

## NANOFLUIDICS

## Atomic-scale ion transistor with ultrahigh diffusivity

Yahui Xue<sup>1†</sup>, Yang Xia<sup>1†</sup>, Sui Yang<sup>1</sup>, Yousif Alsaied<sup>1</sup>, King Yan Fong<sup>1</sup>, Yuan Wang<sup>1</sup>, Xiang Zhang<sup>2\*</sup>

Biological ion channels rapidly and selectively gate ion transport through atomic-scale filters to maintain vital life functions. We report an atomic-scale ion transistor exhibiting ultrafast and highly selective ion transport controlled by electrical gating in graphene channels around 3 angstroms in height, made from a single flake of reduced graphene oxide. The ion diffusion coefficient reaches two orders of magnitude higher than the coefficient in bulk water. Atomic-scale ion transport shows a threshold behavior due to the critical energy barrier for hydrated ion insertion. Our in situ optical measurements suggest that ultrafast ion transport likely originates from highly dense packing of ions and their concerted movement inside the graphene channels.

**B**iological ion channels with atomic-scale selectivity filters not only allow extremely fast and precisely selective permeation of alkali metal ions but also behave as life's transistors, with the ability to gate their on-off responses to external stimuli so as to sustain important biological activities (1, 2). Efforts have been made to develop artificial pore structures to probe ion diffusion dynamics mimicking biological systems for

fundamental understanding and applications in life science, filtration, and energy storage (3–5). Ion transport theory in a continuum framework has been developed with pores fabricated by conventional nanofabrication processes (6, 7), but these pore sizes exceed the diameters of hydrated ions, negating ion selectivity (8). Single-walled carbon nanotubes have emerged as interesting candidates for transporting ions (9). Nonetheless, these channels are mostly at the 1-nm scale, and they still exhibit poor selectivity given the typical angstrom-level size of hydrated ions and the measured diffusion coefficient, which is comparable to or even slower than that in bulk water ( $\sim 1.9 \times 10^{-9} \text{ m}^2/\text{s}$ ) (10, 11). Recently, graphene layer structures

have demonstrated their superiority over many others [e.g., graphene nanopores (12), metal-organic frameworks (13), and porous polymer (14)] in achieving elevated selectivity of monovalent metal ions with precisely controlled channel dimensions at the angstrom scale (15). However, these angstrom-scale channels preclude fast diffusion (on the order of  $10^{-11}$  to  $10^{-13} \text{ m}^2/\text{s}$ ) because hydrated ions encounter steric resistance when entering a narrower channel space (16, 17). There is also a lack of gating ability at atomic scale to mimic the transistor-like behavior of biological channels. Although ion transport in so-called nanofluidic transistors and rectifiers has been reported in nanoscopic channels (18, 19), it still remains a grand challenge to realize gated ultrafast and simultaneously selective ion diffusion through atomic-scale channels to mimic the full functionalities of biological ones.

We report an atomic-scale ion transistor based on electrically gated graphene channels  $\sim 3 \text{ \AA}$  in height, possessing simultaneously ultrafast and selective ion transport that is two orders of magnitude faster than ion diffusion in bulk water. By applying electrical gating, the average surface potential on the graphene layer can be controlled, thus changing the energy barrier for ion intercalation into the channel. Our graphene channel device is made of a single flake of multilayer reduced graphene oxide (rGO) with interlayer spacing  $\lambda \approx 0.45 \text{ nm}$  (20). The device

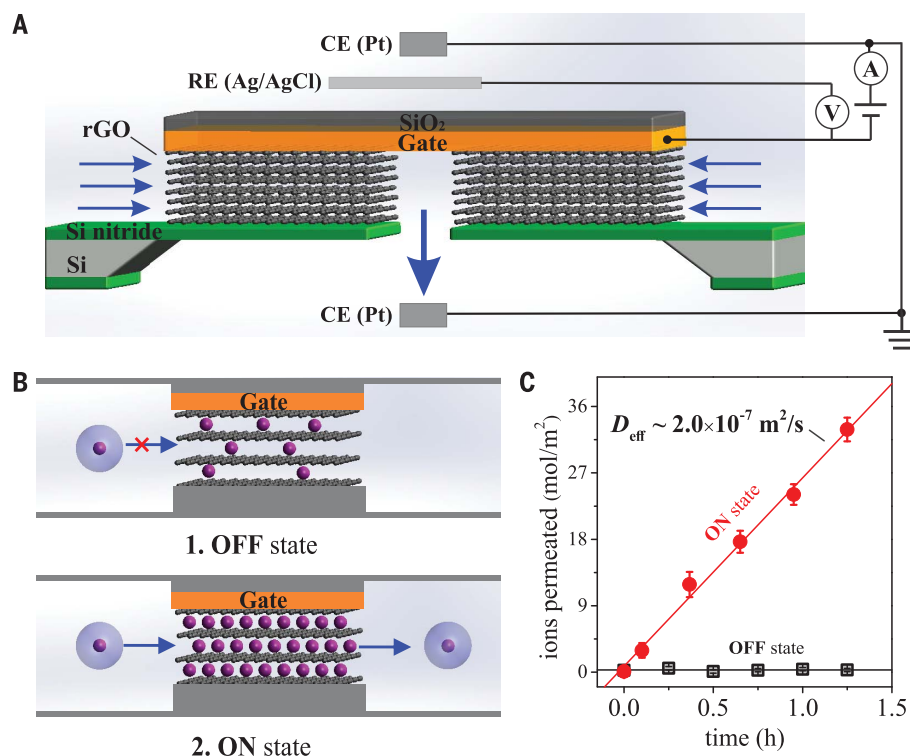
<sup>1</sup>Nanoscale Science and Engineering Center, University of California, Berkeley, CA, USA. <sup>2</sup>Faculty of Science and Faculty of Engineering, University of Hong Kong, Hong Kong, China.

†These authors contributed equally to this work.

\*Corresponding author. Email: president@hku.hk

### Fig. 1. Experimental setup and ultrafast ion permeation.

(A) Schematic of our atomic-scale graphene channel device with electric potential control using a three-electrode configuration. Gold is used as the gate electrode. Ag/AgCl in saturated KCl aqueous solution is used as the reference electrode (RE) and platinum wires as counter electrodes (CE). The arrows indicate the direction of ion flux driven by concentration gradient. Multiple graphene layers are electrically connected with the gate electrode in the out-of-plane direction (see fig. S6). (B) Schematics of "ON" and "OFF" states of ion permeation. Purple dots, alkali metal ions; light blue circles, hydration shells. In the "OFF" state, ions could be trapped from the previous round of ion intercalation as a result of cation- $\pi$  interactions (17). (C) Experimental observation of potassium ion permeation through our graphene channels driven by a concentration gradient of 0.2 M at  $-1.2 \text{ V}$  (ON state) and OCP (OFF state), respectively.

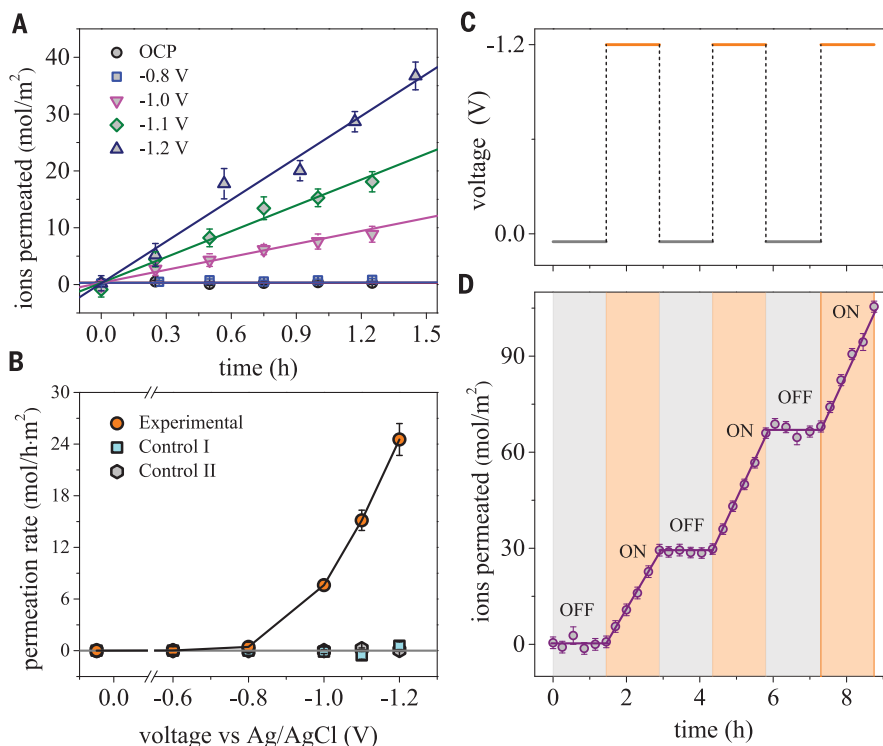


**Fig. 2. Electrically controlled ion permeation.**

(A) Potassium ion permeation through atomic-scale graphene channels of thickness  $t = 25$  nm, driven by a concentration gradient of 0.2 M and at different electric potentials. Symbols are experimental data; lines are linear fittings.

(B) Permeation rate as a function of applied electric potential. Orange dots correspond to the experimental data in (A), obtained by the slopes of best linear fittings. Other symbols are data from two control experiments to exclude the leakage effect from the interfaces of the rGO flake with the silicon nitride substrate and the metal electrode, respectively (20).

(C and D) Potential control scheme (C) and ON-OFF responses (D) of ion permeation with switching potential between  $-1.2$  V and OCP.



is supported on a free-standing silicon nitride membrane with a rectangular hole for ion flow and clamped with gate electrode and insulation layers for electric potential control (Fig. 1A). This configuration offers the advantages of intact layer structures (with diminished pinholes and defects relative to self-assembled graphene oxide laminates) for fundamental property investigation while preserving flexibility for scaling-up fabrication. Such two-dimensional graphene channels are clipped into rectangular shapes with length  $L \approx 6 \mu\text{m}$  and width  $W \approx 20 \mu\text{m}$  to facilitate ion permeation. The whole device as a membrane is clamped between two reservoirs (referred to as feed and permeate compartments), which are filled with highly conductive alkaline buffer electrolytes that can negate the electrophoretic effect and establish a 0.2 M concentration gradient of investigated cations [see (20) for detailed discussion on the electrophoretic effect].

To explore the possibility of controllable ion permeation through our graphene channels, we probed potassium ion diffusion purely driven by a concentration gradient (20). Because the channel size is smaller than the hydration diameters of alkali metal ions, it creates an intrinsic energy barrier that forbids ion entry in the open-circuit condition, indicating the OFF state for ion permeation (Fig. 1B, top). The electrical potential is applied to mimic the electric charge on the walls of biological channels. In this scenario, the hydration shell can be distorted or partially stripped off to

overcome the ion-entry energy barrier, enabling ion intercalation as capacitive charge (27). Beyond a percolation threshold as the intercalated ions accumulate inside the channels, permeable ion transport is initialized, indicating the ON state of ion permeation (Fig. 1B, bottom).

With this configuration, an ultrafast permeation of potassium ions is observed at  $-1.2$  V (Fig. 1C, ON state), corresponding to a typical linear model driven by a concentration gradient and exhibiting an effective diffusion coefficient,  $D_{\text{eff}} \approx 2.0 \times 10^{-7} \text{ m}^2/\text{s}$ , within graphene channels whose height is comparable to the selectivity filter diameter of biological channels. This diffusion coefficient is two orders of magnitude higher than that in bulk water and surpasses the intrinsic diffusion coefficient observed in biological channels (20). In contrast, potassium ions show negligible diffusion at the open-circuit potential (OCP) because of the steric hindrance of large-sized hydrated ions (Fig. 1C, OFF state).

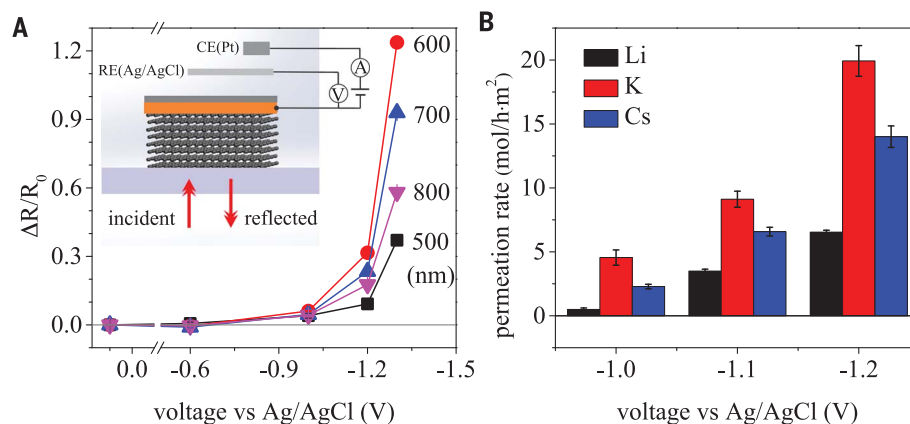
To gain more insight into the effect of pore surface charge on ion permeation through atomic-scale channels, we investigated the permeation results under different electric potentials (Fig. 2A). Driven by a concentration gradient, the linear increase of ion concentration with time and with applied electric potential is observed beyond a threshold potential ( $-1.0$  to  $-1.2$  V). The higher the electric potential, the stronger the ion permeation. This suggests increased ion intercalation into atomic-scale graphene channels under strong

physical confinement with higher electrical driving force. Below the threshold (from OCP to  $-0.8$  V), negligible change of ion permeation is observed. A plot of the potential-dependent permeation rate (Fig. 2B) shows that the threshold voltage behavior is evident, which indicates the onset electric potential to overcome the ion-entry energy barrier. Experimental evaluation of the energy barrier reveals a value of  $\sim 24$  kJ/mol for potassium ions, which agrees reasonably well with predictions reported in the literature (15, 20, 22).

We further studied the switching capability of ionic permeation through the atomic-scale channels. We monitored the ion permeation by repeatedly switching the gate voltage below and beyond the threshold (Fig. 2C). It is seen that ion permeation happens linearly and rapidly with time at  $-1.2$  V (beyond the threshold). When the potential is switched to OCP (below the threshold), the permeation immediately stops (Fig. 2D). This ON-OFF switchable sequence is repeatable over several cycles.

We explored the ion intercalation and packing density inside the channels under different electric potentials. Because the electronic structure of a material strongly affects its optical properties, we explored the intercalated charge density in our atomic-scale graphene channels by in situ optical reflection measurements (20). We observed enhanced optical reflection with respect to the open-circuit condition in the spectrum region from 450 to 900 nm beyond a threshold voltage (Fig. 3A

**Fig. 3. Charge intercalation and ionic selectivity.** (A) Relative optical reflection change induced by charge intercalation as a function of electric potential at wavelengths of 500, 600, 700, and 800 nm.  $R_0$  is reflection intensity at OCP, and  $\Delta R$  is relative change at different potential. Inset: schematic experimental setup for in situ optical reflection measurements. (B) Comparison of permeation rates of  $\text{Li}^+$ ,  $\text{K}^+$ , and  $\text{Cs}^+$  ions in atomic-scale graphene channels at  $-1.0$ ,  $-1.1$ , and  $-1.2$  V.



and fig. S14), consistent with our potential-dependent ion diffusion measurements. Such observation is attributed to the doping level increase as ions intercalate into the graphene channels. We modeled the optical reflection measurements by approximating the optical property of rGO with Fermi level-dependent multiple graphene layers (20). The modeling results capture well the overall trend of optical reflection change (fig. S16), revealing a charge density on the order of  $1.8 \times 10^{14} \text{ cm}^{-2}$  at  $-1.2$  V. Such a charge density is quite high and compares well with the measurements in the electrochemical charging of bilayer graphene (23) and ultrathin graphite (24).

We further probed how ion packing density promotes ultrafast ion diffusion. Note that ultimate confinement largely reduces the dielectric constant of aqueous solutions (25). The high packing density of charges observed in our graphene channels could impart strong Coulomb interaction among adjacent ions and promote their concerted movement with decreasing energy barrier (26, 27). We adopted a mean-field theoretical model to correlate the dependence of the effective ion diffusion coefficient on the charge density and their mutual interactions (20). For a charge density of  $1.8 \times 10^{14} \text{ cm}^{-2}$ , the model yields an enhancement of the diffusion coefficient from  $1.9 \times 10^{-9} \text{ m}^2/\text{s}$  to  $\sim 0.8 \times 10^{-7} \text{ m}^2/\text{s}$ , which reasonably agrees with our experimental results. The accelerated diffusion dynamics can be understood in terms of Coulomb interaction-induced concerted ion movement (27, 28). The theoretical underestimation may be caused by uncertainty due to modeling assumptions and the omission of factors such as the low friction of graphene surfaces (29) and phonon-enhanced ion diffusion (30).

Elevated selectivity of monovalent metal ions is also observed in our atomic-size graphene channels. To reasonably compare the permeation rates of different alkali metal ions, we filled the feed compartment with a mixture of  $\text{LiCl}$ ,  $\text{KCl}$ , and  $\text{CsCl}$ , 0.2 M each in the same

solution. Fig. 3B shows the permeation rates of different cations in a potential range from  $-1.0$  to  $-1.2$  V (see also fig. S17). A selection ratio of  $\text{K}^+/\text{Li}^+$  as high as 9.0 is achieved at  $-1.0$  V. The overall permeation rates increase with the electric potential, consistent with the single-potassium ion measurements in Fig. 2A. It is also interesting to observe a constant selection sequence in the studied potential range—that is,  $\text{K}^+ > \text{Cs}^+ > \text{Li}^+$ —which resembles the selection sequence of biological potassium channels. This implies a controlling mechanism combined with ion dehydration and electrostatic interaction with ion-binding sites in our charged graphene channels (31), in contrast to previous artificial channels (13, 14).

Our atomic-scale ionic transistors can switch ion transport effectively and selectively. The ultrahigh ion diffusivity is explained by their dense packing and resultant concerted movement. The reversible and switchable ion permeation is attributed to the steric ion-entry energy barrier overcome by applied electrical potential. The synergetic contribution of atomic-scale confinement and surface potential renders the ion transport highly selective. This demonstration not only provides fundamental understanding of fast ion sieving in biological systems but also leads to highly controllable and ultrafast ion transport of relevance to ion batteries, seawater desalination, and medical dialysis.

#### REFERENCES AND NOTES

- B. Eisenberg, *Fluct. Noise Lett.* **11**, 1240001 (2012).
- F. J. Sigworth, *Nature* **423**, 21–22 (2003).
- J. C. T. Eijkel, A. van den Berg, *Microfluid. Nanofluidics* **1**, 249–267 (2005).
- J. R. Werber, C. O. Osuji, M. Elimelech, *Nat. Rev. Mater.* **1**, 16018 (2016).
- C. C. Chen, L. Fu, J. Maier, *Nature* **536**, 159–164 (2016).
- C. Duan, A. Majumdar, *Nat. Nanotechnol.* **5**, 848–852 (2010).
- C. Dekker, *Nat. Nanotechnol.* **2**, 209–215 (2007).
- H. B. Park, J. Kamcev, L. M. Robeson, M. Elimelech, B. D. Freeman, *Science* **356**, eaab0530 (2017).

- J. Geng *et al.*, *Nature* **514**, 612–615 (2014).
- F. Fornasiero *et al.*, *Proc. Natl. Acad. Sci. U.S.A.* **105**, 17250–17255 (2008).
- J. Wu, K. Gerstandt, H. Zhang, J. Liu, B. J. Hinds, *Nat. Nanotechnol.* **7**, 133–139 (2012).
- R. C. Rollings, A. T. Kuan, J. A. Golovchenko, *Nat. Commun.* **7**, 11408 (2016).
- H. Zhang *et al.*, *Sci. Adv.* **4**, eaq0066 (2018).
- P. Wang *et al.*, *Nat. Commun.* **9**, 569 (2018).
- J. Abraham *et al.*, *Nat. Nanotechnol.* **12**, 546–550 (2017).
- A. Esfandiari *et al.*, *Science* **358**, 511–513 (2017).
- L. Chen *et al.*, *Nature* **550**, 380–383 (2017).
- R. Karnik *et al.*, *Nano Lett.* **5**, 943–948 (2005).
- L. Cantley *et al.*, *Nanoscale* **11**, 9856–9861 (2019).
- See supplementary materials.
- M. M. Hantel, T. Kaspar, R. Nesper, A. Wokaun, R. Kotz, *Electrochem. Commun.* **13**, 90–92 (2011).
- Y. Yu *et al.*, *Nanoscale* **11**, 8449–8457 (2019).
- M. Kühne *et al.*, *Nat. Nanotechnol.* **12**, 895–900 (2017).
- W. Bao *et al.*, *Nat. Commun.* **5**, 4224 (2014).
- L. Fumagalli *et al.*, *Science* **360**, 1339–1342 (2018).
- D. A. Köpfer *et al.*, *Science* **346**, 352–355 (2014).
- S. Kondrat, P. Wu, R. Qiao, A. A. Kornyshev, *Nat. Mater.* **13**, 387–393 (2014).
- X. He, Y. Zhu, Y. Mo, *Nat. Commun.* **8**, 15893 (2017).
- T. Mouterde *et al.*, *Nature* **567**, 87–90 (2019).
- S. Muy *et al.*, *Energy Environ. Sci.* **11**, 850–859 (2018).
- B. Hille, *Ionic Channels in Excitable Membranes* (Sinauer, ed. 2, 1992).

#### ACKNOWLEDGMENTS

**Funding:** Supported by King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research award OSR-2016-CRG5-2996. **Author contributions:** X.Z. conceived the project and guided the research; Y. Xue designed and conducted the permeation experiments; Y. Xia and Y. Xue fabricated the devices and, with assistance from S.Y., performed the optical measurements and modeling; Y.A. performed sample characterization by XRD; K.Y.F. assisted with building the experimental setup; Y. Xue, Y. Xia, S.Y., and X.Z. wrote and revised the paper with inputs from all authors. **Competing interests:** The authors declare no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and the supplementary materials.

#### SUPPLEMENTARY MATERIALS

science.sciencemag.org/content/372/6541/501/suppl/DC1  
Materials and Methods  
Figs. S1 to S17  
References (32–46)

28 February 2020; accepted 5 March 2021  
10.1126/science.abb5144

## Atomic-scale ion transistor with ultrahigh diffusivity

Yahui Xue, Yang Xia, Sui Yang, Yousif Alsaied, King Yan Fong, Yuan Wang and Xiang Zhang

*Science* **372** (6541), 501-503.  
DOI: 10.1126/science.abb5144

### Gated ion flow in graphene oxide membranes

Cells are adept at fast, gated ion flow through tailored channels, which is key to many biological processes. Xue *et al.* developed ion transistors from reduced graphene oxide membranes and observed a field-enhanced diffusivity of the ions (see the Perspective by Hinds). By applying electrical gating, the average surface potential on the graphene layer could be controlled, thus altering the energy barrier for ion intercalation into the channel and leading to very high diffusion rates. The authors observed selective ion transport two orders of magnitude faster than the ion diffusion in bulk water.

*Science*, this issue p. 501; see also p. 459

ARTICLE TOOLS	<a href="http://science.sciencemag.org/content/372/6541/501">http://science.sciencemag.org/content/372/6541/501</a>
SUPPLEMENTARY MATERIALS	<a href="http://science.sciencemag.org/content/suppl/2021/04/28/372.6541.501.DC1">http://science.sciencemag.org/content/suppl/2021/04/28/372.6541.501.DC1</a>
RELATED CONTENT	<a href="http://science.sciencemag.org/content/sci/372/6541/459.full">http://science.sciencemag.org/content/sci/372/6541/459.full</a>
REFERENCES	This article cites 46 articles, 7 of which you can access for free <a href="http://science.sciencemag.org/content/372/6541/501#BIBL">http://science.sciencemag.org/content/372/6541/501#BIBL</a>
PERMISSIONS	<a href="http://www.sciencemag.org/help/reprints-and-permissions">http://www.sciencemag.org/help/reprints-and-permissions</a>

Use of this article is subject to the [Terms of Service](#)

---

*Science* (print ISSN 0036-8075; online ISSN 1095-9203) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. The title *Science* is a registered trademark of AAAS.

Copyright © 2021 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works