

Scaling Behavior and Conductance Mechanisms of Ion Transport in Atomically Thin Graphene Nano/Sub-Nanopores

Xiao-Yu Huang,¹ Yangjun Cui,¹ Cuifeng Ying,^{2*} Jianguo Tian,¹ Zhibo Liu^{1,3*}

¹ *The Key Laboratory of Weak Light Nonlinear Photonics, Ministry of Education, School of Physics and Teda Applied Physics Institute, Renewable Energy Conversion and Storage Center, State Key Laboratory of Photovoltaic Materials and Cells, Nankai University, Tianjin 300071, China*

² *Advanced Optics & Photonics Laboratory, Department of Engineering, School of Science & Technology, Nottingham Trent University, Nottingham NG11 8NS, UK*

³ *The collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, China*

* Corresponding author: liuzb@nankai.edu.cn, cuifeng.ying@ntu.ac.uk

ABSTRACT

Ion transport through atomically thin nano/sub-nanopores, such as those in monolayer graphene, presents challenges to traditional ion conduction models, primarily due to extreme confinement effects and hydration interactions. Under these conditions, existing models fail to account for conductance behaviors at the nano and sub-nanometer scales. In this study, we perform a combined experimental and theoretical investigation of ion transport in monolayer graphene nano/sub-nanopores across varying salt concentrations. We introduce a conductance model that accurately

predicts the observed scaling behavior by addressing the interaction between counterions and the edges of atomically thin pores, where counterion movement is constrained by the pore's structure. This model also quantifies the hydration energy barrier, highlighting the impact of hydration shell structures on ion transport efficiency. Our findings reveal that hydrated potassium ions traverse these pores with higher efficiency than previously estimated, offering new insights into ion transport mechanisms under atomic-scale confinement.

KEYWORD: graphene nanopores, ion transport, scaling behavior, conductance mechanism

The anomalous transport of water and ions in extremely confined spaces presents a fundamental challenge to classical mechanics and continuity equations¹⁻⁶. Solid-state nanopores are key nanofluidic devices used to study ion transport under extreme confinement⁵⁻¹¹. The conventional Maxwell-Hall access resistance model (MH model) is used to explain the ion transport in nanopores initially with surface charge ignored as simplification¹². For surface-charged nanopores, the effects of the electrical double layer (EDL) on the ion transport are significant, particularly under low salt concentrations. Based on Stein et al.'s work on the surface-charge governed ion transport in nanofluidic channels¹³, Lee et al. proposed a surface conductance model (Lee's model) that successfully predicted the saturation conductance behavior for nanopores at 100 nm scales¹⁴. As the length and diameter of nanopores decrease to sub-10 nm, the conductance exhibit scaling behavior, making Lee's model inequitable¹⁰. By employing the electric-potential leakage, Noh et al. presented a conductance theory (Noh's model) capable of explaining the scaling behavior of nanopores at nanometer scale⁹. This scaling behavior is attributed to the breakdown of

electroneutrality in nanopores, a phenomenon observed in various nanofluid systems, such as carbon nanotube¹⁵⁻¹⁷.

The above models, however, cannot accurately describe the conductance of nano/sub-nanopores in monolayer graphene as observed experimentally by us (see Supplementary Note 1 C in Supplementary Information for details). This discrepancy arises because these models are based on assumptions fundamentally unsuitable for graphene nano/sub-nanopores. The atomic thick pore length makes the electroneutrality condition unsatisfied in Lee's model, and Noh's model ignores the influence of counterions at pore entrance, which significantly affects the conductance of monolayer graphene nanopores. The nano/sub-nanometer pore diameter also contradicts Lee's assumption of neglecting the thickness of the EDLs. Additionally, the traditional models cannot capture the complex EDL structure in atomically thin sub-nanopores effectively¹⁸. Moreover, the interaction between the ion hydration shell and sub-nanopores, given their comparable sizes, significantly influence the ion transport¹⁹⁻²¹. Qualifying the energy barrier for hydrated ions passing through sub-nanopores remains challenging. Although nanopores in two-dimensional (2D) materials provide an ideal platform to study the ion transport under extreme confinement, there are few experimental works available due to the challenges in forming stable sub-nanopores.

Here, we systematically studied the ion transport mechanisms in nano/sub-nanopores within monolayer graphene. We observed conductance scaling behavior in these graphene nano/sub-nanopores across various salt concentrations. Subsequently, we proposed a conductance model for atomically thin nano/sub-nanopores, which demonstrates excellent agreement with the experimental results. This model provides a semi-classical description of how counterions interact with the edge of atomically thin pores, suggesting that the scaling behavior arises because the pore edge prevents counterions from translocating along the pore wall. By analyzing free energies of

counterions interacting with the pore edge across different pore diameters, we successfully quantified the hydration barrier, leading to a better understanding of the structure of the hydration shell.

Ionic transport and scaling behavior

To ensure accurate and stable conductance measurements over long-term and across various ion concentrations, we prepared nano/sub-nanopores in high-quality monolayer graphene prepared by mechanical exfoliation and controlled electrochemical reaction (CER) techniques^{22, 23}. The fabrication and stability tests of these nanopores are detailed in Fig. S1-S4, S8 in the Supplementary Information. Figure 1 displays the measured conductance (G) of nanopores and sub-nanopores in monolayer graphene at pH values of 7.5 and 5.0, for nanopores, across salt concentration n_0 ranging from 10^{-5} M to 1 M. As the salt concentration decreases, the conductance of nanopores in Fig. 1(b) and 2(c) shows four phases: (1) conductance decreases linearly with salt concentration (2) this decrease slows down at 10^{-1} M, indicating a first saturation (3) at 10^{-2} M, the conductance decreases rapidly with reduced salt concentration, and (4) the second saturation appears at 10^{-4} M. This phenomenon is consistently observed in monolayer graphene nanopores, as demonstrated in Figs. S5-S6 in the Supplementary Information. Unlike nanopores, the conductance of sub-nanopores in Fig. 1(d) and 1(e) exhibits a biphasic reduction with decreasing salt concentration: an initial rapid decline transitions to a more gradual decrease. Figure 1(g) illustrates that as the nanopore diameter decreases, the conductance decline transitions from four phases to two phases.

We fit these experimental data using Lee's and Noh's models with surface charge density σ and pore diameter d as open parameters; the dashed lines in Fig. 1(b)-(e) represent their best fitting curves. Fitting curves with other parameters are shown in Figs. S10-S11 in the Supplementary

Information. As shown in Fig. 1(b) and 1(c), Lee's model failed in capture the scaling behavior observed in the nanopores in monolayer graphene, while Noh's model shows a more rapid decrease in conductance at low salt concentrations compared to the experimental results. Both models cannot describe the conductance of nano/sub-nanopores at different salt concentrations.

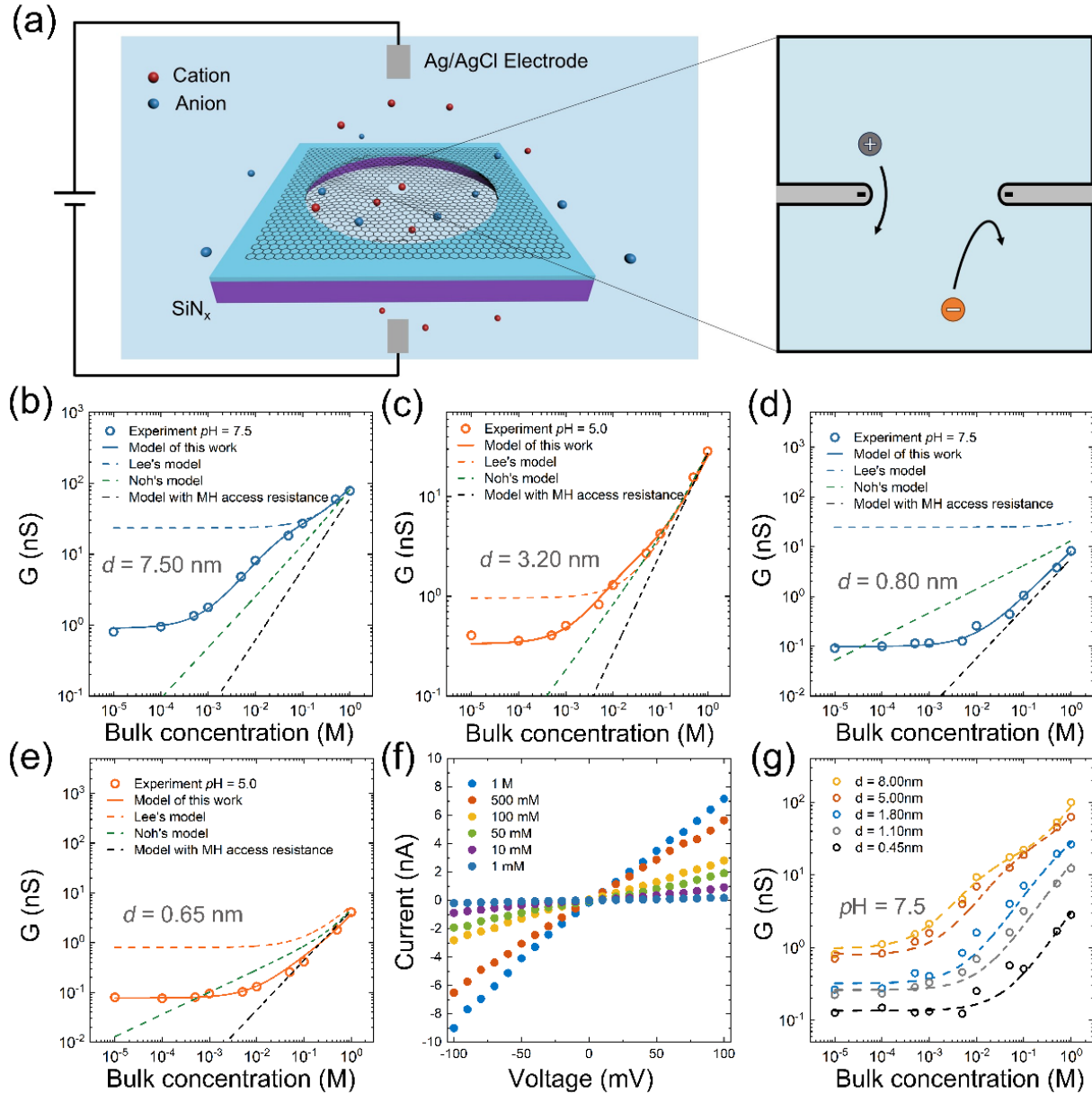


Figure 1. Ion transport through charged graphene nano/sub-nanopores under the influence of an external electric field. **a** The schematic of the ion transportation through atomically thin nanopore;

The dashed lines in (b)-(g) plot the calculation results of existing models (see Supplementary Information Fig. S5-S7 for details), while the solid lines represent the model proposed in this work. **b** $d = 7.50$ nm, pH = 7.5; **c** $d = 3.20$ nm, pH = 5.0; **d** $d = 0.80$ nm, pH = 7.5; **e** $d = 0.65$ nm, pH = 5.0; **f** I-V data of the nanopore presented in panel (b); **g** Fitting curves of our model in comparison with the experimental data obtained from nanopores with various diameters.

Here, we propose a semi-classical conductance model to describe the various linear behaviors of monolayer graphene pores from nano to sub-nano scales. The solid curves in Fig. 1(b-e) represent the theoretically predicted conductance, which agree well with the experimental results obtained from pores ranging from 0.45 nm to 8 nm. This model incorporates classical continuum physics quantities such as surface charge density σ and ion spatial number density n , and simplifies nanopore shape to a cylinder. The coarse-grained approach for this model is detailed in Figs. S12 and S13 in the Supplementary Information.

Determination of surface charge density

For the phenomenon of solid surface charging in ionic solutions, two widely accepted explanations exist. One is the hydrolysis of oxygen-containing groups on the solid surface, and the other is the specific adsorption of hydroxide ions onto the solid surface. Both explanations describe the process by which the solid surface consumes hydroxide ions from the aqueous solution, being negatively charged. Considering the hydroxide ion adsorption, Secchi et al. proposed a relationship between surface charge density σ and the pH of the solution in carbon nanotubes¹⁷. Unlike nanotubes, the defect-free surface of graphene exhibits low chemical activity and consequently low hydroxide ion absorption. Therefore, hydroxide ions are exclusively adsorbed at the edge of graphene

nanopores with limited assessable sites due to geometric constrain, as illustrated in Fig. 2(a). Since the exchange of adsorbed hydroxide ions only happens near the pore edge, the consumed hydroxide ions could be immediately compensated by the ionization of rich accessible water molecules, reaching to an equilibrium of chemical potential:

$$\mu_{\text{OH}^-}[s] = \mu_{\text{OH}^-}[p] \quad (1)$$

where $\mu_{\text{OH}^-}[s]$ and $\mu_{\text{OH}^-}[p]$ are the chemical potential of OH^- ions on pore edge and in pore interior space respectively. The electrical potential inside the pore, which cannot be ignored in nano/sub-nanometer confinements, is simplified as an average electrostatic potential known as the Donnan potential ψ_D ²⁴. Assuming that the interior surface can trap OH^- ions with an adsorption energy $U_{\text{trap}} < 0$, the chemical potential in equation (1) can be written as

$$\mu_{\text{OH}^-}[s] = k_B T \log([\text{OH}^-]_s \lambda^2) - e\psi_s + U_{\text{trap}} \quad (2)$$

$$\mu_{\text{OH}^-}[p] = k_B T \log([\text{OH}^-]_p \lambda^3) - e\psi_D \quad (3)$$

where e is the elementary charge, k_B is the Boltzmann constant, $T = 293$ K is room temperature, $[\text{OH}^-]_s = |\sigma|/e$ is the surface density of OH^- ions on the pore wall, $[\text{OH}^-]_p = 1000 \cdot N_A \cdot 10^{\text{pH}-14} \text{ m}^{-3}$ is the space density of hydroxide ions inside the pore (N_A is the Avogadro's constant), ψ_s is the surface electrostatic potential and λ is microscopic normalizing length in

expression of $\lambda = \left(\frac{h^2}{2\pi m_{\text{OH}^-} k_B T} \right)^{\frac{1}{2}}$.

When the pore edge is negatively charged, graphene nanopore attracts potassium ions and repels chloride ions. Consequently, potassium ions have a higher probability of passing through the nanopores compared to chloride ions. We approximate this process using the Poisson-Boltzmann (PB) equation. By solving the self-consistent equations formed by equation (1) and the PB equation, we establish the relationship between surface charge density σ , salt concentration n_0 ,

and pH. To determine the surface charge of sub-nanopores, we used the U_{trap} obtained from fitting the nanopore data, assuming that adsorption energy remains same for different the pore sizes. The numerical results in Fig. 3(a) suggest that after accounting for the compensation of hydroxide ions by the ionization of water, the surface charge density does not decrease indefinitely with decreasing salt concentration but rather reaches saturation. This finding provides new insights into studying nanopore conductance assuming fixed surface charge density^{11, 25}, and partially explains the lower exponent of scaling behavior observed in nanopores in some 2D material, compared to the 1/3 predicted by Secchi et al¹⁷.

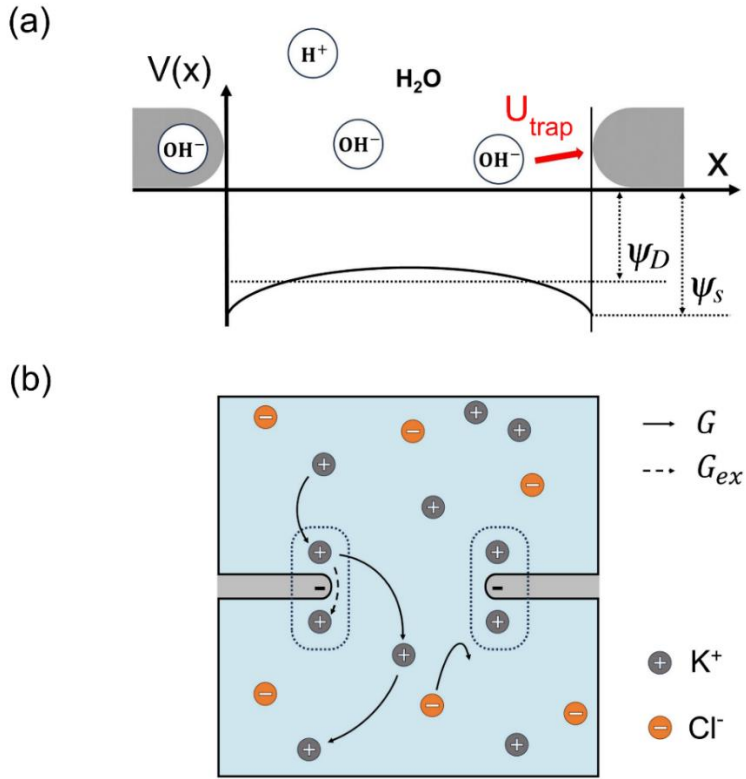


Figure 2. Schematic diagram of the model in this work. **a** Adsorption of OH^- ions occur on the pore edge in graphene nano/sub-nanopore. The OH^- ions are trapped with adsorption energy of U_{trap} . The consumed OH^- inside the pore are compensated by the ionization of water

molecular; **b** Two conductance mode of graphene nano/sub-nanopore with electroneutrality breakdown.

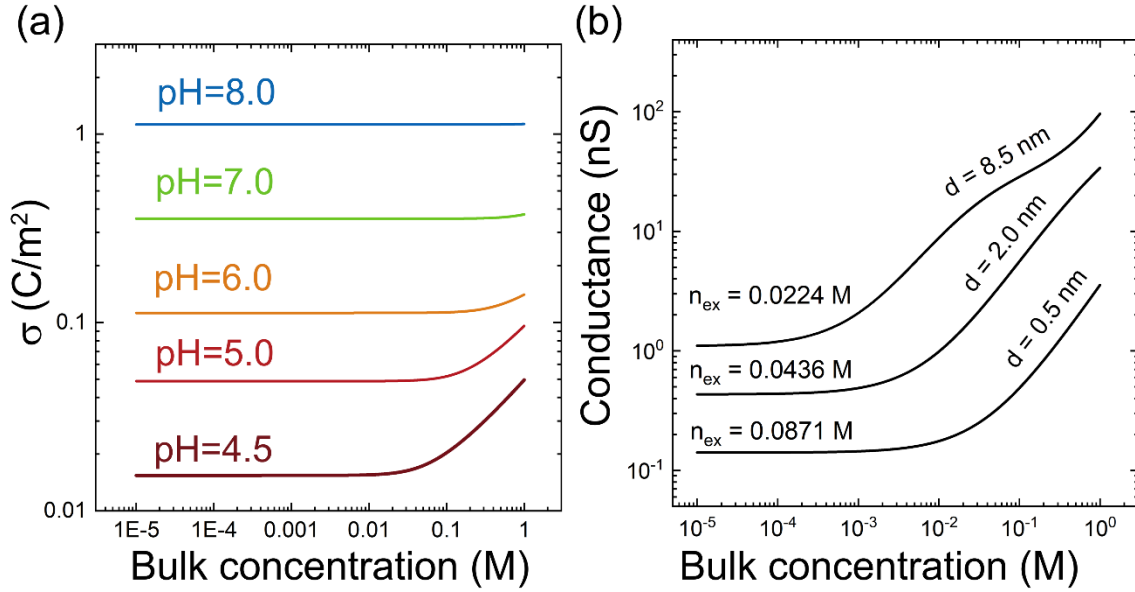


Figure 3. Numerical result for the model developed in this work. **a** Surface charge density changes with bulk salt concentration at different pHs. The nanopore diameter is fixed to $d = 5.50$ nm; **b** Scaling behavior transition of graphene nano/sub-nanopores with the breakdown of electroneutrality. The black lines represent calculations based on equation (6), with fixed values of $\text{pH} = 7.5$ and $U_{trap} = -0.6$ eV. As the pore diameter decreases from the nanometer to the sub-nanometer scale, the scaling behavior transitions from a four-stage reduction to a two-stage reduction.

Conductance model of atomically thin sub-nanopore with electroneutrality breakdown

The counter ions attracted by the charged pore edge are symmetric on both sides of the pore entrance⁵. Under an applied bias, potassium ions in the bulk solution are driven by the electric field towards the pore entrance. Two ion translocation processes can occur [see Fig. 2(b)]: (1) ions pass the nanopore directly, which dominates at high concentrations, and (2) ions replace the counterions in the EDLs at the pore entrance. Meanwhile, chloride ions in the bulk solution are repelled by the negative charged nanopore edge. These processes are closely related to the concentration of ions in the bulk solution and can be derived by introducing the condition of electroneutrality disruption into the classical nanopore conductance model. Assume that the concentration of potassium ions in the nanopore is n_K , and the concentration of chloride ions is n_{Cl} . When electroneutrality is disrupted, potassium ions in the bulk solution are adsorbed at the pore entrance, affecting the probability of potassium ions inside the pore, leading to $n_K = n_0$ inside the pore. The repulsion of chloride ions remains unchanged as $n_{Cl} = \sqrt{n_0^2 + \left(\frac{2\sigma}{de}\right)^2} - \frac{2\sigma}{de}$. The conductance inside the pore (G_p) with diameter of d and atomically thickness L can be written as:

$$G_p = eN_A \mu (n_{K^+} + n_{Cl^-}) \frac{\pi d^2}{4L} \quad (4)$$

where $\mu = \frac{1}{2}(\mu_{K^+} + \mu_{Cl^-})$ is the ion mobility. The conductance resulting from potassium ions transport from the bulk solution to the pore access (G_a) can be calculated using the Maxwell-Hall (MH) access resistance model, which has been validated for graphene nanopore^{26, 27}. When considering the distribution of counterions at the pore entrance, the MH model adapts to an extended form

$$G_a = 2eN_A \mu (n_{K^+} + n_{Cl^-})d + 2N_A\mu\sigma \quad (5)$$

Aside from potassium ions being replaced from the bulk solution, counterions located at the pore entrance can directly pass through the nanopore under the electric field driving force. This

process occurs relatively infrequently since counter ions tend to be trapped on both sides of the charged pore edge⁵. The conductance, induced by this process, G_{ex} , need to be calculated independently and integrated to determine the overall nanopore conductance (see Supplementary Information Supplementary Note D for demonstration). Assuming the concentration of counter ions is n_{ex} , the total conductance of the nanopore under breakdown of electroneutrality can be expressed as:

$$G_{tol} = (G_p^{-1} + 2G_a^{-1})^{-1} + G_{ex} \quad (6)$$

where $G_{ex} = eN_A \mu n_{ex} \left[\frac{4L}{\pi d^2} + \frac{1}{d} \right]^{-1}$ (see Supplementary Note2: G for derivation details). Using equation (6), Figure 3(b) illustrates the scaling behaviors transitioning from a four-stage decrease to a two-stage decrease by varying d and n_{ex} while keeping U_{trap} constant. It is necessary to point out that equation (6) simplifies the interaction model between ions and the nanopore. The first term on the right side of equation (6) represents the influence of bulk solution ions and counter-ions on the nanopore conductance, neglecting the influence of ion size. The second term on the right side of equation (6) reflects the interactions between counter ions and the nanopore edge, which lead to the breakdown of electroneutrality.

Quantification of hydration barrier

The interaction between hydrated ions and sub-nanometer ion channels has long been a topic of significant interest²⁸. The process of hydrated ions passing through graphene sub-nanopores is considered even more complex²⁹. Although equation (6) effectively fits the measured conductance of graphene sub-nanopores [see Fig. 1(c) (d)], the mechanism of ion transportation through such extreme confinement is worth further discussion. In 2017, Sahu et al. proposed that due to their atomic thickness, graphene sub-nanopores remove only a small portion of water molecules in the

hydration shell of ions, unlike longer sub-nanometer channels where complete dehydration occurs³⁰. Because only partial dehydration occurs, the hydration barrier is significantly lower than the hydration energy of the ions (the hydration energy of K^+ is about $20 k_B T$ ³¹), which leads to relatively high conductance when pore edge is negatively charged. In this work, we calculate the conductance of a sub-nanopore using the linear segments of I-V curves [see black points in Fig. 4(a) for example], where the hydration barrier is suppressed. The electroneutral breakdown in sub-nanopores can be attributed to two parts, the leakage of EDLs and the repulsion of the hydration barrier. Numerical calculation result in Fig. 4(b) shows that at $d < 2.50$ nm, $n = 1$ M, only single ion exists inside the pore. Therefore, the repulsion from the pore wall can be regarded as acting on a single ion. The chemical potential equilibrium of potassium ions inside the pore is given by

$$k_B T \log(n_0) = k_B T \log(n_0 + n_{ex}) + U_{leak} + U_{hyd} + e\psi_D \quad (7)$$

where U_{leak} is the equivalent repulsive energy describing the EDLs leakage as an effective repulsive potential for counter ions and U_{hyd} denotes the hydration barrier when ions go through the pore. At the sub-nanometer scale, the potential inside the pore is close to the ζ potential, thus chloride ions are virtually absent in sub-nanopores. Considering the Donnan equilibrium leads to

$$n_0^{-\frac{e\psi_D}{k_B T}} = \frac{4\sigma}{ed} \quad (8)$$

Combining equations (7) and (8) we obtain

$$U_{leak} + U_{hyd} = k_B T \log \left[\frac{4\sigma}{(n_0 + n_{ex})ed} \right] \quad (9)$$

At high bulk concentration, only potassium ions near the pore edge are attracted by the negative potential. To ensure the broad applicability of equation (9) across sub-nanopore to nanopore scales, we assume $n_0 \approx 0$. Circles in Fig. 4(c) illustrates the relationship between the free energy difference and the radius of the nanopore, predicted by equation (9). If the free energy difference

caused by ion dehydration is considered as potential energy difference caused by the dielectric environment variation, free energy loss caused by the repulsion between hydrated ions and the nanopore scales as $1/R^{32}$. Thus, we assume

$$U_{hyd} = k_B T \frac{a_H}{R} \quad (10)$$

where a_H is the critical radius at which the hydration barrier equals $1 k_B T$. When $R < a_H$, the hydration barrier becomes significant. And equation (9) becomes

$$\log\left(\frac{4\sigma}{en_{ex}d}\right) = \frac{a_H}{R} + \frac{U_{leak}}{k_B T} \quad (11)$$

The blue and red dashed lines in Fig. 4(c) illustrate the fit of equation (11) to the experimental results. When pH = 7.5, the fitting yields to $a_H = 0.78$ nm and $U_{leak} = 5.05 k_B T$. When pH = 5.0, we obtain $a_H = 0.07$ nm and $U_{leak} = 3.41 k_B T$. We note that the values of U_{leak} and U_{hyd} at pH = 5.0 are significantly lower than those at pH = 7.5. This is because the relatively high concentration of hydrogen ions in the bulk solution, reaching 10^{-5} M. Hydrogen ions have a higher mobility compared to potassium ions and encounter less hinderance by the sub-nanopore. Therefore, their contribution to conductance cannot be ignored at low bulk concentrations. This results in an underestimated predicted value of energy barrier when calculating equation (11). At pH = 7.5, the concentration of hydrogen ions in the solution is consistently much lower than that of potassium ions, making the prediction of equation (11) more accurate. Figure 4(c) compares Sahu's MD simulation results (black triangles) with the U_{hyd} obtained in this work (blue circles) at pH = 7.5, showing that they are of the same order of magnitude. Equation (11) fit well with Sahu's results, demonstrating the accuracy of the theoretical analysis in predicting the experimental results³⁰.

This result suggests that the graphene sub-nanopore may facilitate the passage of hydrated ions without experiencing significant dehydration penalties. Similar behavior has been recently observed in carbon nanotubes, demonstrating that hydrated ions would pass through charged nanotubes with ease². Figure 4(d) sketches the hydrated ion transport behavior [from left to right, corresponding to I, II and III regions in Fig. 4(c)], which is in agreement with previous work²⁹.

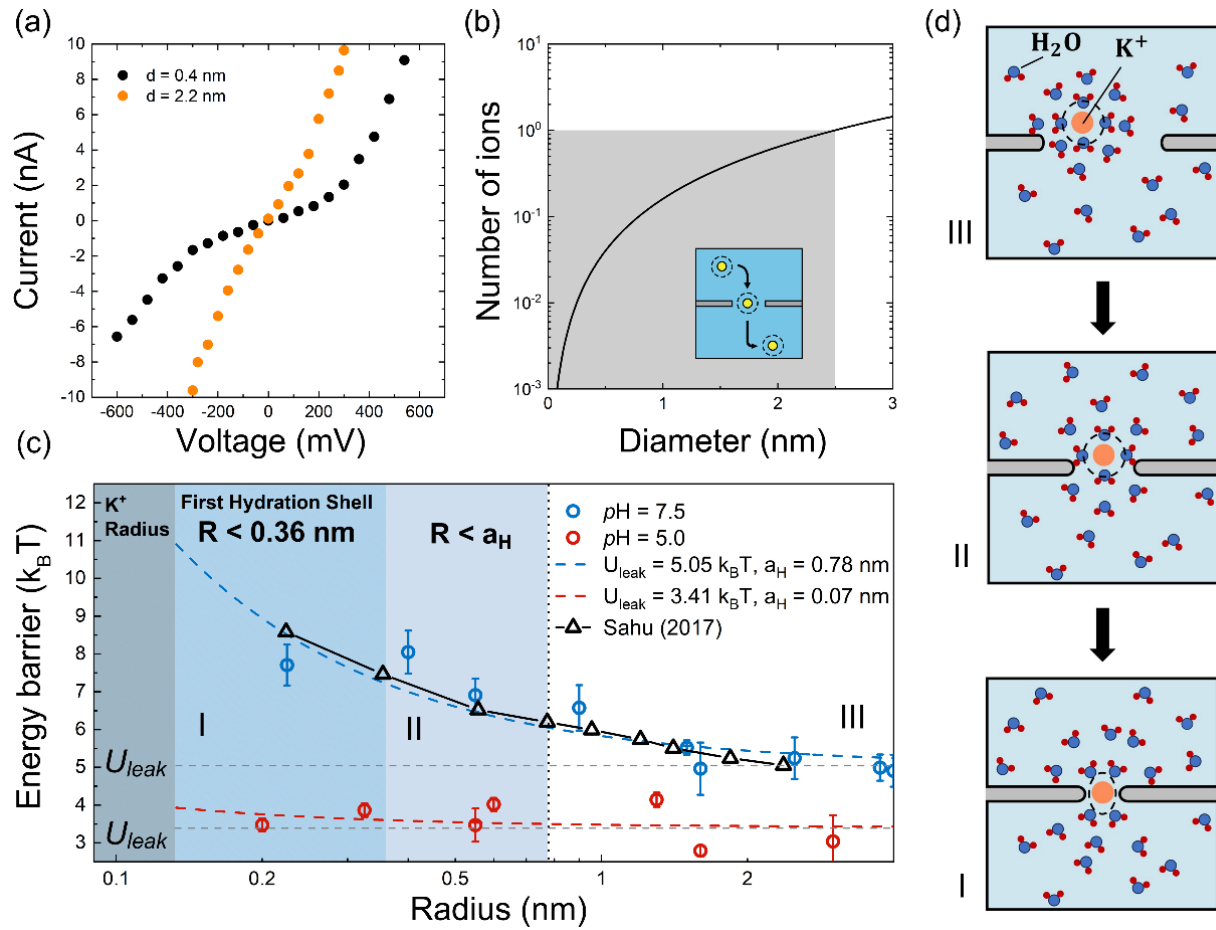


Figure 4. Ion transportation in graphene sub-nanopore. **a** I-V curves of sub-nanopore ($d = 0.6$ nm) and nanopore ($d = 2.2$ nm) at $n_0 = 1$ M, $pH = 7.5$; **b** Number of ions in pore interior calculated by $N = n \times (\pi d^2)/(4 L)$, $n = 1$ M; The inset cartoon illustrates the situation when

ion number is less than 1. **c** The energy barrier $\Delta E = U_{hyd} + U_{leak}$ changing with pore radius at different pH values. Dashed curves are fitted with equation (11); **d** Schematic of a hydrated ion transporting through graphene nanopores corresponding to the phases indicated in panel (c), pH = 7.5. Left, region I; middle, region II; right, region III.

In summary, the model proposed in this work successfully predicts the mechanisms of ion transport in atomically thin nanopores. The extremely thin thickness results in the complete leakage of the EDLs, which leads to electroneutral breakdown inside the pore and conductance scaling behavior. The hydration barrier further suppresses ion transport as the pore diameter decreases to the sub-nanometer scale. Our experimental results confirm that hydrated ions undergo only partial dehydration when passing through monolayer graphene sub-nanopores. As more experimental data become available in the future, the understanding of the interaction processes between hydrated ions and nano/sub-nano channels will undoubtedly deepen.

ASSOCIATED CONTENT

Supporting Information

Supplementary note 1. experimental setup: A. Fabrication of graphene nanopore; B. Pore conductance measurement; C. Discussion about Noh's and Lee's models.

Supplementary note 2. supplementary theory: A. Assumption and simplification; B. The approximation of the Poisson-Boltzmann equation in an infinitely long charged cylinder; C. Hydroxide ions adsorption theory; D. Conductance of an atomically thin graphene nanopore with electroneutrality breakdown.

Corresponding Author

Zhibo Liu - *The Key Laboratory of Weak Light Nonlinear Photonics, Ministry of Education, School of Physics and Teda Applied Physics Institute, Renewable Energy Conversion and Storage Center, State Key Laboratory of Photovoltaic Materials and Cells, Nankai University, Tianjin 300071, China; The collaborative Innovation Center of Extreme Optics, Shanxi University, Taiyuan, Shanxi 030006, China; Email:*

liuzb@nankai.edu.cn

Cuifeng Ying - *Advanced Optics & Photonics Laboratory, Department of Engineering, School of Science & Technology, Nottingham Trent University, Nottingham NG11 8NS, UK; Email:* cuifeng.ying@ntu.ac.uk

Authors

Xiao-Yu Huang - *The Key Laboratory of Weak Light Nonlinear Photonics, Ministry of Education, School of Physics and Teda Applied Physics Institute, Nankai University, Tianjin 300071, China*

Yangjun Cui - *The Key Laboratory of Weak Light Nonlinear Photonics, Ministry of Education, School of Physics and Teda Applied Physics Institute, Nankai University, Tianjin 300071, China*

Jianguo Tian - *The Key Laboratory of Weak Light Nonlinear Photonics, Ministry of Education, School of Physics and Teda Applied Physics Institute, Renewable Energy Conversion and Storage Center, State Key Laboratory of Photovoltaic Materials and Cells, Nankai University, Tianjin 300071, China.*

Author contributions

X. H. and Z. L. realised the conceptualization and written the original draft; X. H. investigated and designed the experiment; X. H. and Y. C. visualized the physical image; Z. L., C. Y. and J. T. supervised the whole study; C. Y. and Z. L. reviewed and edited the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This work was supported by the National Natural Science Foundation of China (Grant 12174207). C.Y. acknowledges the funding by UK-India Education and Research Initiative (UKIERI).

References

- (1) Duan, C.; Majumdar, A. Anomalous ion transport in 2-nm hydrophilic nanochannels. *Nat. Nanotechnol.* **2010**, 5 (12), 848-852.
- (2) Li, Z.; Misra, R. P.; Li, Y.; Yao, Y. C.; Zhao, S.; Zhang, Y.; Chen, Y.; Blankschtein, D.; Noy, A. Breakdown of the Nernst-Einstein relation in carbon nanotube porins. *Nat. Nanotechnol.* **2023**, 18 (2), 177-183.
- (3) Luo, Z. X.; Xing, Y. Z.; Ling, Y. C.; Kleinhammes, A.; Wu, Y. Electroneutrality breakdown and specific ion effects in nanoconfined aqueous electrolytes observed by NMR. *Nat. Commun.* **2015**, 6, 6358.
- (4) Tunuguntla, R. H.; Henley, R. Y.; Yao, Y.-C.; Pham, T. A.; Wanunu, M.; Noy, A. Enhanced water permeability and tunable ion selectivity in subnanometer carbon nanotube porins. *Science* **2017**, 357 (6353), 792-796.
- (5) Xiong, M.; Athreya, N.; Chakraborty, R.; Leburton, J. P. Ion Trapping and Thermionic Emission across Sub-nm Pores. *Nano Lett.* **2023**, 23 (24), 11719-11726.
- (6) Feng, J.; Liu, K.; Graf, M.; Dumcenco, D.; Kis, A.; Di Ventra, M.; Radenovic, A. Observation of ionic Coulomb blockade in nanopores. *Nat. Mater.* **2016**, 15 (8), 850-855.

- (7) Wang, J.; Cheng, C.; Zheng, X.; Idrobo, J. C.; Lu, A. Y.; Park, J. H.; Shin, B. G.; Jung, S. J.; Zhang, T.; Wang, H.; et al. Cascaded compression of size distribution of nanopores in monolayer graphene. *Nature* **2023**, 623 (7989), 956-963.
- (8) Rollings, R. C.; Kuan, A. T.; Golovchenko, J. A. Ion selectivity of graphene nanopores. *Nat. Commun.* **2016**, 7, 11408.
- (9) Noh, Y.; Aluru, N. R. Ion Transport in Electrically Imperfect Nanopores. *ACS Nano* **2020**, 14 (8), 10518-10526.
- (10) Smeets, R. M. M.; Keyser, U. F.; Krapf, D.; Wu, M.-Y.; Dekker, N. H.; Dekker, C. Salt Dependence of Ion Transport and DNA Translocation through Solid-State Nanopores. *Nano Lett.* **2006**, 6 (1), 89-95.
- (11) Feng, J.; Graf, M.; Liu, K.; Ovchinnikov, D.; Dumcenco, D.; Heiranian, M.; Nandigana, V.; Aluru, N. R.; Kis, A.; Radenovic, A. Single-layer MoS₂ nanopores as nanopower generators. *Nature* **2016**, 536 (7615), 197-200.
- (12) Hall, J. E. Access resistance of a small circular pore. *J. Gen. Physiol.* **1975**, 66 (4), 531-532.
- (13) Stein, D.; Kruithof, M.; Dekker, C. Surface-charge-governed ion transport in nanofluidic channels. *Phys. Rev. Lett.* **2004**, 93 (3), 035901.
- (14) Lee, C.; Joly, L.; Siria, A.; Biance, A. L.; Fulcrand, R.; Bocquet, L. Large apparent electric size of solid-state nanopores due to spatially extended surface conduction. *Nano Lett.* **2012**, 12 (8), 4037-4044.
- (15) Levy, A.; de Souza, J. P.; Bazant, M. Z. Breakdown of electroneutrality in nanopores. *J. Colloid Interface Sci.* **2020**, 579, 162-176.

- (16) Uematsu, Y.; Netz, R. R.; Bocquet, L.; Bonthuis, D. J. Crossover of the Power-Law Exponent for Carbon Nanotube Conductivity as a Function of Salinity. *J. Phys. Chem. B* **2018**, *122* (11), 2992-2997.
- (17) Secchi, E.; Nigues, A.; Jubin, L.; Siria, A.; Bocquet, L. Scaling Behavior for Ionic Transport and its Fluctuations in Individual Carbon Nanotubes. *Phys. Rev. Lett.* **2016**, *116* (15), 154501.
- (18) Wang, L.; Boutilier, M. S. H.; Kidambi, P. R.; Jang, D.; Hadjiconstantinou, N. G.; Karnik, R. Fundamental transport mechanisms, fabrication and potential applications of nanoporous atomically thin membranes. *Nat. Nanotechnol.* **2017**, *12* (6), 509-522.
- (19) Fu, Y.; Su, S.; Zhang, N.; Wang, Y.; Guo, X.; Xue, J. Dehydration-Determined Ion Selectivity of Graphene Subnanopores. *ACS Appl. Mater. Interfaces* **2020**, *12* (21), 24281-24288.
- (20) Barabash, M. L.; Gibby, W. A. T.; Guardiani, C.; Smolyanitsky, A.; Luchinsky, D. G.; McClintock, P. V. E. Origin and control of ionic hydration patterns in nanopores. *Commun. Mater.* **2021**, *2* (1), 65.
- (21) Sint, K.; Wang, B.; Král, P. Selective Ion Passage through Functionalized Graphene Nanopores. *J. Am. Chem. Soc.* **2008**, *130* (49), 16448-16449.
- (22) Kuan, A. T.; Lu, B.; Xie, P.; Szalay, T.; Golovchenko, J. A. Electrical pulse fabrication of graphene nanopores in electrolyte solution. *Appl. Phys. Lett.* **2015**, *106* (20), 203109.
- (23) Feng, J.; Liu, K.; Graf, M.; Lihter, M.; Bulushev, R. D.; Dumcenco, D.; Alexander, D. T.; Krasnozhan, D.; Vuletic, T.; Kis, A.; et al. Electrochemical Reaction in Single Layer MoS₂: Nanopores Opened Atom by Atom. *Nano Lett.* **2015**, *15* (5), 3431-3438.
- (24) Bocquet, L.; Charlaix, E. Nanofluidics, from bulk to interfaces. *Chem. Soc. Rev.* **2010**, *39* (3), 1073-1095.

- (25) Jiang, X.; Zhao, C.; Noh, Y.; Xu, Y.; Chen, Y.; Chen, F.; Ma, L.; Ren, W.; Aluru, N. R.; Feng, J. Nonlinear electrohydrodynamic ion transport in graphene nanopores. *Sci. Adv.* **2022**, *8* (2), eabj2510.
- (26) Heerema, S. J.; Schneider, G. F.; Rozemuller, M.; Vicarelli, L.; Zandbergen, H. W.; Dekker, C. 1/f noise in graphene nanopores. *Nanotechnology* **2015**, *26* (7), 074001.
- (27) Sahu, S.; Zwolak, M. Colloquium: Ionic phenomena in nanoscale pores through 2D materials. *Rev. Mod. Phys.* **2019**, *91*, 021004.
- (28) Zwolak, M.; Lagerqvist, J.; Di Ventra, M. Quantized ionic conductance in nanopores. *Phys. Rev. Lett.* **2009**, *103* (12), 128102.
- (29) Jain, T.; Rasera, B. C.; Guerrero, R. J.; Boutilier, M. S.; O'Hern, S. C.; Idrobo, J. C.; Karnik, R. Heterogeneous sub-continuum ionic transport in statistically isolated graphene nanopores. *Nat. Nanotechnol.* **2015**, *10* (12), 1053-1057.
- (30) Sahu, S.; Di Ventra, M.; Zwolak, M. Dehydration as a Universal Mechanism for Ion Selectivity in Graphene and Other Atomically Thin Pores. *Nano Lett.* **2017**, *17* (8), 4719-4724.
- (31) Richards, L. A.; Schafer, A. I.; Richards, B. S.; Corry, B. Quantifying barriers to monovalent anion transport in narrow non-polar pores. *Phys. Chem. Chem. Phys.* **2012**, *14* (33), 11633-11638.
- (32) Parsegian, A. Energy of an Ion crossing a Low Dielectric Membrane: Solutions to Four Relevant Electrostatic Problems. *Nature* **1969**, *221* (5183), 844-846.

SYNOPSIS

Xiao-Yu Huang, Yangjun Cui, Cuifeng Ying*, Jianguo Tian, Zhibo Liu*

Scaling Behavior and Conductance Mechanisms of Ion Transport in Atomically Thin Graphene Nano/Sub-Nanopores

ToC figure

