

1 Suggested Title:

## 2 **A Gateway to Understanding Confined Ions**

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4 If a charged electrode with a flat surface is immersed in a liquid containing ions, it is relatively well  
5 understood that the oppositely-charged ions will be attracted to the interface, forming a so-called  
6 electrical double layer. However, what happens if the surface of the electrode is not flat but contains  
7 nanopores or channels? The answer to this seemingly simple question is surprisingly complex and  
8 is not yet fully understood. Moreover, it is central to understanding how important and emerging  
9 technologies such as electrochemical supercapacitors function on the molecular level.<sup>1</sup> Much of  
10 what we do know about the behaviour of nanoconfined ions has come from modelling and  
11 simulations,<sup>2</sup> but recently new experimental approaches are starting to provide tantalising insight  
12 into real-life systems.<sup>3</sup> Writing in *Nature Nanotechnology*, Xiao *et al.*, have demonstrated a new  
13 approach based on electrolyte gating which may expand the experimental toolkit and provide an  
14 additional lens through which to view the behaviour of nanoconfined ions in real-time.<sup>4</sup>

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16 The technique of electrolyte gating involves putting a semiconductor electrode into contact with an  
17 ionic liquid or solution, and applying a gate voltage to set up an electrical double layer at the  
18 interface (Fig. 1a).<sup>5</sup> The accumulation of electrons or holes within the electrode surface increases  
19 the conductivity of the semiconductor. Measurement of gating-induced conductance changes has  
20 been widely used to study insulator-to-metal transitions, superconductivity, and other electronic  
21 phase transitions in materials. The work by Xiao *et al.* turns electrolyte gating on its head: instead  
22 studying the electronic structure of the solid electrode, they set out to see if it could be used to study  
23 the behaviour of the ions in the liquid electrolyte.

24  
25 Part of the challenge with applying electrolyte gating in this context is that the effect is only  
26 observed in semiconductors, whereas many model electrode materials are based on graphite-like  
27 nanoporous carbon which has metallic conducting properties. However, reduced graphene oxide  
28 behaves like a *p*-type semiconductor due to the presence of structural defects. In previous work, the  
29 same group has developed an approach for fabricating multi-layered graphene membranes (MGMs)  
30 from reduced graphene oxide, in which the interlayer distances between the graphene sheets are  
31 controllable from 10 nm down to subnanometre separations.<sup>6</sup> The researchers hypothesise that,  
32 providing the MGM sheets are sufficiently separated, the electronic structure of the electrode  
33 should be more like defective graphene (semiconducting) than graphite (conducting) and the  
34 electrolyte gating effect should be observable. Furthermore, since the MGM pore width is tuneable,  
35 these materials provide an ideal model system for studying adsorbed ion behaviour.

36  
37 Using a specially-designed two-electrode cell with an additional platinum contact to measure the  
38 trans-membrane conductance (Fig. 1b), Xiao *et al.* performed a electrochemical measurements on a  
39 MGM with 10 nm layer spacing in an aqueous KCl electrolyte. As the cell voltage was swept across  
40 a range of  $\pm 0.8$  V, the trans-membrane conductance was found to approximately double. Additional  
41 analysis ruled out contributions from redox reactions, electrode expansion or changes in contact  
42 resistance, leaving electrolyte gating as the most likely source of the observed results. Further  
43 confirmation came from conventional back gating measurements on reduced graphene oxide in a  
44 field-effect transistor, where very similar conductance changes were observed.

45  
46 Having successfully identified electrolyte gating, the next step was to see if this effect is sensitive to  
47 the electrolyte ion dynamics. To do this, measurements were performed on a set of MGMs with  
48 layer spacings of between 5 – 0.6 nm. For larger layer spacings, very similar behaviour to the proof-  
49 of-concept experiment was observed, indicating free movement of ions in and out of the  
50 nanochannels during charging (Fig. 1c). Intriguingly, different behaviour was observed for layer  
51 spacings below 1.0 nm, particularly when electrolytes containing large molecular ions were used. In  
52 these experiments, a marked hysteresis was observed between the cell voltage and trans-membrane

53 conductance. Similar results were observed in constant current experiments where the peak  
54 conductance was seen several seconds after the ionic current was reversed (Fig. 1d). These  
55 observations point towards increased nanoconfinement and reduced ion mobility when the pore  
56 width approaches the bare ion diameter – a phenomenon which is particularly pertinent in the field  
57 of supercapacitor energy storage devices, where confinement effects have been predicted to yield  
58 significant capacitance increases.<sup>2</sup>

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60 The work by Xiao *et al.* provides a new perspective from which to view the behaviour and  
61 dynamics of confined ions, something which is currently of high interest yet notoriously difficult to  
62 do. One of the advantages of electrolyte gating is that it is intrinsically a real-time technique and  
63 can therefore potentially capture some of the fast timescale processes that are difficult to track with  
64 other methods. However, further work will be required to better understand the detailed origins of -  
65 and the factors influencing - the gating effect, and to determine the resolution with which it can  
66 probe the structure of the electrical double layer. Of particular interest is how the arrangement and  
67 solvation states of ions within the electrical double layer is affected by the electrode structure and  
68 the chemical properties of the electrolyte. If electrolyte gating can help to answer some of these  
69 questions it could have a very big impact in the field.

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#### 71 References

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1. Salanne, M. *et al.* *Nature Energy* **1**, 16070 (2016).

73

2. Federov, M. V.; Kornyshev, A. A. *Chem. Rev.* **114**, 2978-3036 (2014).

74

3. Forse, A. C.; Merlet, C.; Griffin, J. M.; Grey, C. P. *J. Am. Chem. Soc.* **138**, 5731-5744  
75 (2016).

75

4. Xiao, J. *et al.* *Nature Nano.*

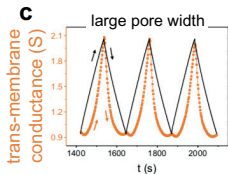
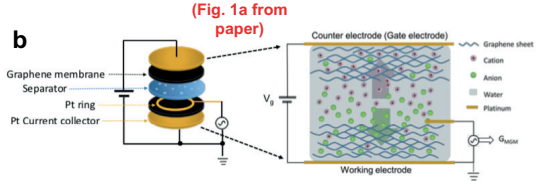
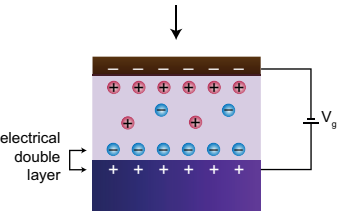
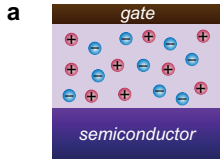
76

5. Leighton, C. *Nature Mater.* **18**, 13-18, (2019).

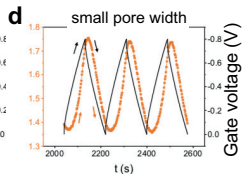
77

6. Yang, X.; Cheng, C.; Wang, Y.; Qiu, L.; Li, D. *Science* **341**, 534-537 (2013).

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(Fig. 4a from paper)



(Fig. 4d from paper)