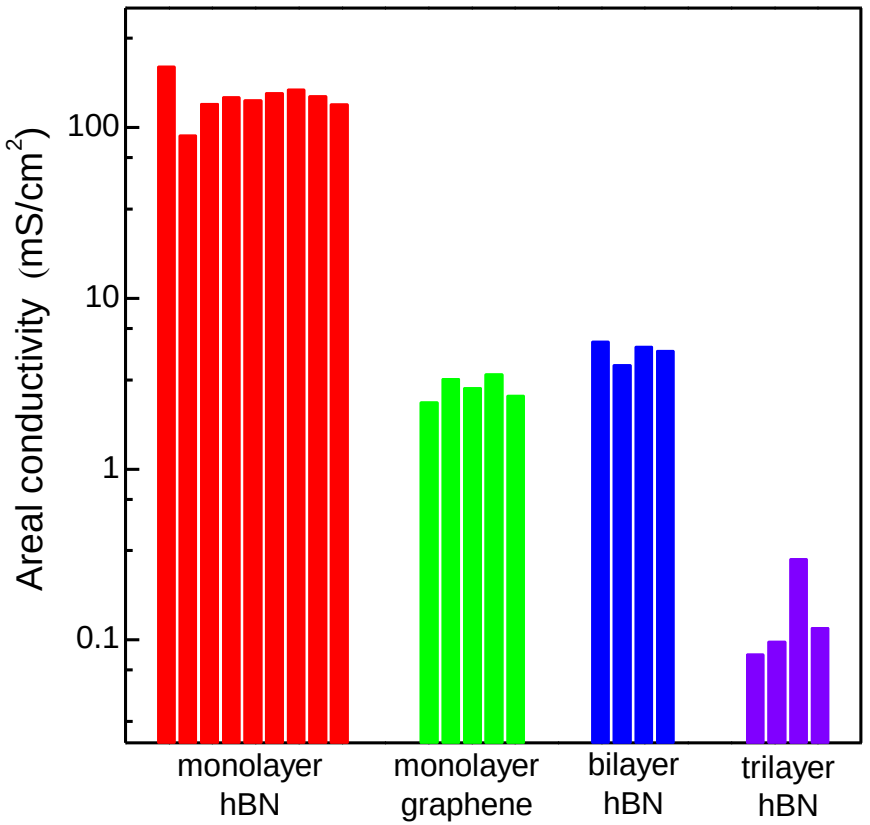
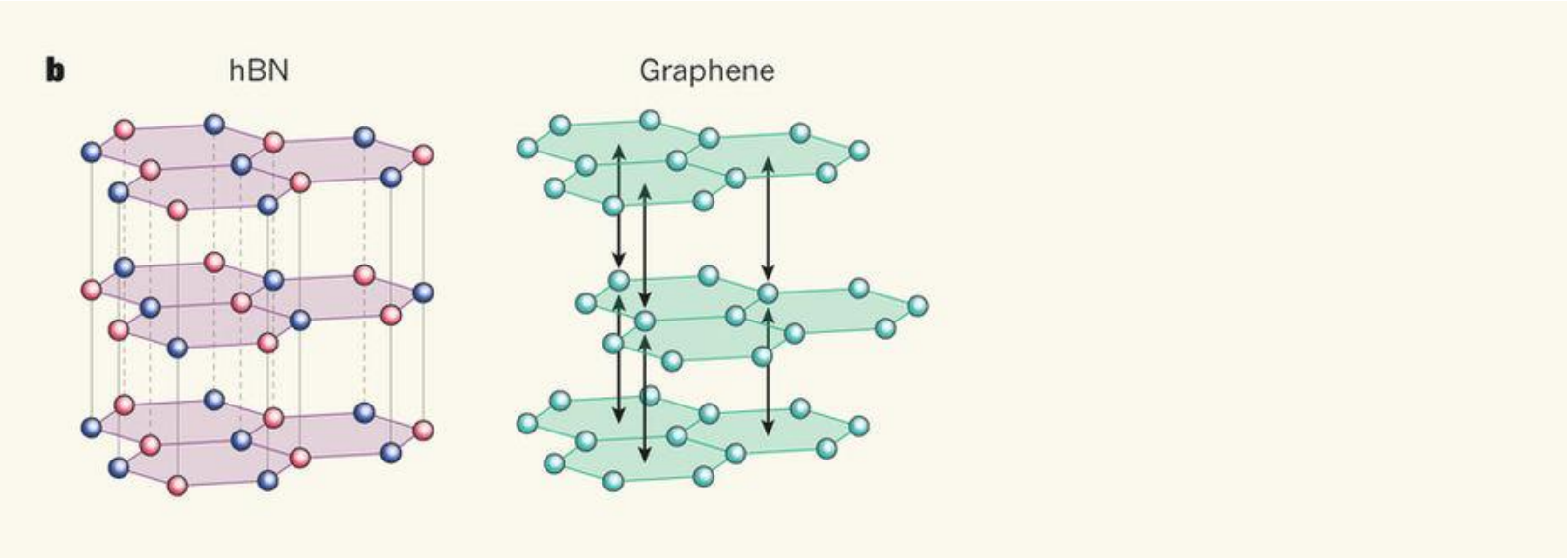




S. Hu, et al *Nature* (2014)

Interpreation: Protons pierce the pristine crystal lattice



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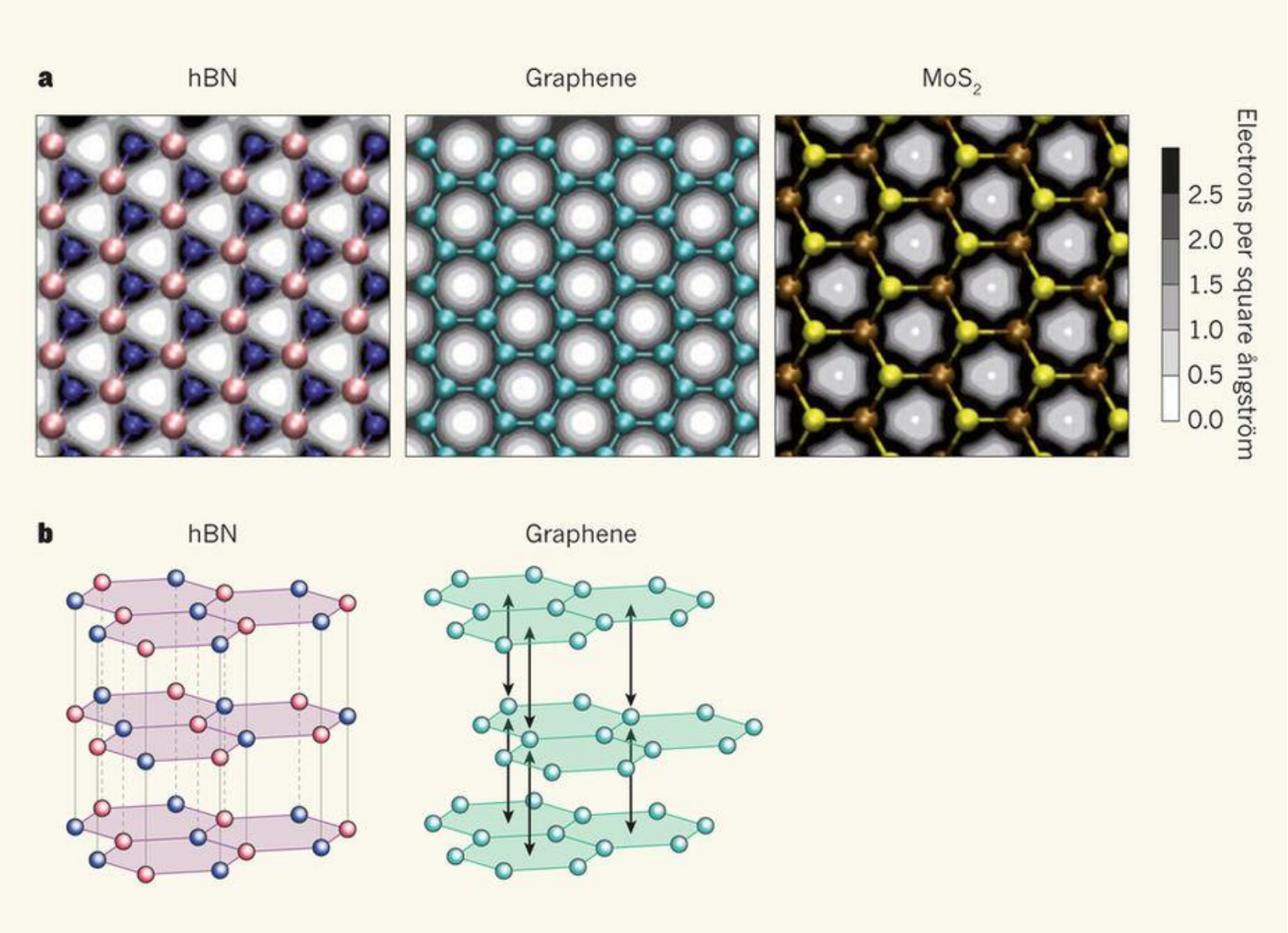
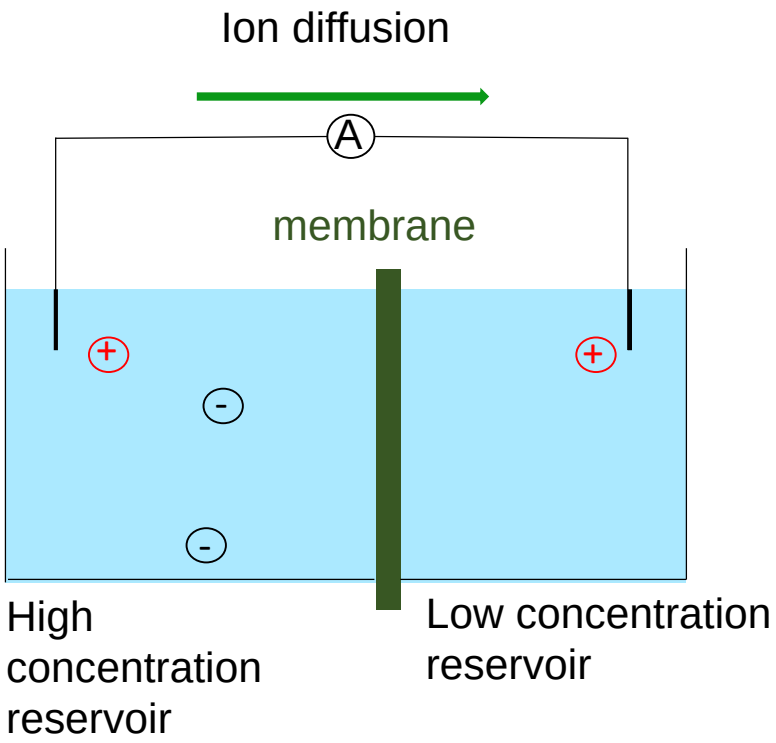
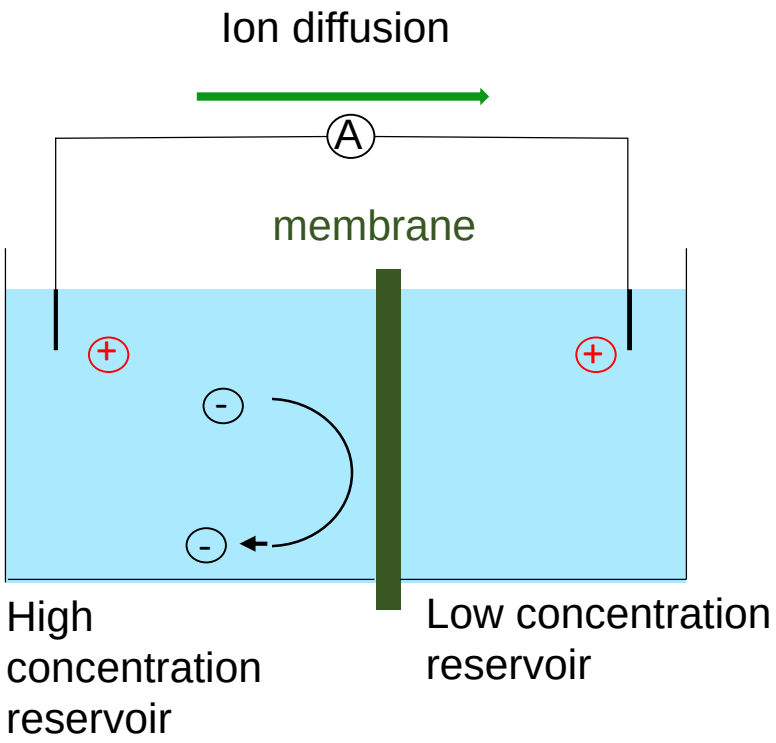
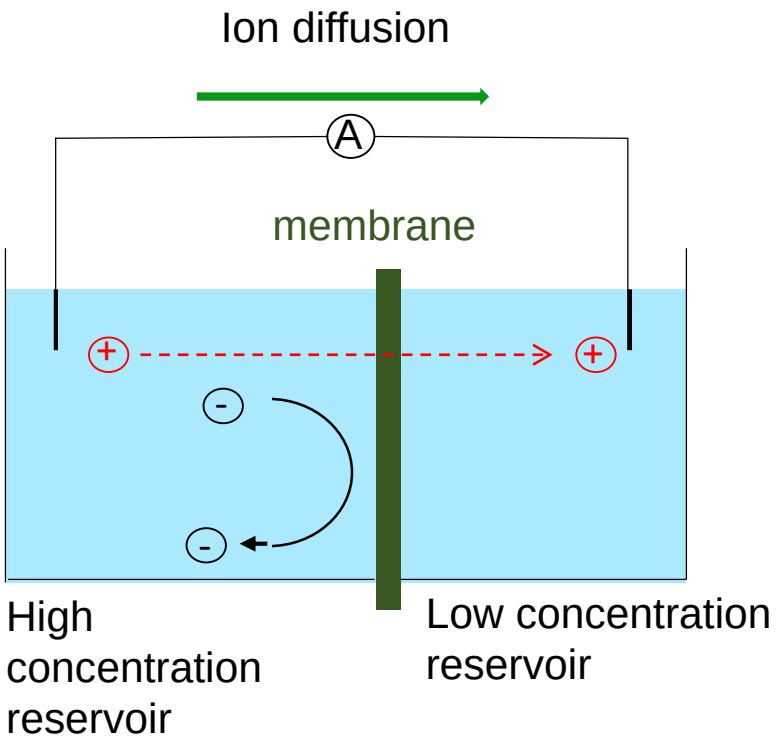


Ion selectivitiy




Ion diffusion
A
membrane
+
+
-
-
High concentration reservoir
Low concentration reservoir


Ion diffusion
A
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+
+
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High concentration reservoir
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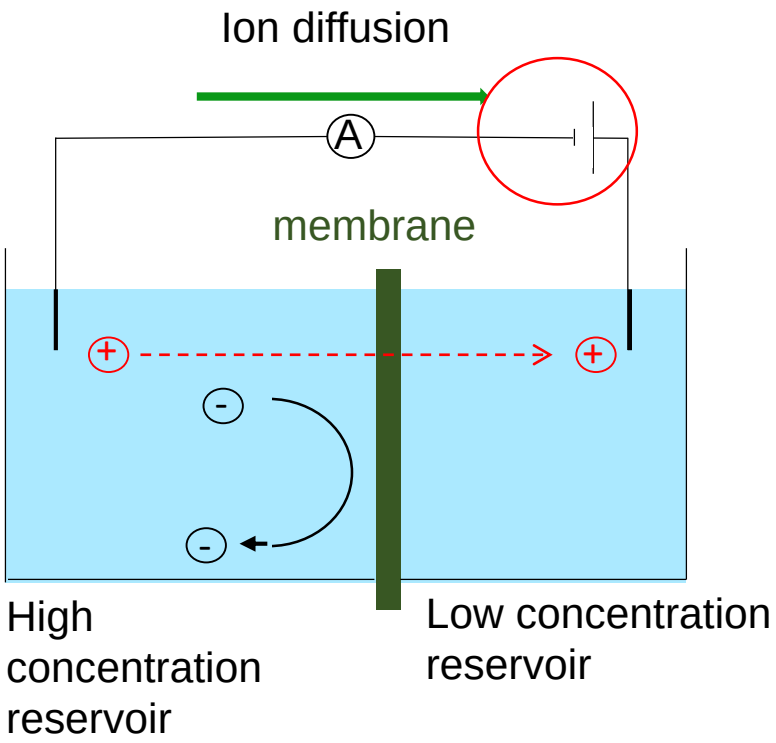
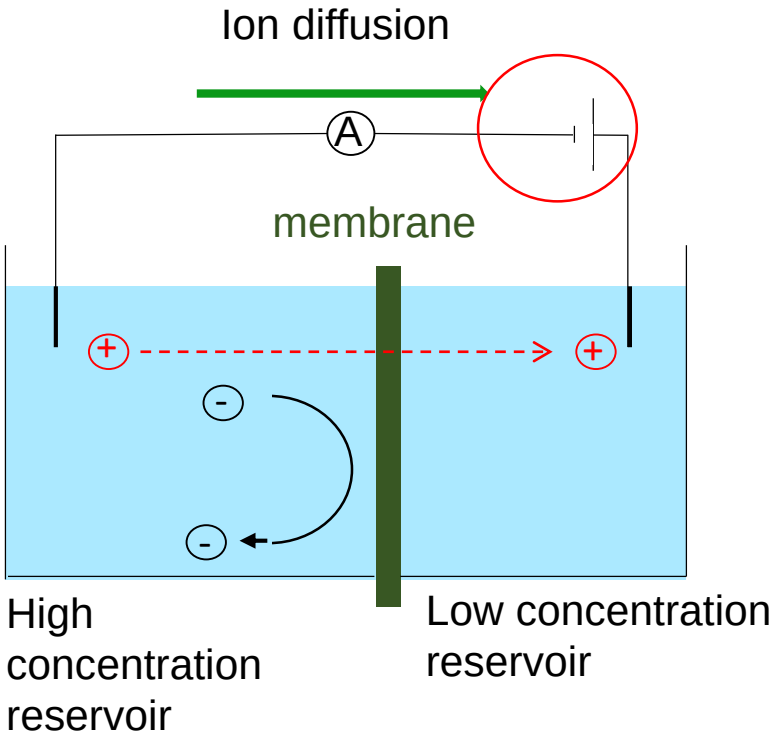
Nernst potential – stops current

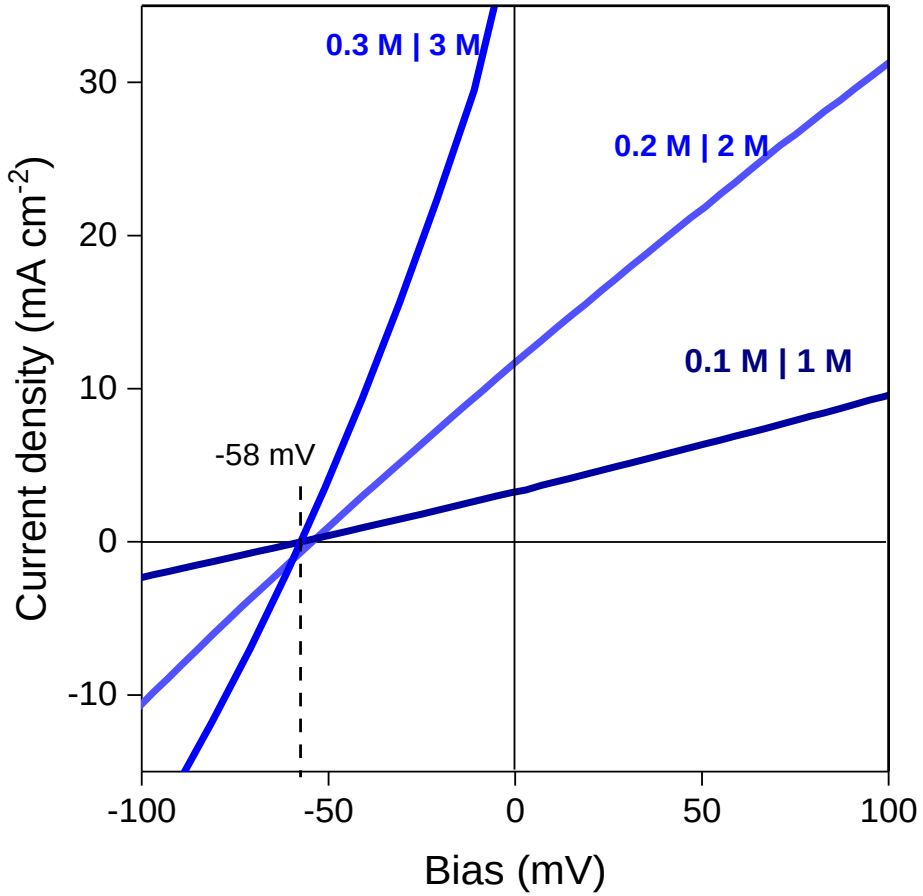


$V_0 = -(k_B T/e) \ln(\Delta C)$

Nernst relation

Perfect proton selectivity





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L. Mogg et al. *Nature Comms* (2019)

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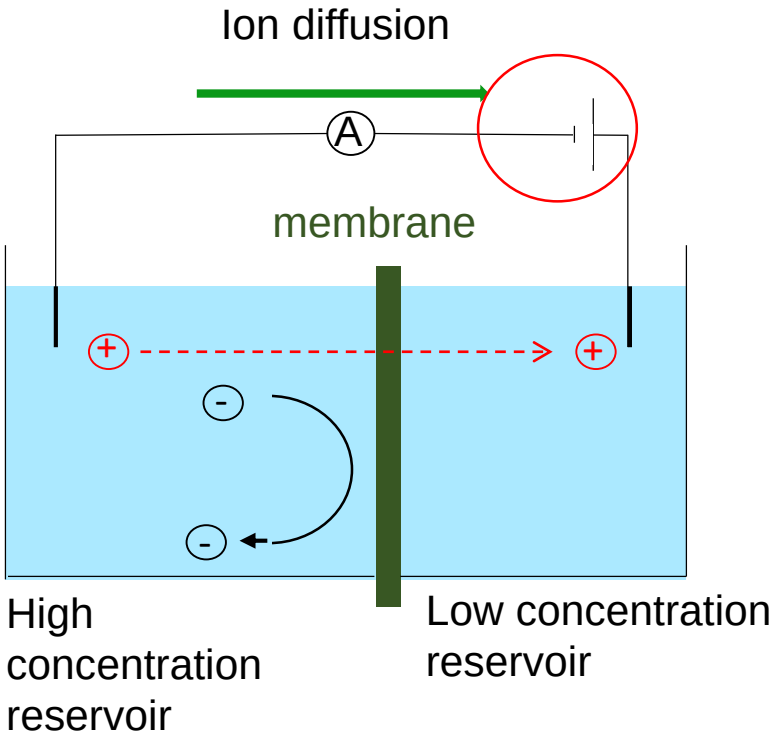

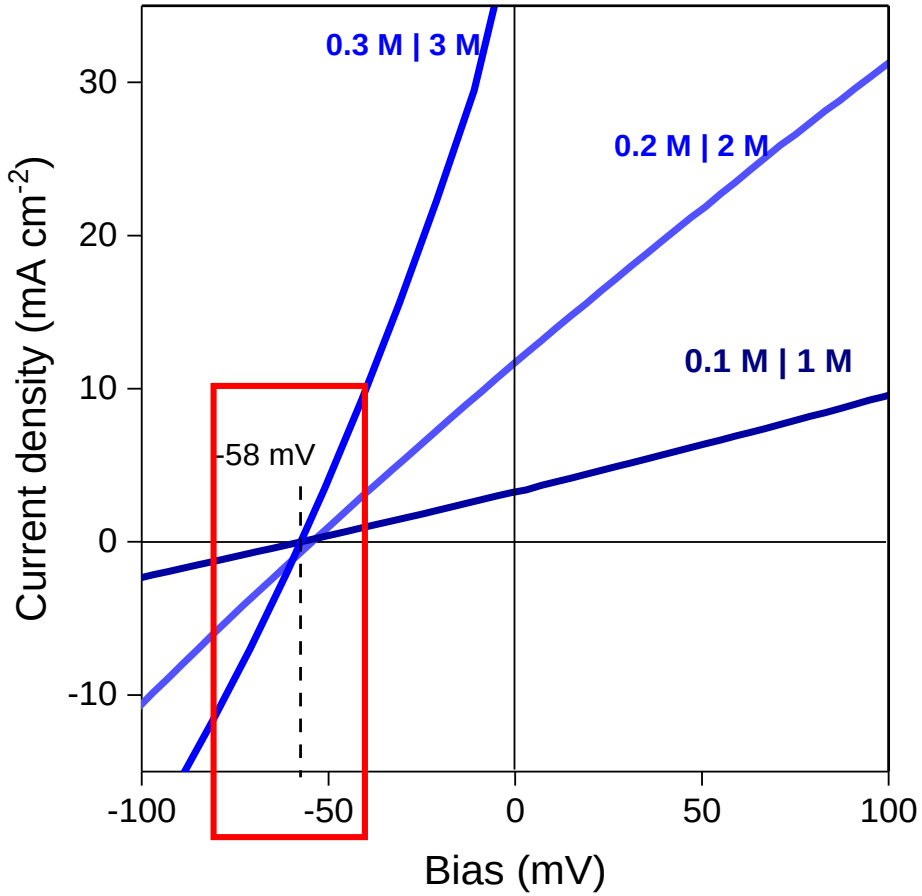

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L. Mogg et al. *Nature Comms* (2019)

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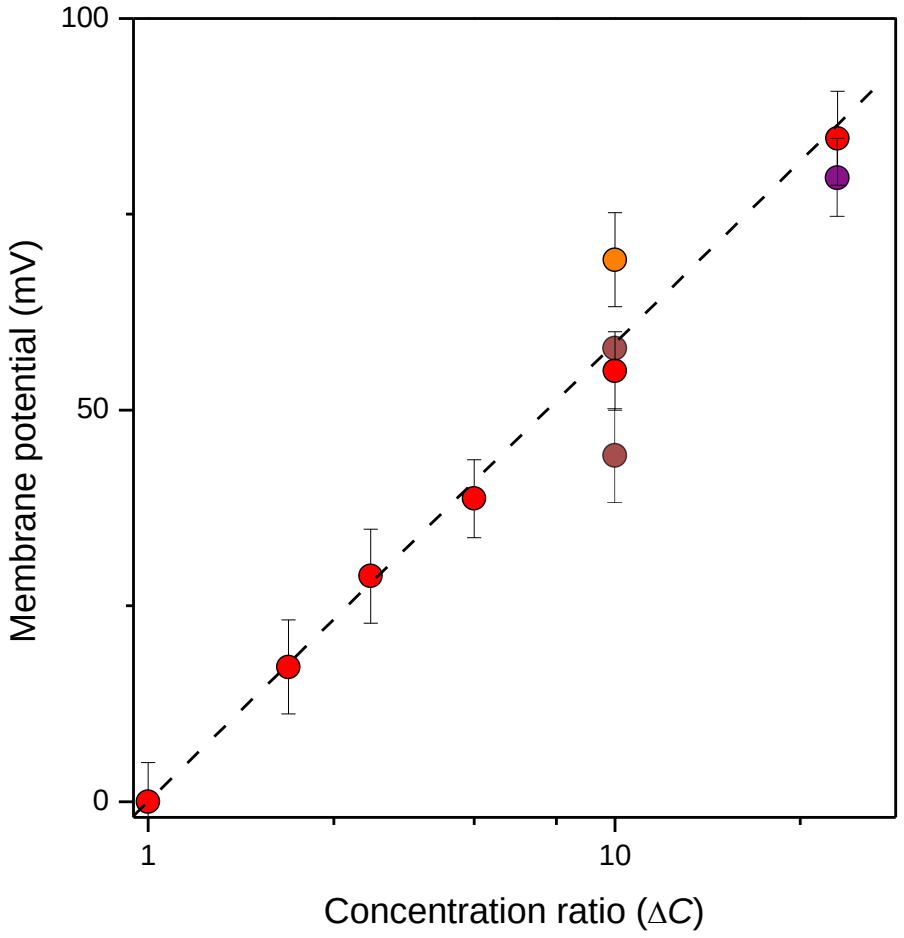
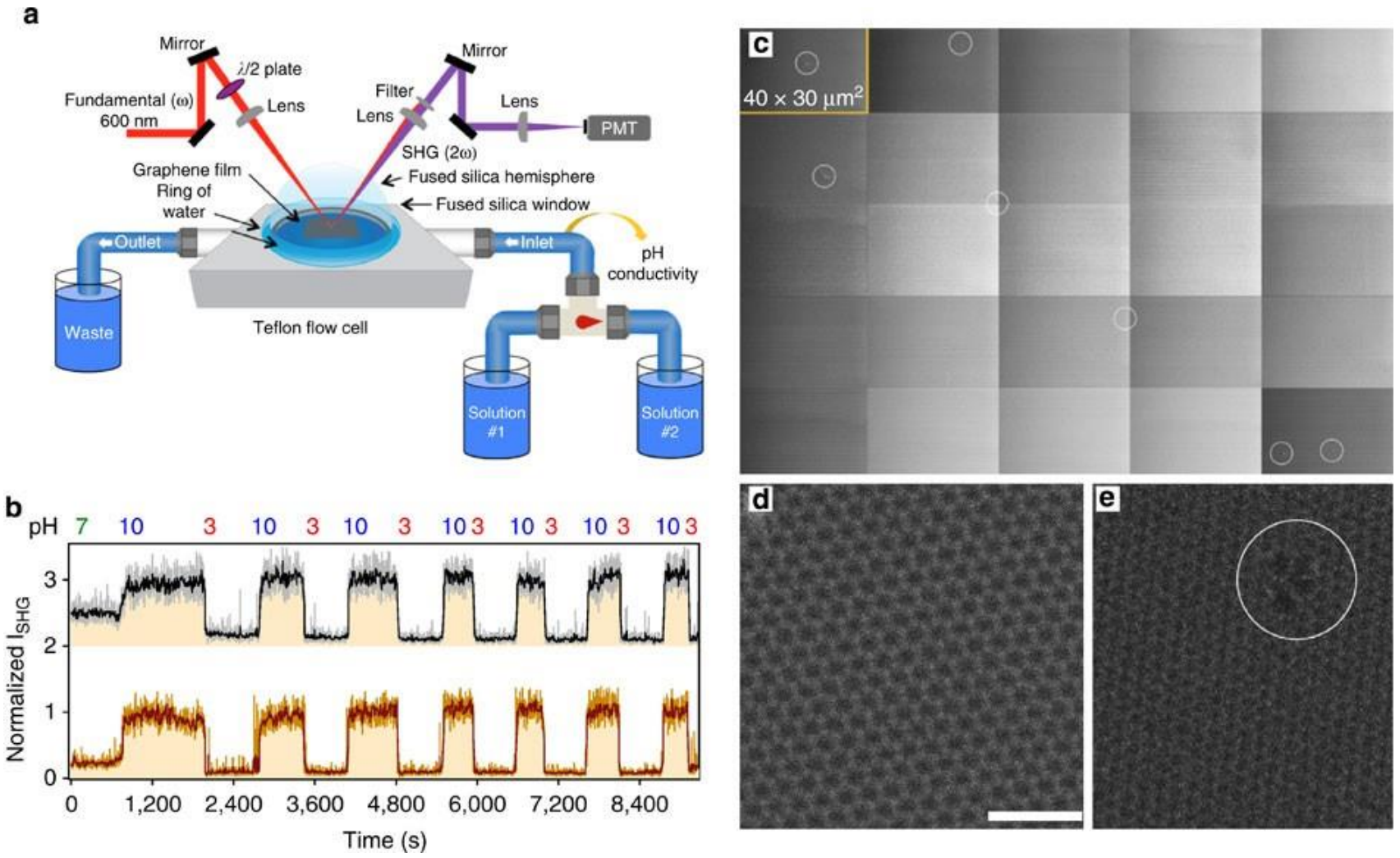
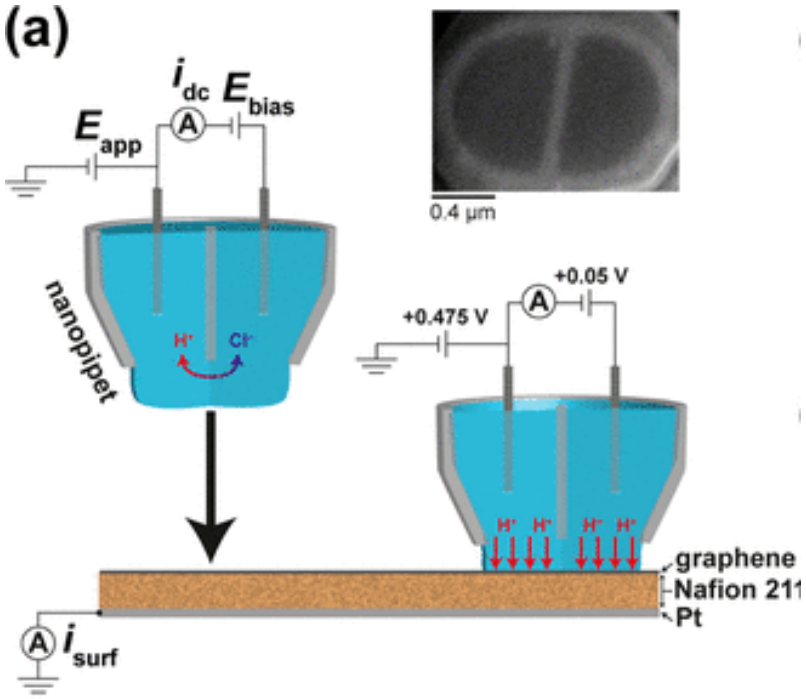


Alternative interpretation: transport through small defects



J. Achtyl et al. *Nat. Comms.* (2014).

SECCM of CVD devices: huge currents (nA) scattered in rare spots



C. Bentley et al. *ACS Nano.* (2022).

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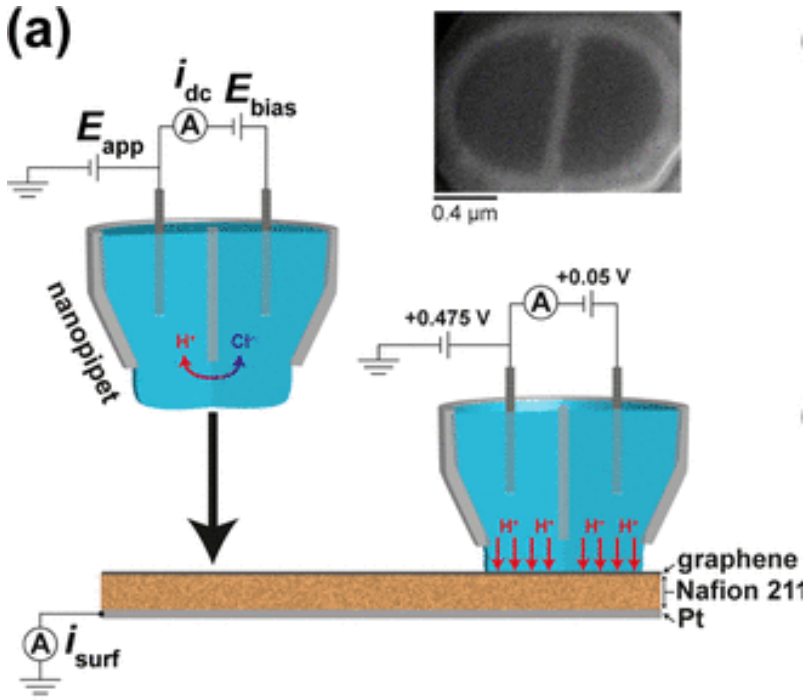
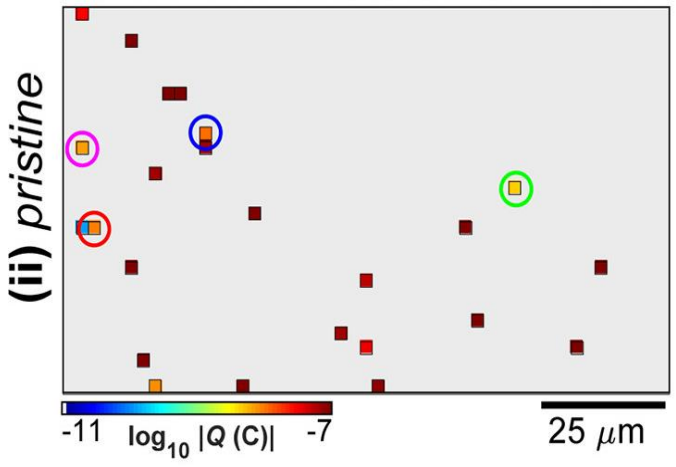
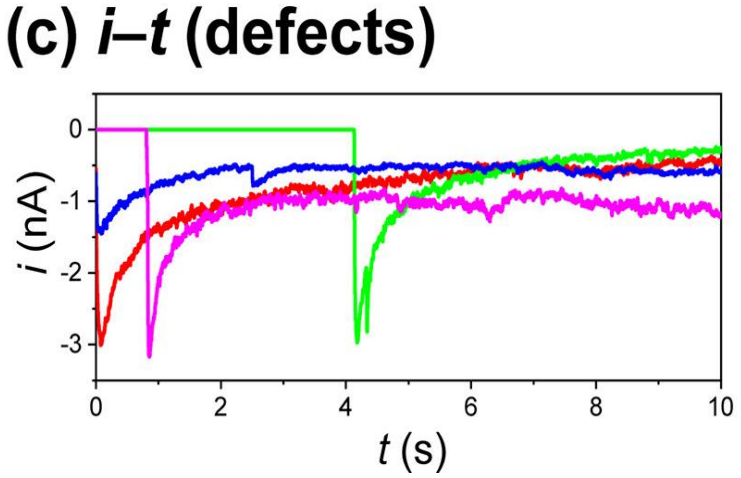
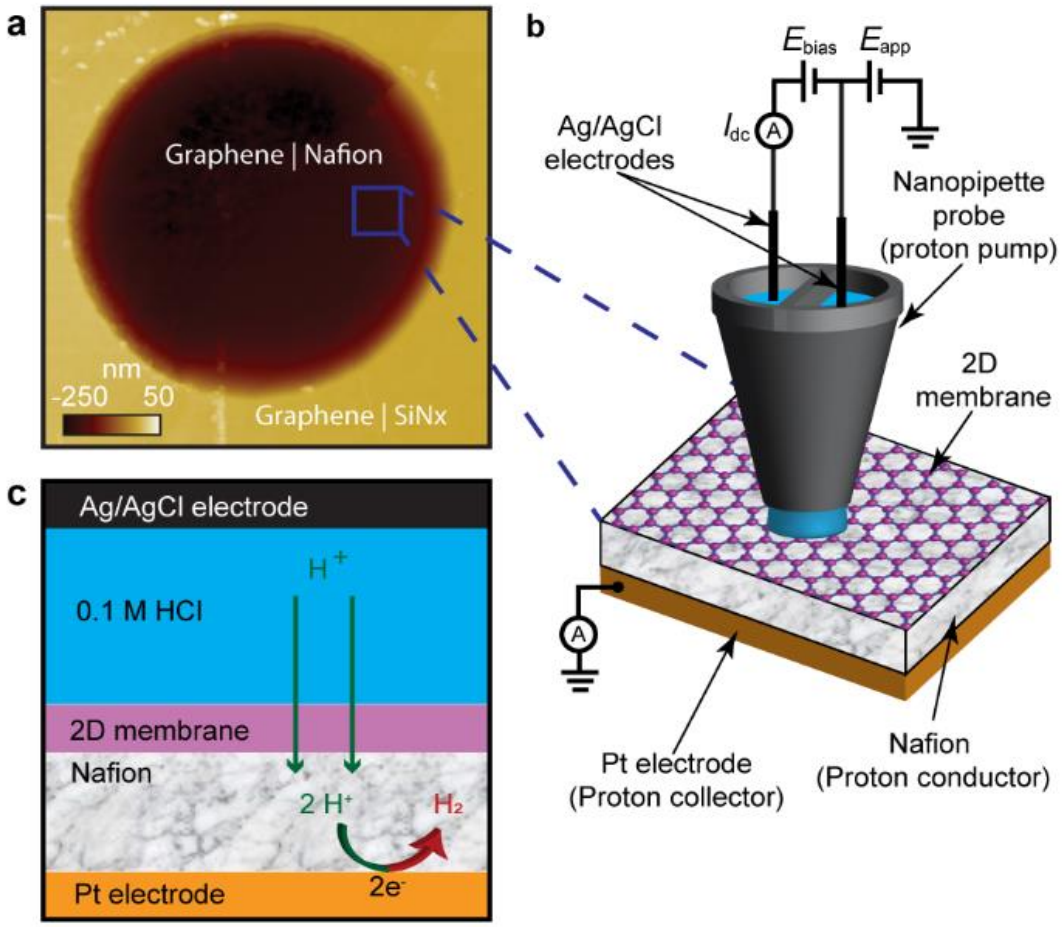






C. Bentley et al. *ACS Nano.* (2022).

SECCM of mechanically exfoliated graphene



Collaboration with Prof. Pat Unwin, Warwick

O. Wahab et al. *Nature.* In press.

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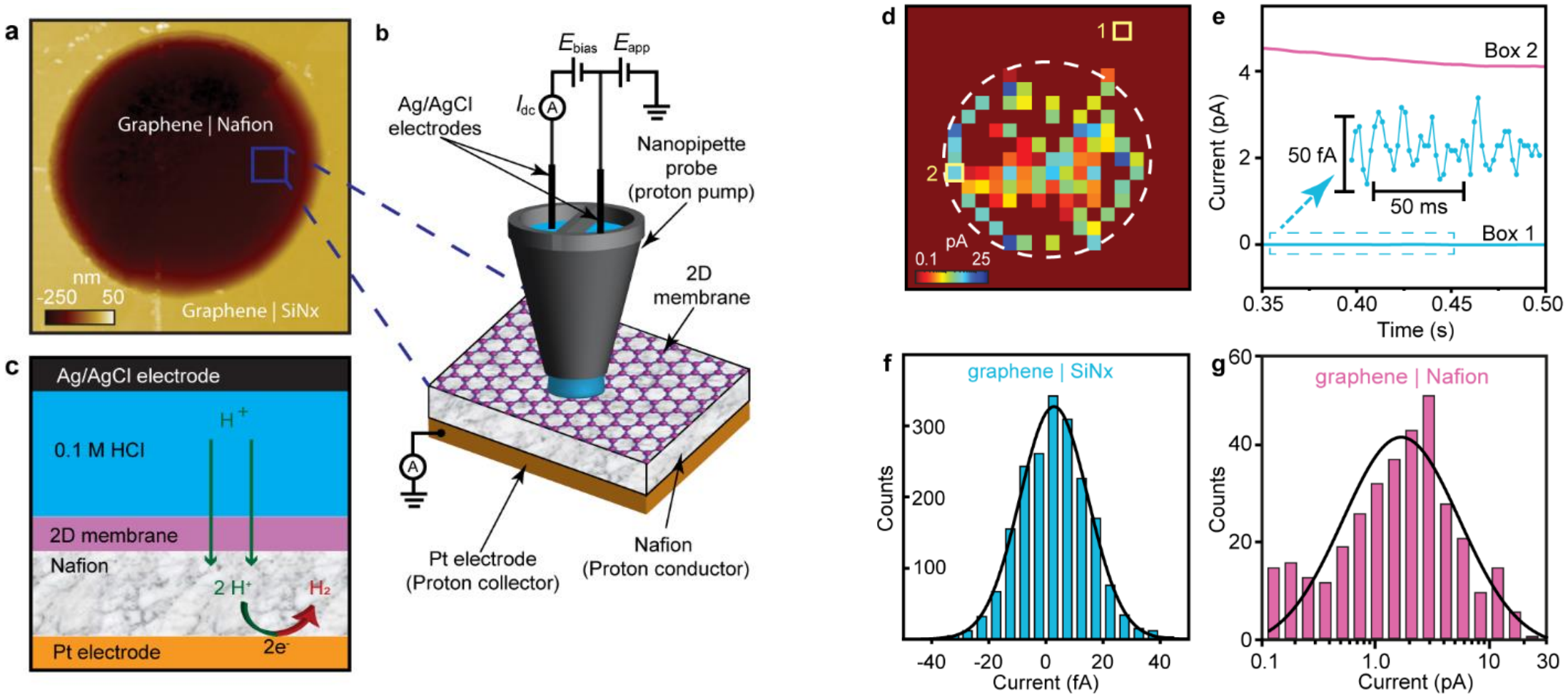

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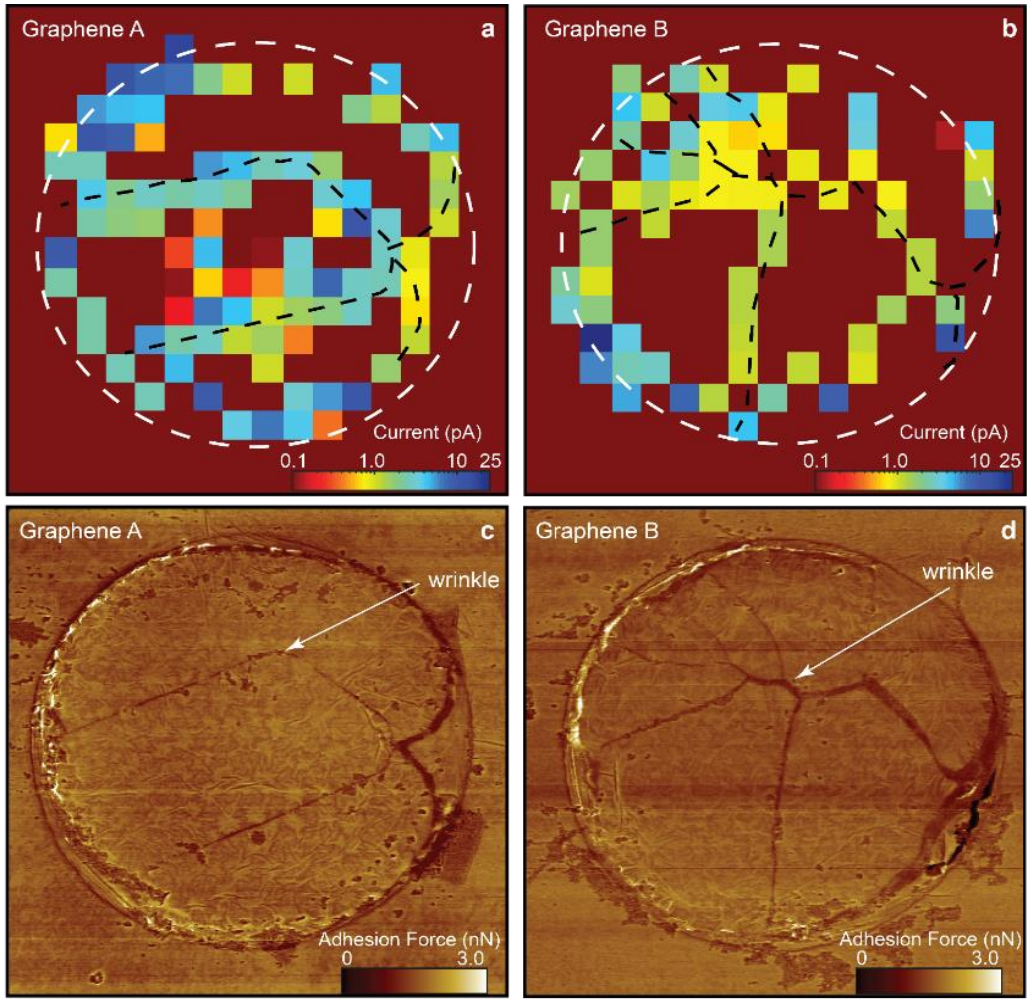
Nanoscale non-flatness accelerates proton transport



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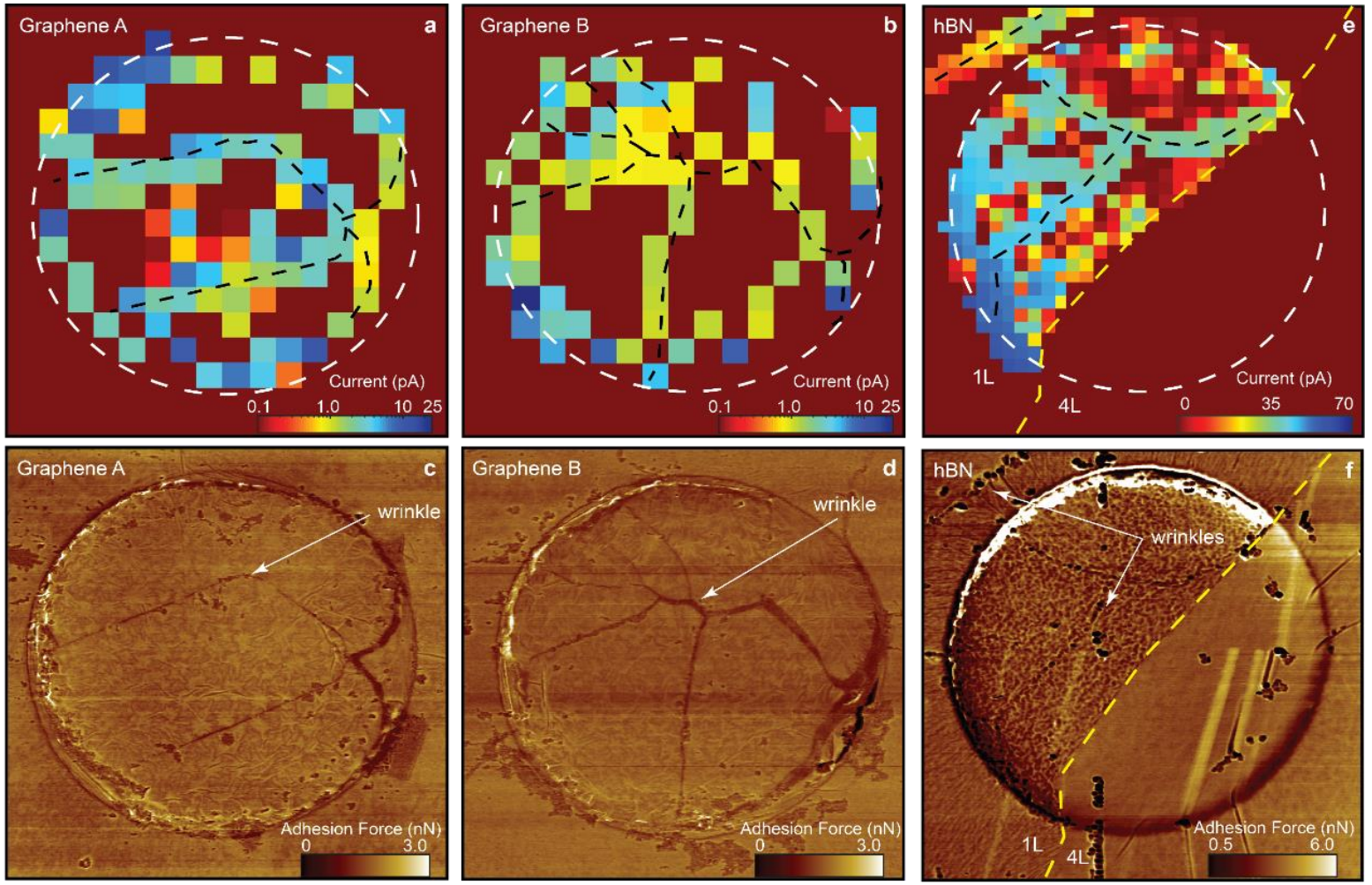

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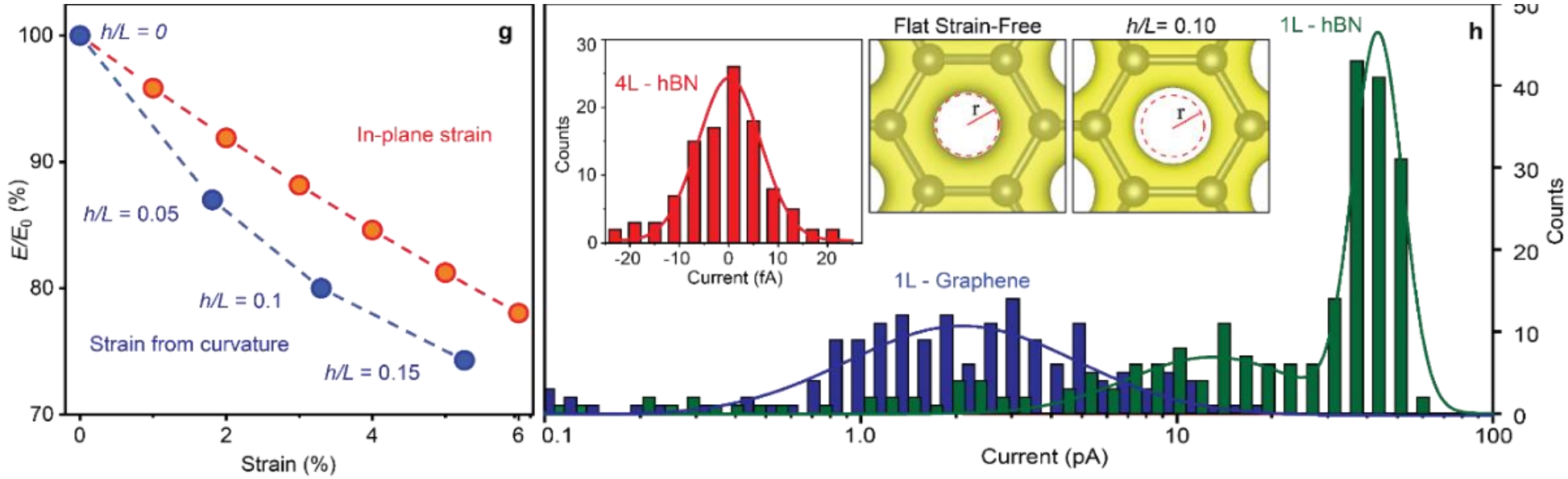
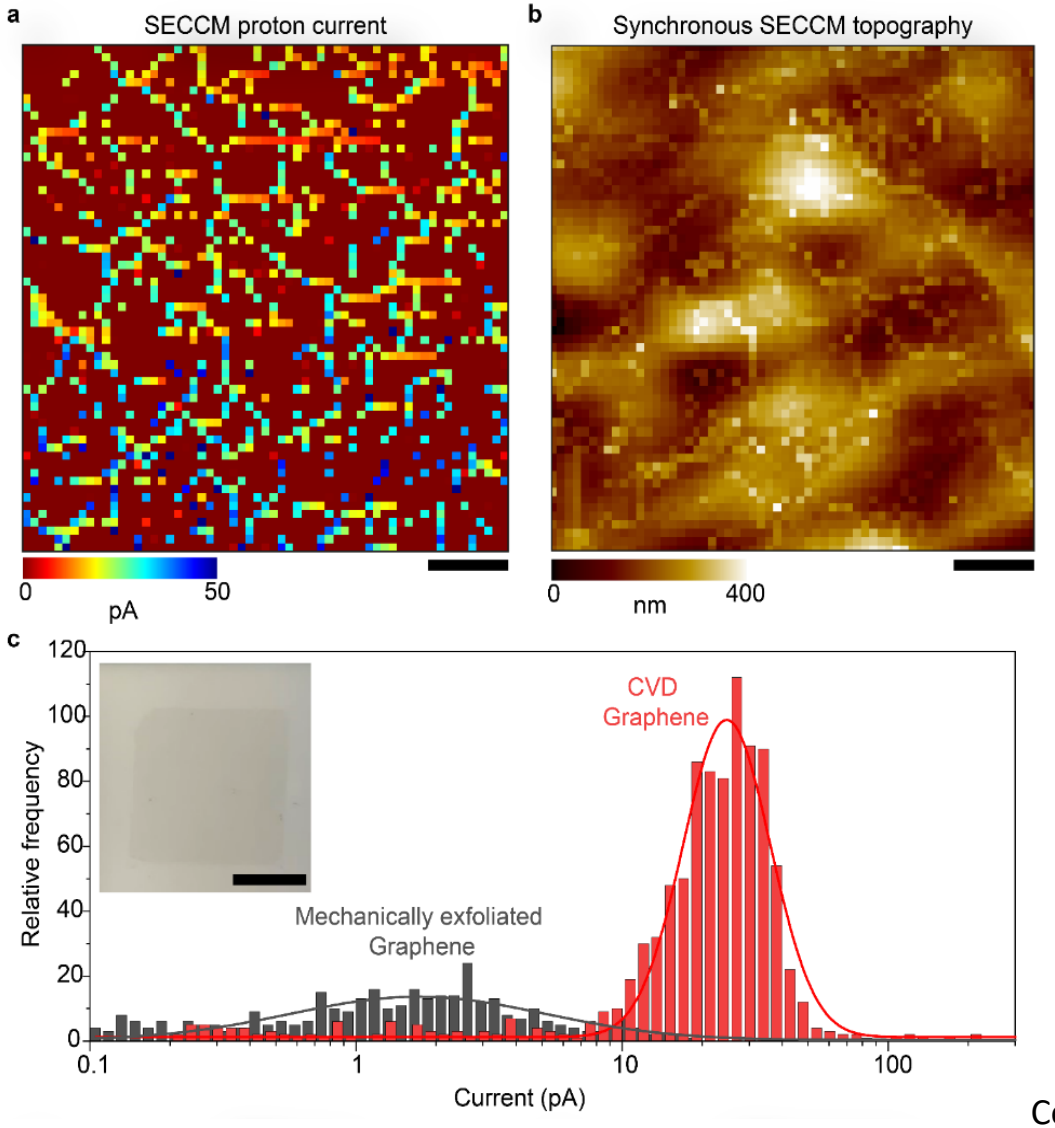
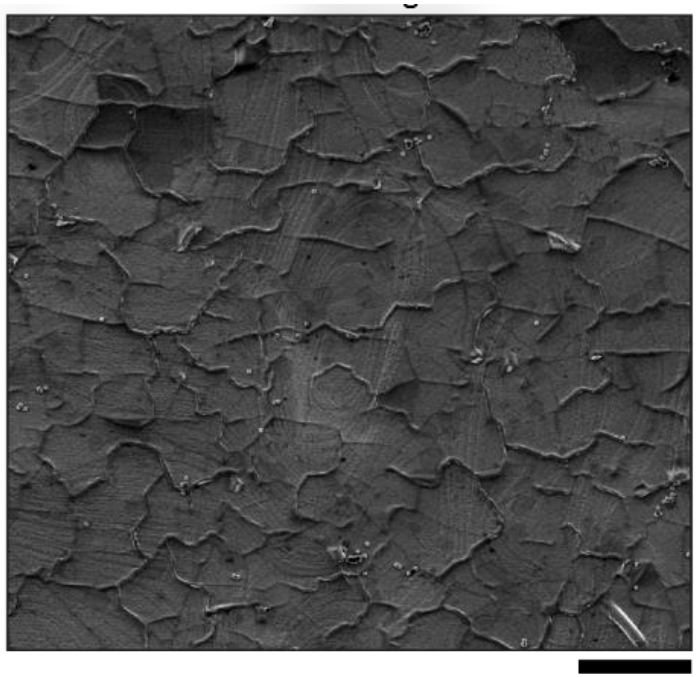


Collaboration with Prof. Pat Unwin, Warwick

O. Wahab et al. *Nature.* In press.

Scans of our CVD devices: no large fluxes, no holes. Enhanced activity in grain boundaries





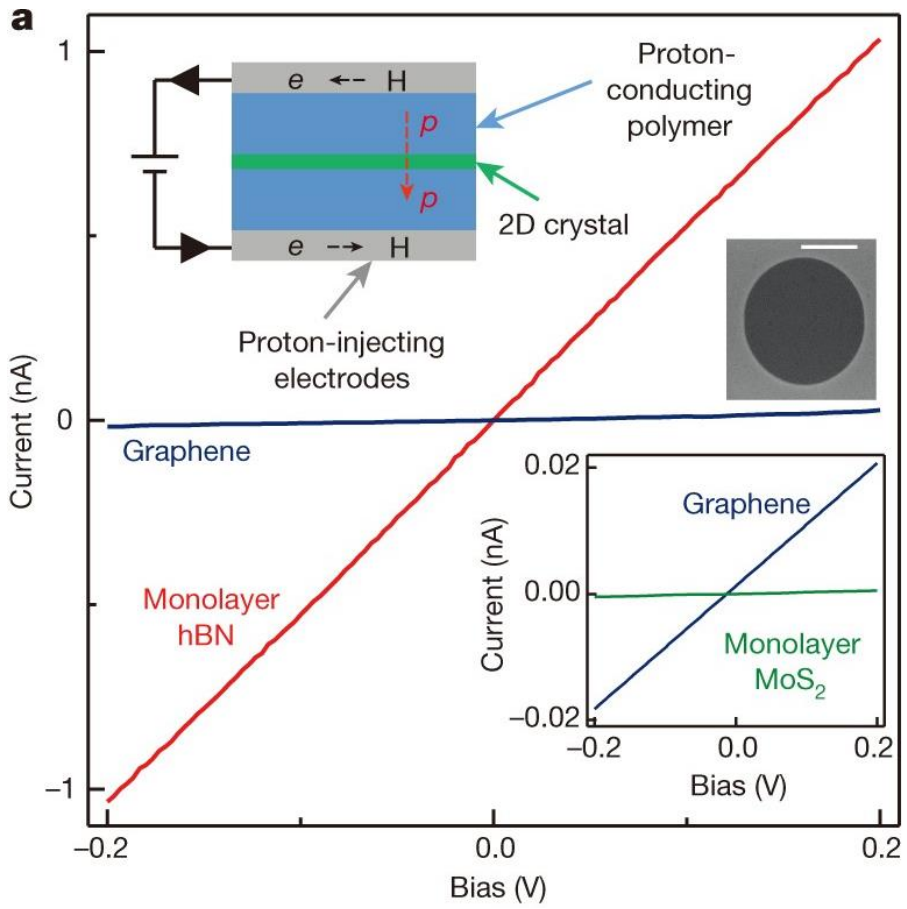
Collaboration with Prof. Pat Unwin, Warwick

O. Wahab et al. *Nature.* In press.

Interfacial water dissociation

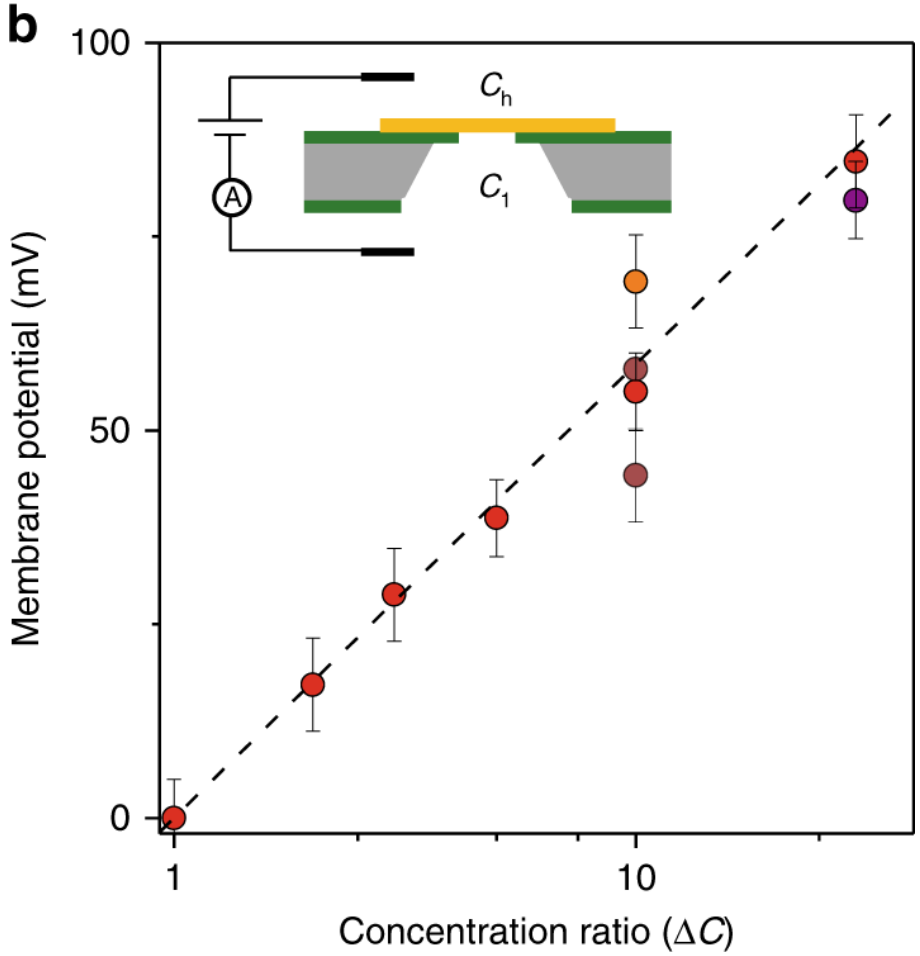
Graphene is perfectly selective proton conductor

Excellent out-of-plane proton conductor



S. Hu, et al *Nature* (2014)

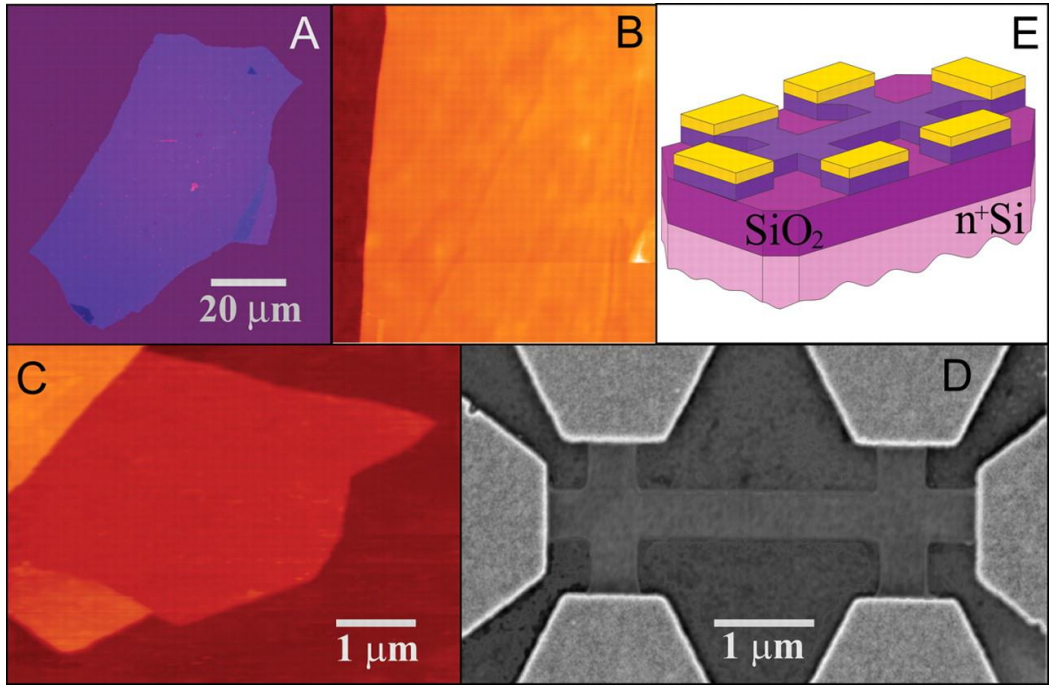
Impermeable to all other ions



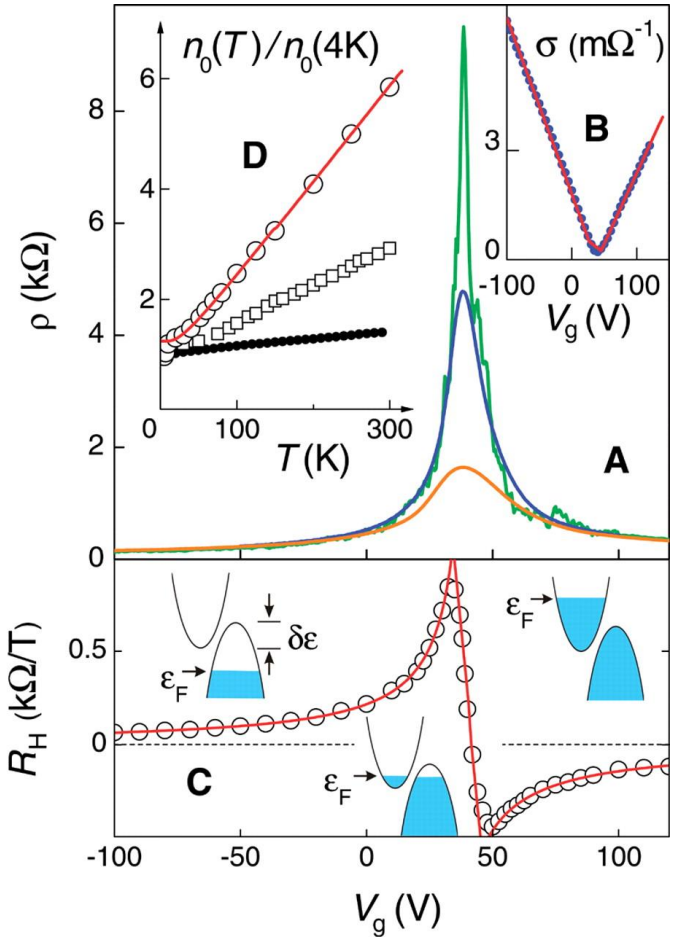
L. Mogg, et al *Nat. Comms.* (2019)

Graphene is an excellent in plane electron conductor

Excellent in-plane electron conductor

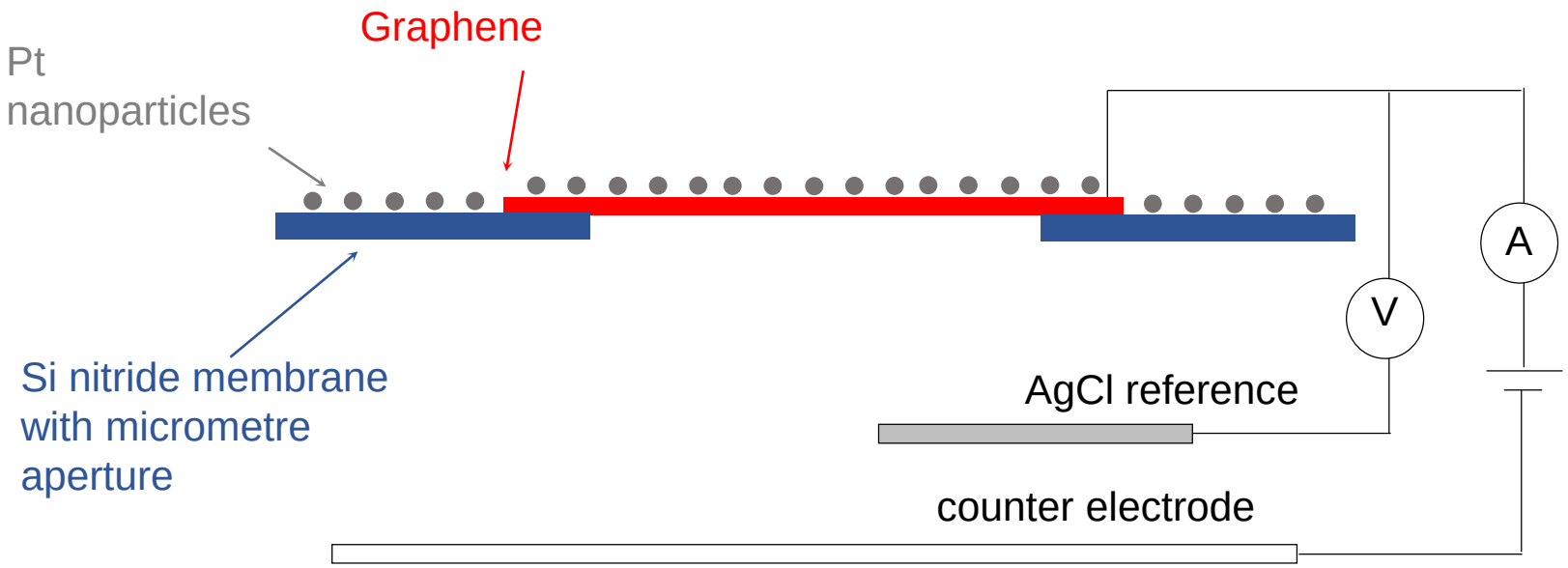


Gate tuneable Fermi energy provides
knowledge of interfacial charge density



K.S. Novoselov, et al *Science* (2004)

Proton permeable graphene electrodes



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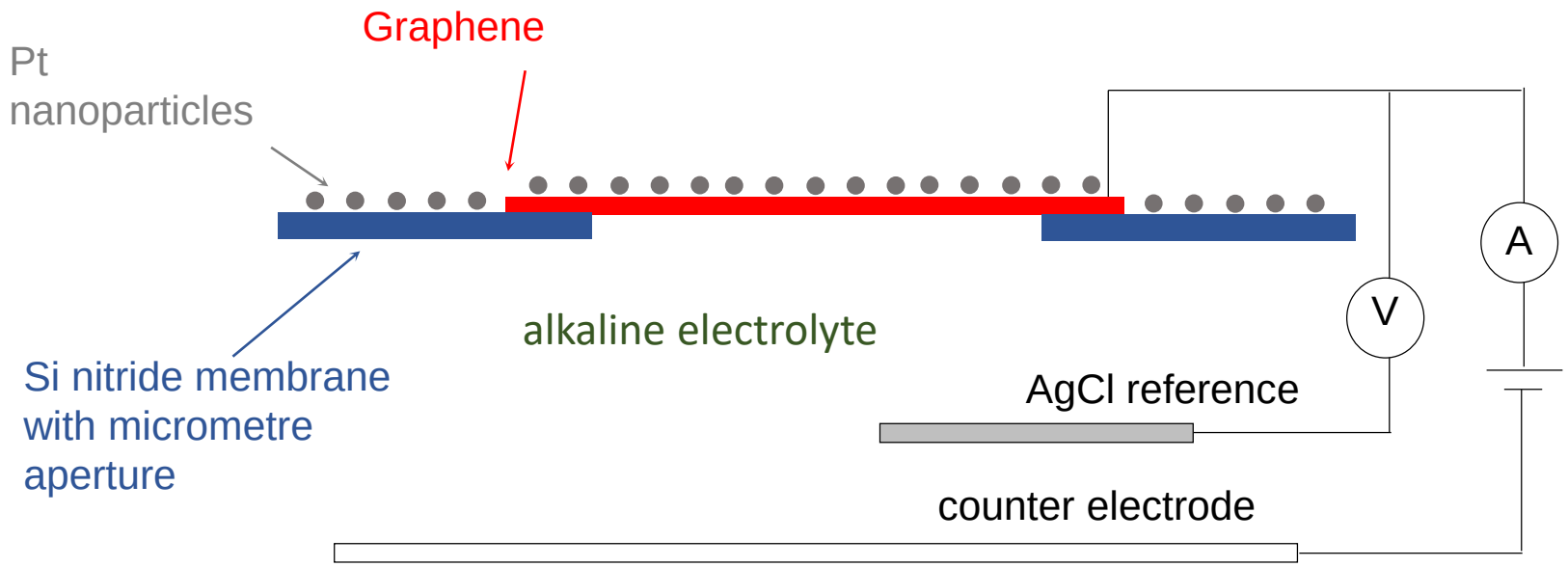
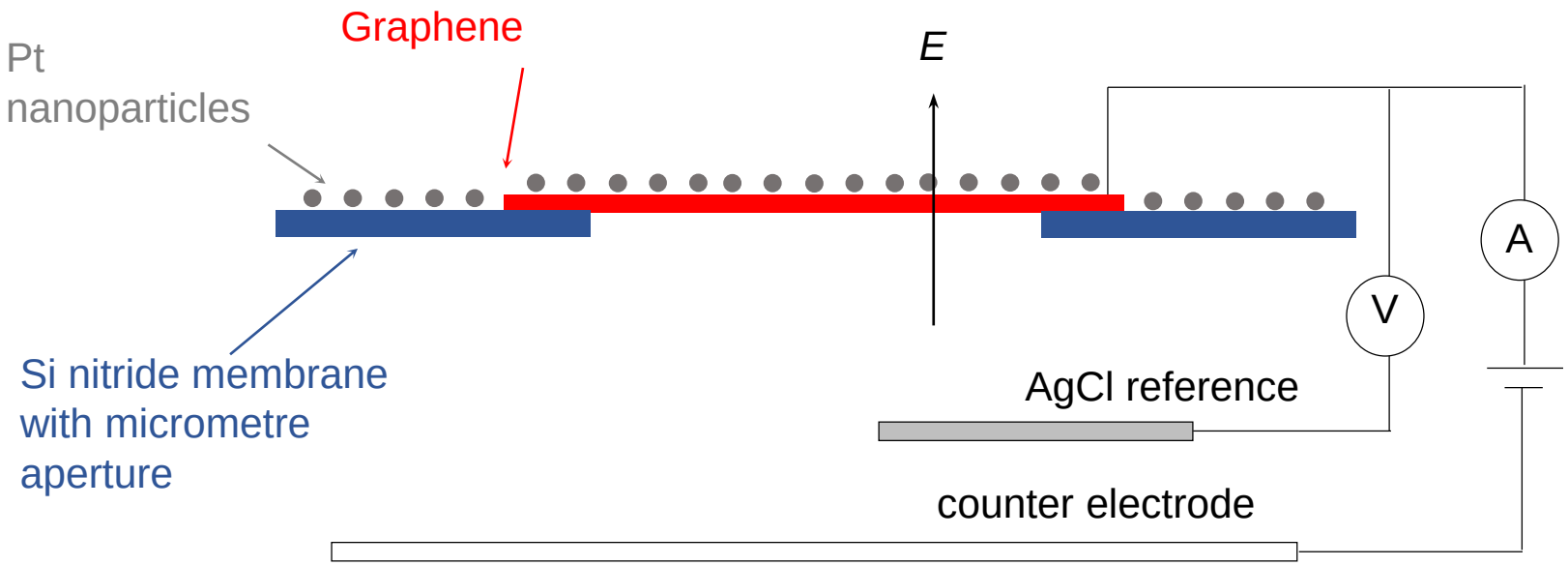


Alkaline pH ensures all protons come from water dissociation

Proton permeable graphene electrodes



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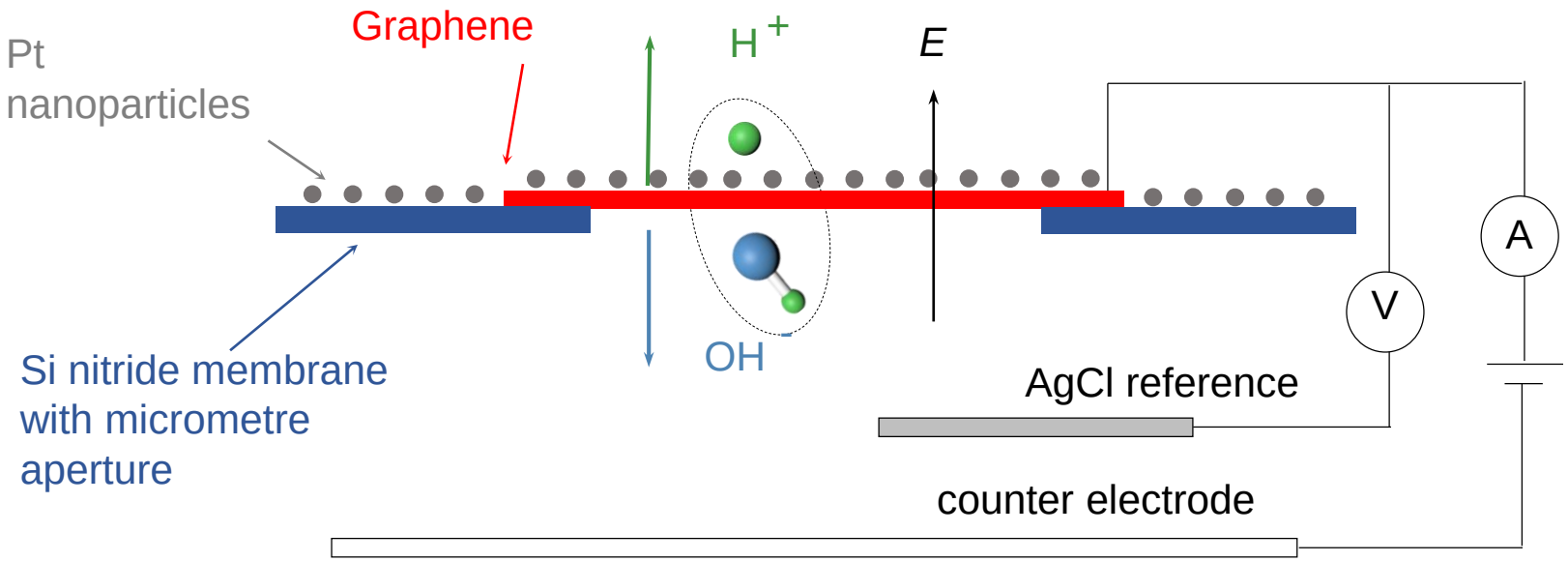
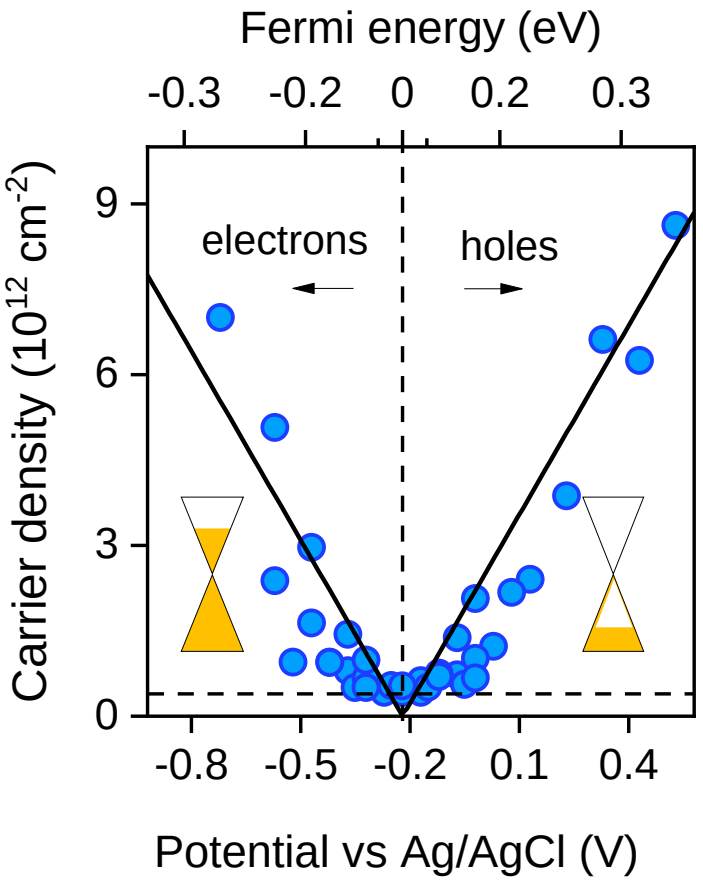
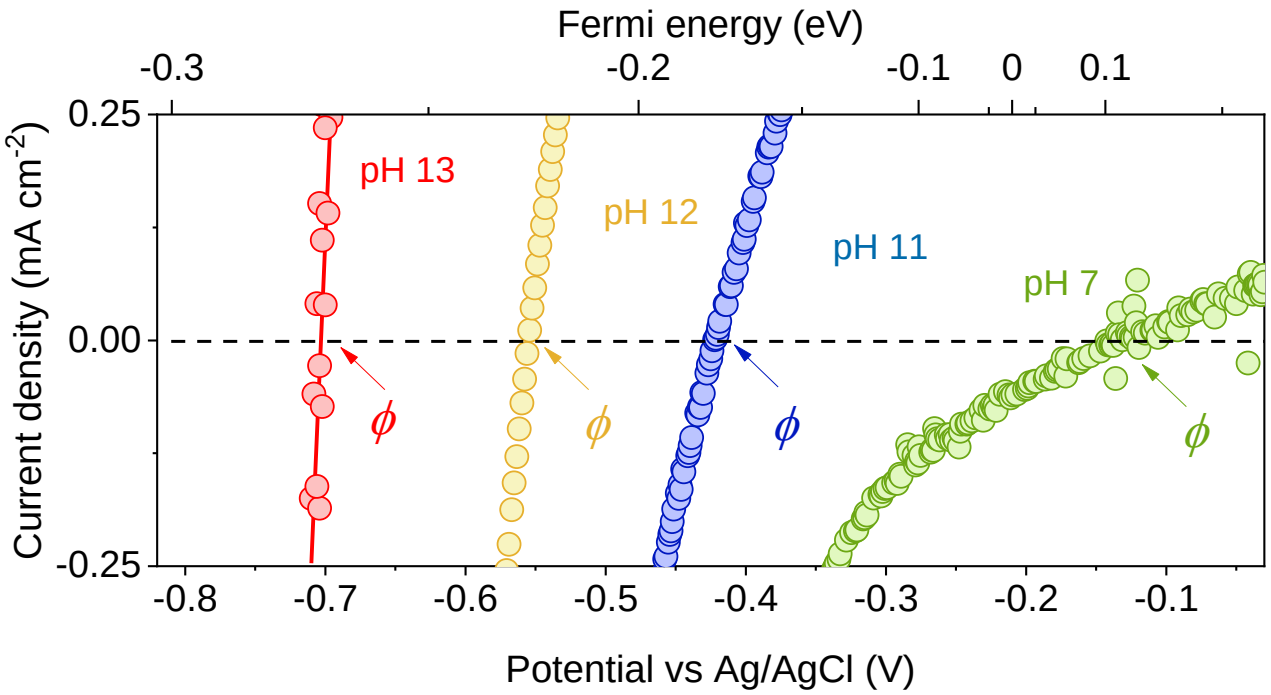


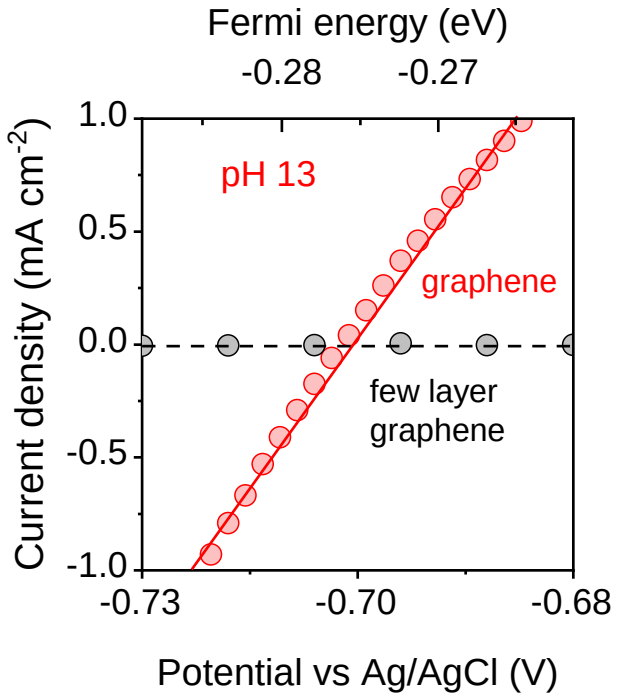
Fermi energy and n can be characterised in situ with Raman



Intrinsic proton currents as a function of pH

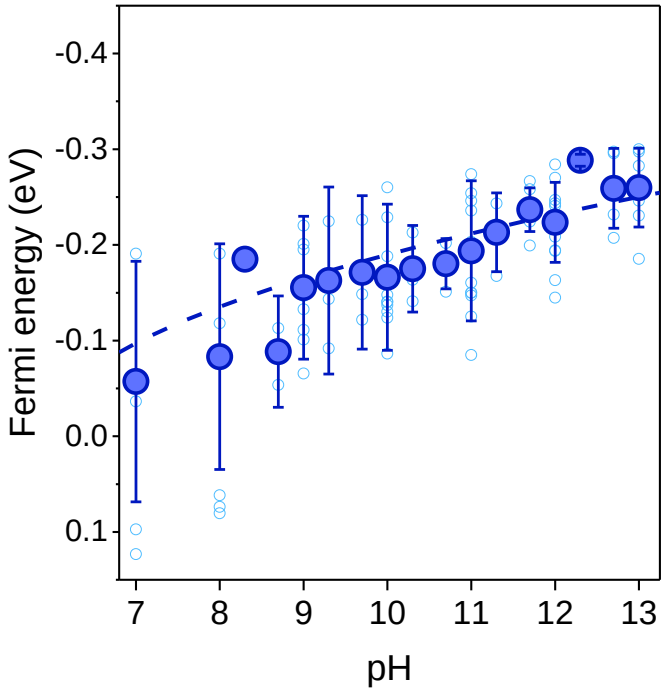


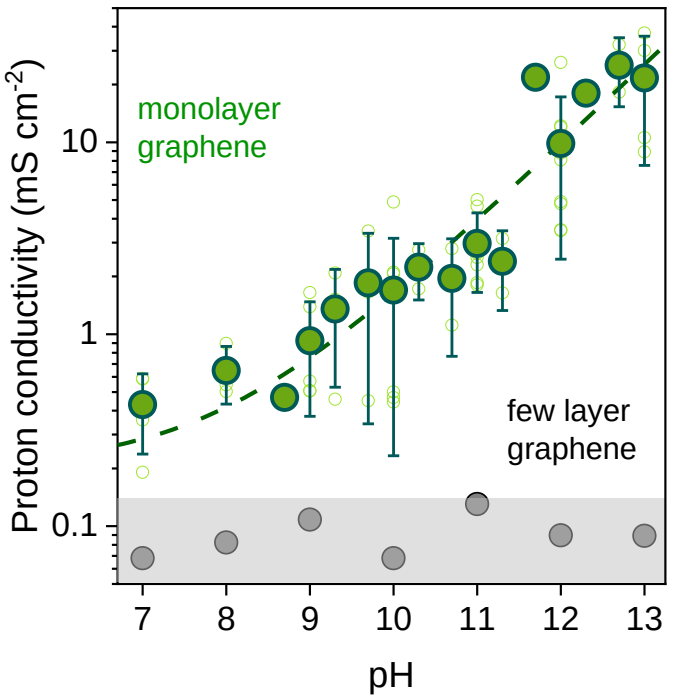
Reference multilayer graphene gave no currents



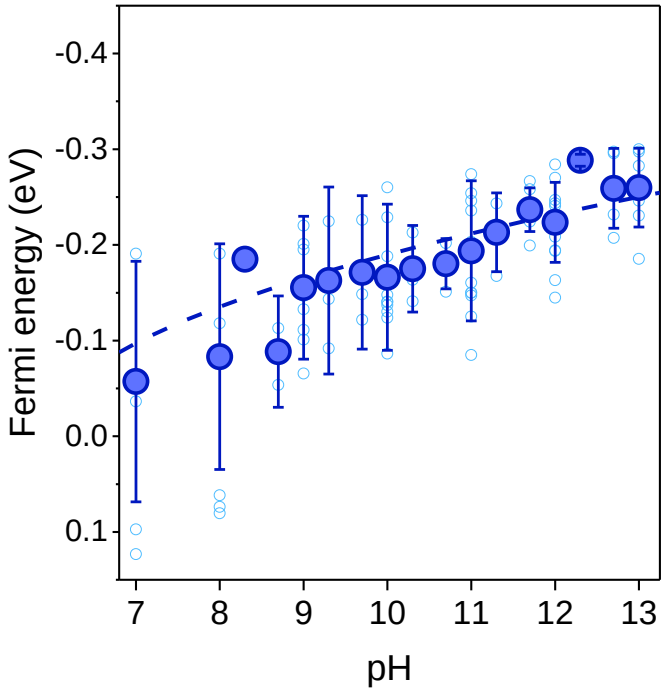
Proton permeability is essential to observe the effect

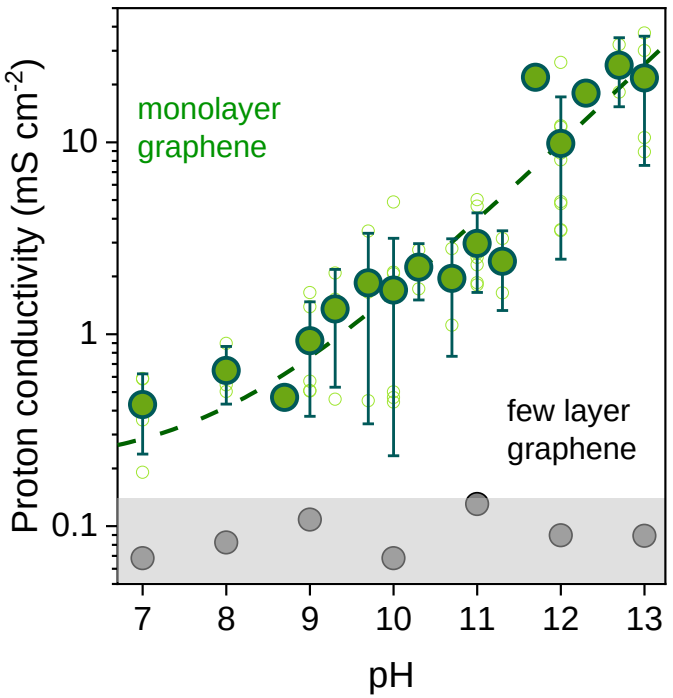
Systematically extracted Fermi energy and proton conductance

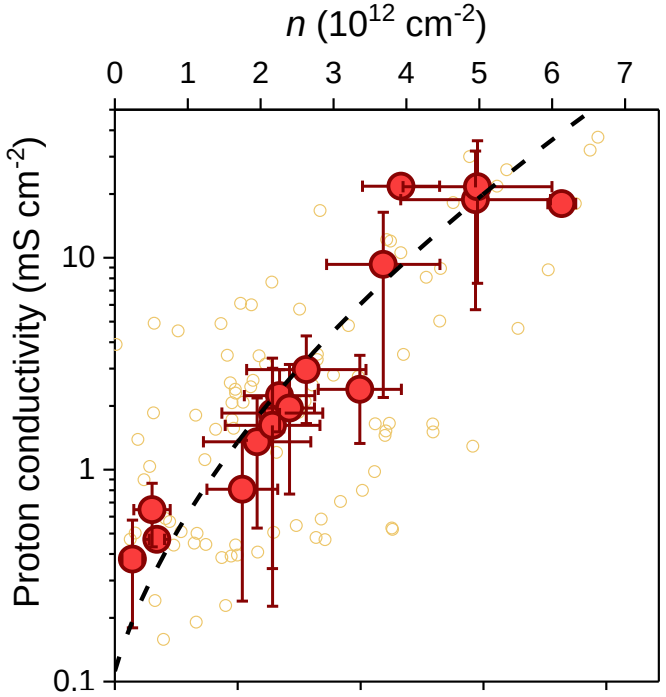




We can correlate both data sets







$E \propto n$

Onsager's theory combines epsilon with conductivity

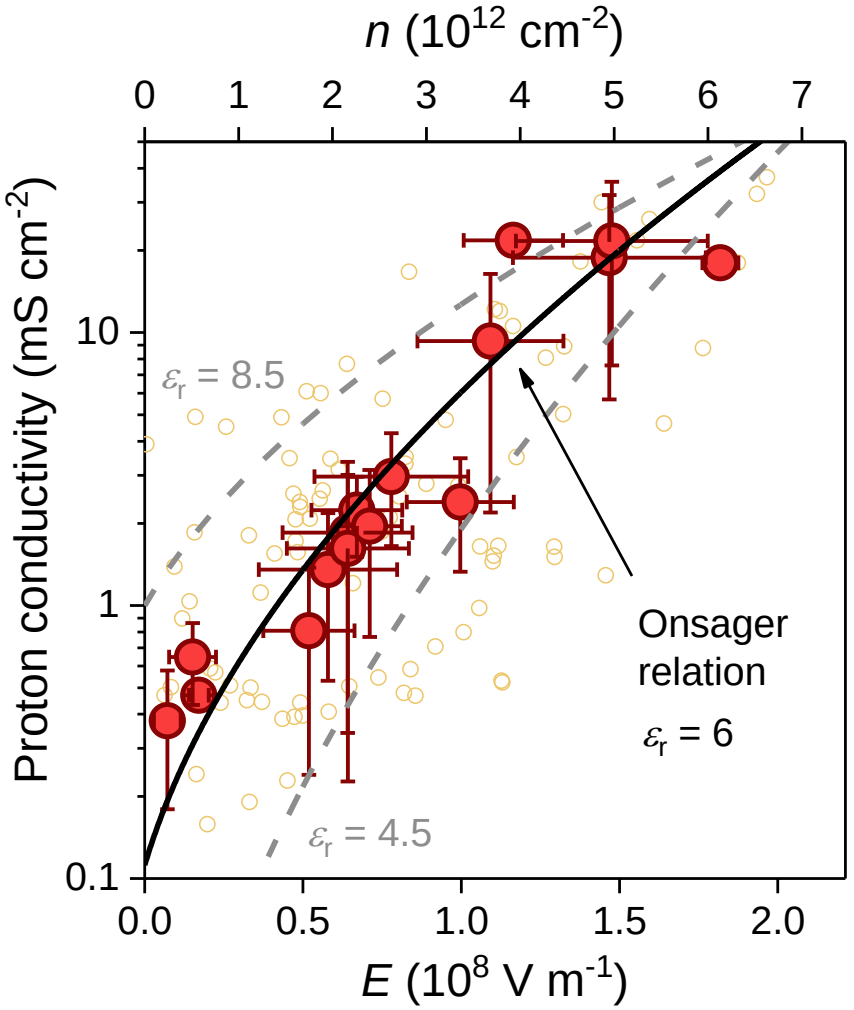
Deviations from Ohm's Law in Weak Electrolytes

LARS ONSAGER,* *Sterling Chemistry Laboratory, Yale University*

(Received May 29, 1934)

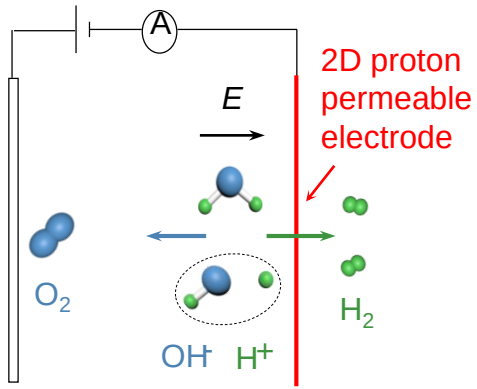
The effect of an external electric field on the electrolytic dissociation is computed kinetically from the equations for Brownian motion in the combined Coulomb and external fields. The result is an increase of the dissociation constant, by the factor $K(X)/K(0)=F(b)=1+b+(1/3)b^2+\cdots$, where the parameter b is proportional to the absolute value of the field intensity, and inversely proportional to the dielectric constant. In water at 25°, $F(b)=F(1)=2.395$ for a field of 723 kilovolt/cm, while in benzene, the same increase of the dissociation constant is obtained for a field of only 21 kilovolt/cm. The theory is quantitatively confirmed by the deviations from Ohm's law which have been observed for solutions of weak electrolytics in water and in benzene. For solutions of salts in acetone, and for solid electrolytes such as glass, mica, celluloid, etc., the observed increments of conductance are smaller than those expected from the theory, but still of the predicted type and order of magnitude. The kinetic constants of dissociation and recombination can be computed separately on the assumption that the recombination proceeds as rapidly as the mutual approach of two ions due to the Coulomb attraction. The derivation is equivalent to that of Langevin, and leads to the same result. In the Langevin case, the coefficient of recombination is independent of the field; that of dissociation is increased by the factor $F(b)$. Slower reactions may occur when a (chemical) rearrangement of the ion pairs is involved. In the most general case, it is necessary to consider the successive reversible reactions *ions*$\rightleftarrows$*pairs*$\rightleftarrows$*molecules*, where the former takes place with the Langevin velocity; only the reaction rate *pairs*$\rightarrow$*ions* depends on the field. On the basis of this picture, the saturation phenomena observed in dielectrics are discussed in relation to the field effect.

From Onsager theory we can extract epsilon and therefore *E*



Water dissociation eventually leads to H2 and O2 gases

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2$$



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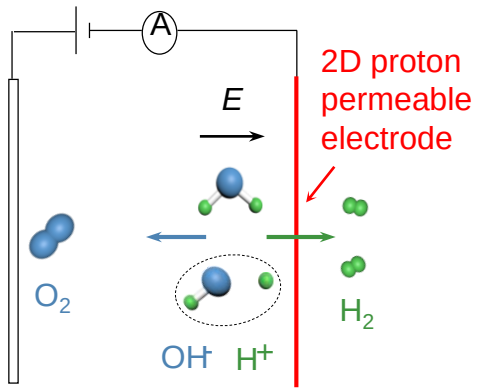
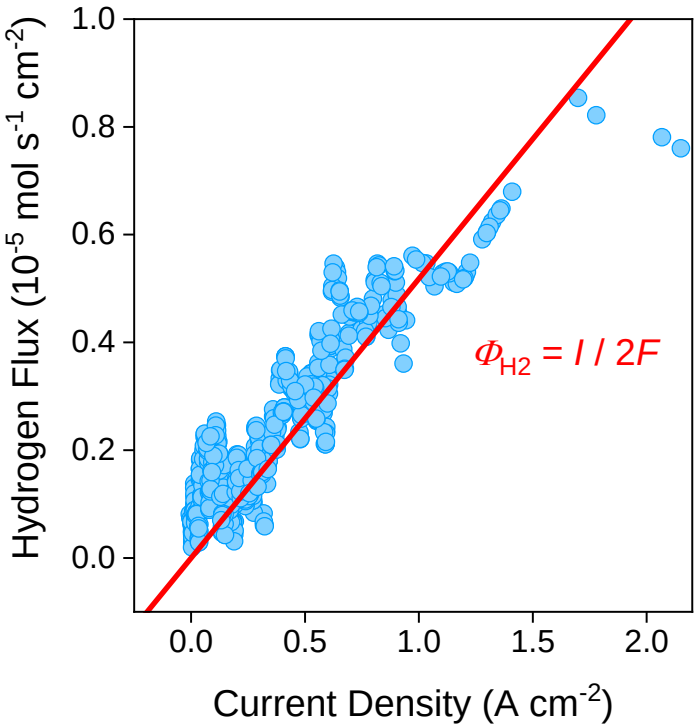
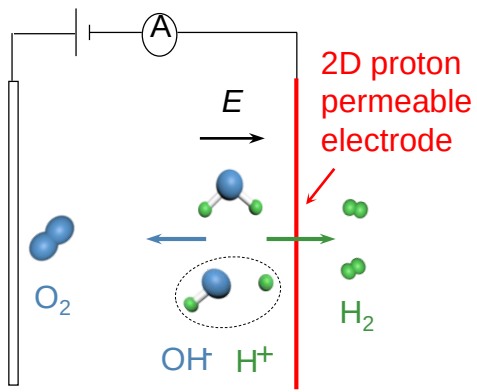
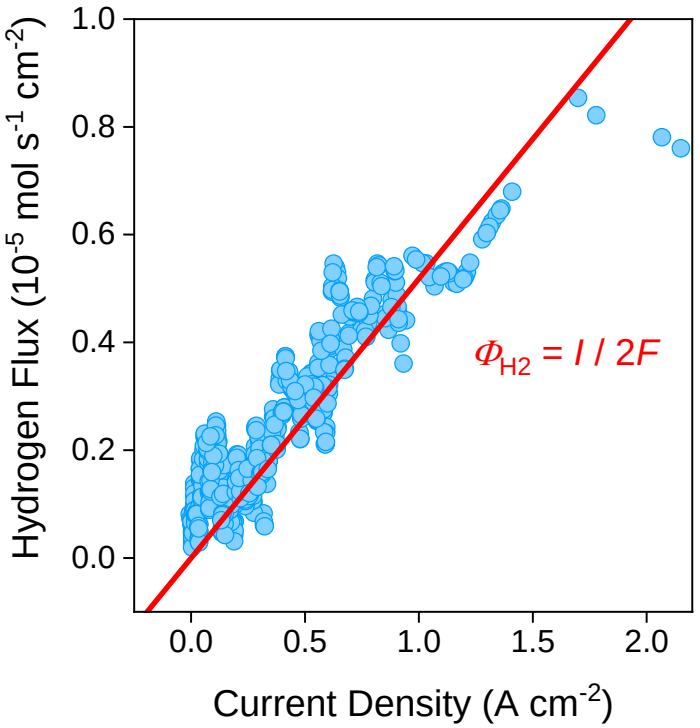


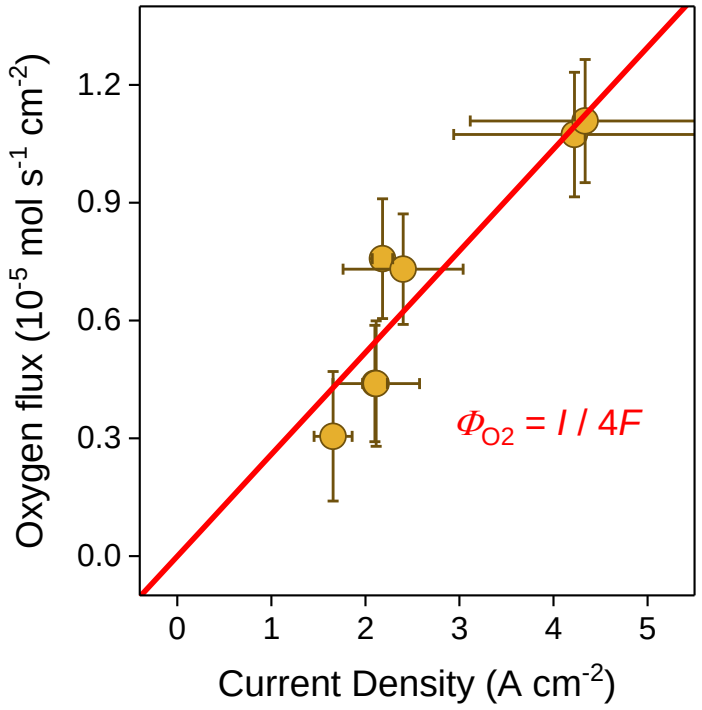


Water dissociation eventually leads to H2 and O2 gases

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2$$







Gases detected in a 2:1 ratio

Take home message

Interfacial water dissociation can be strongly accelerated with *E*

Graphene electrodes are a powerful platform to study interfacial phenomena

Thanks!

Manchester

Junhao Cai

Eoin Griffin

Victor Guarochico-Moreira

Donnchadh Barry

Benhao Xin

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Enrico Daviddi

Pat Unwin

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