

Kinetic Ionic Permeation and Interfacial Doping of Supported Graphene

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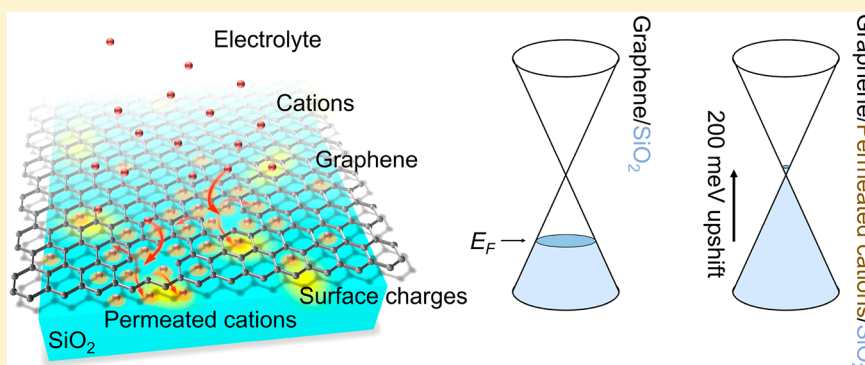
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Supporting Information



ABSTRACT: Due to its outstanding electrical properties and chemical stability, graphene finds widespread use in various electrochemical applications. Although the presence of electrolytes strongly affects its electrical conductivity, the underlying mechanism has remained elusive. Here, we employ terahertz spectroscopy as a contact-free means to investigate the impact of ubiquitous cations (Li^+ , Na^+ , K^+ , and Ca^{2+}) in aqueous solution on the electronic properties of SiO_2 -supported graphene. We find that, without applying any external potential, cations can shift the Fermi energy of initially hole-doped graphene by ~ 200 meV up to the Dirac point, thus counteracting the initial substrate-induced hole doping. Remarkably, the cation concentration and cation hydration complex size determine the kinetics and magnitude of this shift in the Fermi level. Combined with theoretical calculations, we show that the ion-induced Fermi level shift of graphene involves cationic permeation through graphene. The interfacial cations located between graphene and SiO_2 electrostatically counteract the substrate-induced hole doping effect in graphene. These insights are crucial for graphene device processing and further developing graphene as an ion-sensing material.

KEYWORDS: Graphene, terahertz spectroscopy, doping, ionic permeation

Graphene finds extensive use in various electrochemical applications, including ionic sensing,^{1,2} biochemical detection,^{3,4} lithium-ion batteries,⁵ dye-sensitized solar cells,⁶ and supercapacitors,^{7,8} due to its outstanding electrical and mechanical properties, large surface-to-volume ratio, and excellent chemical stability. Despite its critical importance for these applications, the effect of electrolyte solutions on the electronic properties of graphene has remained poorly understood. There is particular debate regarding the microscopic mechanism underlying the effect of aqueous solutions on graphene's conductivity, $\sigma = ne\mu$, where n is the charge

carrier density (related to the Fermi energy via $E_F = \hbar v_F(\pi n)^{1/2}$ where v_F is the Fermi velocity) and μ is the charge carrier mobility. Although it is apparent that the presence of (aqueous) electrolyte solutions affects the conductivity of graphene, it is typically not straightforward to disentangle how μ and n are affected. In the case of polymer

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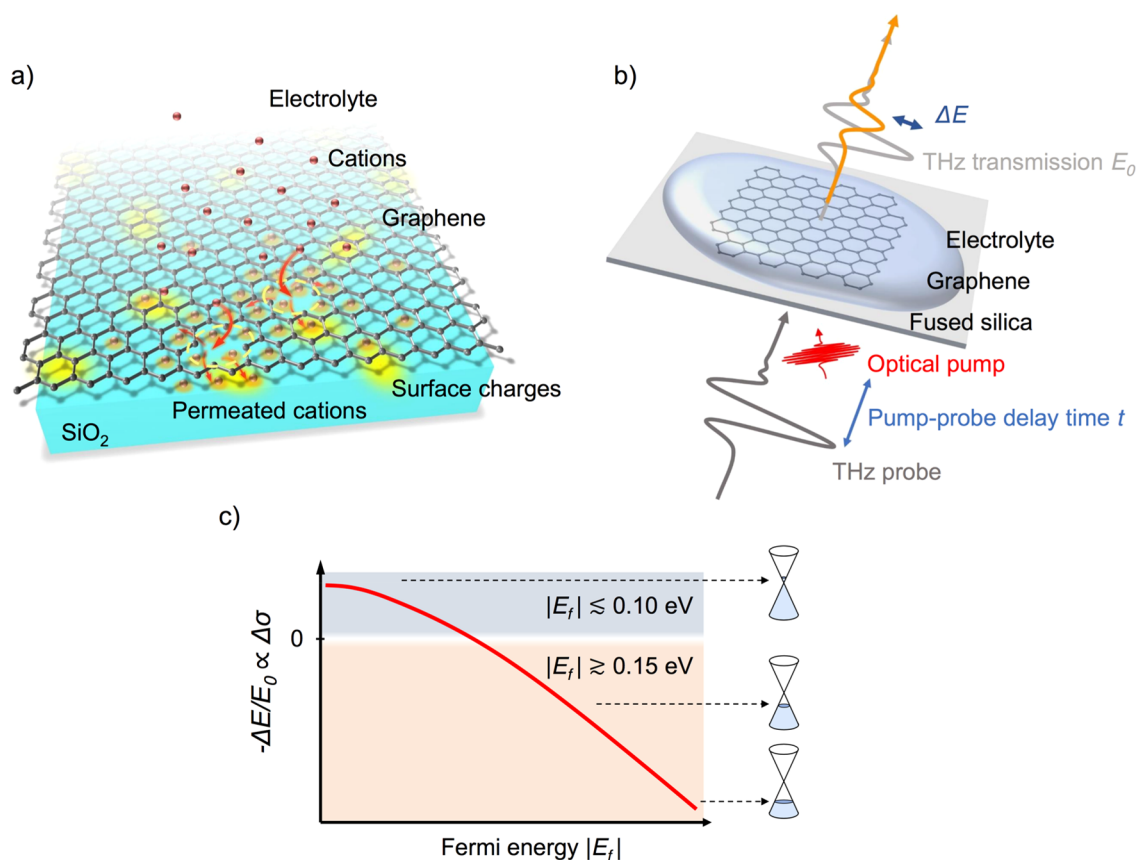


Figure 1. Concept of cation-induced Fermi level shift in graphene and its measurement. (a) Illustration of cation permeation through the graphene sheet to the graphene– SiO_2 interface. Graphene is initially hole-doped due to the presence of negative surface charges (indicated in yellow) on the SiO_2 surface. Intercalated cations lead to a shift of the Fermi level of graphene toward the Dirac point. (b) Schematic picture of optical pump–THz probe spectroscopy on the graphene/electrolyte system, with the graphene supported by fused silica (SiO_2). First, graphene is photoexcited by a femtosecond laser pulse (in red), followed by a THz probe pulse (in light gray). The change in THz transmission, $\Delta E = E - E_0$, is directly proportional to the change in THz conductivity, $\Delta\sigma$. (c) Illustration of typical Fermi energy-dependent THz photoconductivity, $-\Delta E/E_0 \propto \Delta\sigma$, in graphene. The conductivity is positive for graphene with the Fermi energy close to the Dirac point, whereas it becomes increasingly negative upon increasing the Fermi energy.^{25–28} This distinct sign change allows us to assign the effect of cations on the graphene conductivity to a change in Fermi level.

electrolyte solutions, it was found that they are extremely effective at inducing electron/hole doping in graphene through ions located in the Debye layer on top of graphene.⁹ The effect of cations has been primarily ascribed to cations absorbed on the surface of graphene, where they also act as charge-scattering centers,^{10–12} thus affecting μ . On the other hand, ions and water molecules have previously been reported to be able to diffuse between the interlayer space in van der Waals structures,^{13–16} and permeate through the graphene layer via atomic defects.^{17–19} Although these processes have been demonstrated to be useful for molecular separation and ionic sieving,^{17,20} its impact on the electronic and optoelectronic properties of graphene has not been considered and investigated. In addition, for graphene in contact with aqueous solutions, ion-induced variations of the charge carrier density, n , the role of defects in graphene, and the supporting substrate have remained elusive or mostly unexplored.

Here, employing optical pump–terahertz (THz) probe (OPTP) spectroscopy as a noncontact, all-optical method to determine the conductivity, we investigate the impact of a series of cations (based on chloride salts XCl or YCl_2 , with $\text{X} = \text{Li}^+$, Na^+ , K^+ , and $\text{Y} = \text{Ca}^{2+}$) in aqueous solution on the electrical conductivity of graphene supported by SiO_2 . We demonstrate that metal cations affect the conductivity mainly

through a strong electrostatic effect that shifts the Fermi level toward the Dirac point ($\Delta E_F \sim 200$ meV). Through kinetic measurements, we find that it takes tens of minutes for the Fermi energy shift to complete, where the time scale of this process depends critically on the solvation radius of the cations. We rationalize the concentration- and size-dependent cation-induced Fermi level shift that we observe as follows: cations permeate through pores or atomic defects in graphene (as schematically illustrated in Figure 1a) and diffuse further between the graphene– SiO_2 interface. Through electrostatic effects, most likely involving screening of the negatively charged SiO_2 surface by the intercalated cations, the p-type doping effect from the substrate is counteracted. Based on first-principles calculations, we find that, in line with our experimental observations, cations favor residing between graphene and SiO_2 rather than on top of graphene. Our report reveals the process of cation permeability through graphene and its impact on the electronic properties of graphene, highlighting the importance of the interfacial chemistry for graphene's applications in electrochemistry and electronics. These results have implications for graphene-based ion-sensing devices, graphene device processing, and possible applications of graphene in desalination membranes.

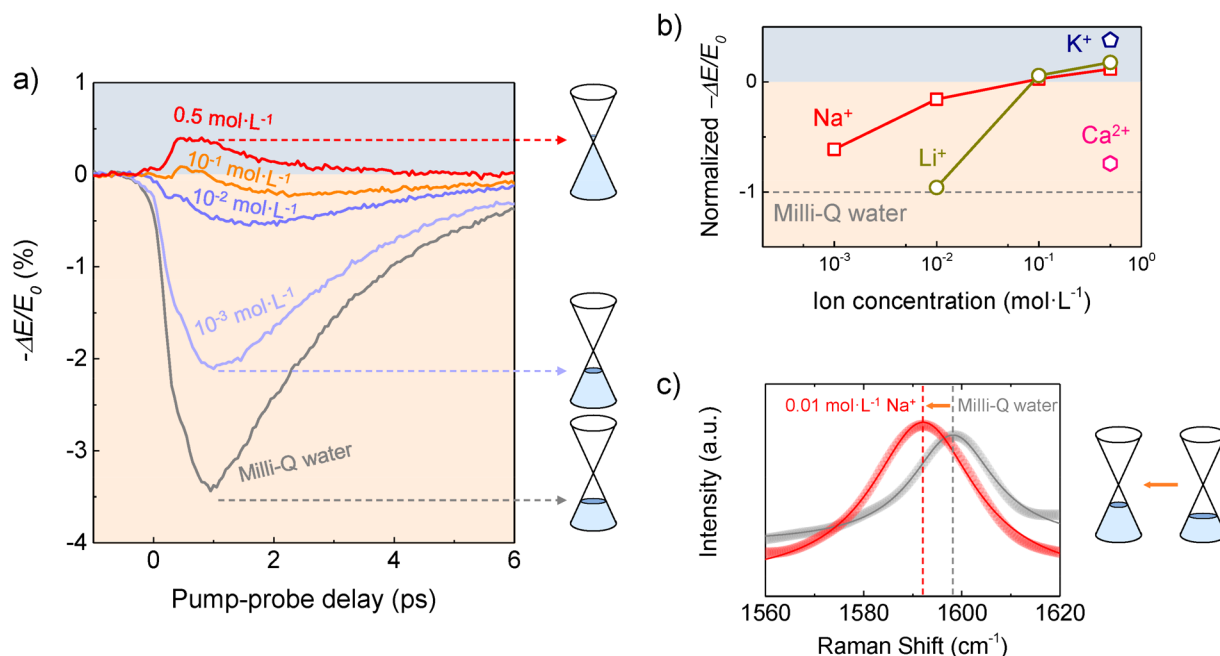


Figure 2. Effect of cations on the THz photoconductivity and Raman spectrum of graphene. (a) Cation (Na^+) concentration-dependent THz conductivity ($-\Delta E/E_0$) dynamics. The dynamics are recorded when the signal is saturated after graphene is in contact with electrolyte. (b) Peak value of the pump-induced THz conductivity for various ions (Li^+ , Na^+ , K^+ , Ca^{2+}) as a function of ion concentration. All data points are normalized to the THz conductivity value in Milli-Q water (shown as the gray dashed line). (c) Raman spectroscopy of graphene in the electrolyte. The G peak positions are 1592.1 cm^{-1} for graphene in 0.01 M Na^+ and 1598.2 cm^{-1} for Milli-Q. This indicates a shift of the Fermi level toward the Dirac point, as shown in the schematics on the right.

Results. We study the electrolyte effect on the electronic properties of graphene using monolayer graphene grown by chemical vapor deposition (CVD) that is transferred onto a fused silica (SiO_2) substrate (details in the [Supporting Information](#)). As typically observed, this leads to hole-doped graphene. The origin of this p-doping effect has been widely studied. Employing first-principles simulations, Nistor et al. identified the (negatively charged) dangling oxygen bonds present in the SiO_2 substrate as one of the main sources.²¹ Other origins, including hole-donating impurities either in the substrate lattice or on the graphene surfaces (such as molecular O_2), have been reported and proposed.^{22–24} We characterize the initial Fermi level of graphene on silica (without electrolyte) by Raman spectroscopy and find it to be $|E_F| = 220\text{--}280\text{ meV}$ (below the Dirac point). We then bring the graphene in contact with electrolytes by sandwiching the electrolyte of interest between the graphene (supported by SiO_2) and a top SiO_2 glass; we limit the thickness of the electrolyte by a Teflon spacer to be $\sim 10\text{ }\mu\text{m}$ to ensure sufficient THz transmission. In our study, the fluence of the laser pump is chosen such that we observe no change of THz conductivity of graphene over 1 h of measurements, as shown in [Figure S1](#). This indicates that our technique is noninvasive and does not create new defects or increase the size of existing defects.

Size-Dependent Cation Induced Doping Effect in Graphene. To monitor how cations affect the graphene conductivity, we employ OPTP spectroscopy. In a typical OPTP measurement, an 800 nm laser pulse with sub-100 fs duration photoexcites graphene. Subsequently, we record the THz transmission change induced by this pump as a function of delay time²⁹ between the optical excitation and THz pulse ([Figure 1b](#)). The change in the transmitted THz field, $\Delta E =$

$E_{\text{pump}} - E_0$ (where E_{pump} and E_0 are the transmissions with and without photoexcitation, respectively), is proportional to the conductivity change ($-\Delta E \propto \Delta\sigma$) of graphene. Whereas this technique is a powerful tool to study the ultrafast charge dynamics and conductivity in graphene,^{25–28,30–34} it also allows for obtaining information on the steady-state Fermi energy in a rather straightforward manner. The reason for this is that the sign and magnitude of the pump-induced THz photoconductivity ($-\Delta E/E_0$ or $\Delta\sigma$) are directly correlated to the Fermi energy in graphene, as we illustrate in [Figure 1c](#): When the Fermi level is close to the Dirac point in graphene ($|E_F| \lesssim 0.10\text{ eV}$), photoexcitation leads to graphene becoming more conductive; that is, the THz conductivity is positive following photoexcitation, whereas with the Fermi level away from the Dirac point ($|E_F| \gtrsim 0.15\text{ eV}$), graphene becomes more resistive after the optical pump, so the THz conductivity is negative.^{25–28,30,32,33} Thus, by monitoring the sign and magnitude of the changes in THz conductivity, we readily obtain the modulation of the Fermi energy in graphene. Importantly, this enables us to unambiguously disentangle changes in carrier density from changes in carrier mobility.

To interrogate the effect of the electrolyte or, more specifically, the role of hydrated cations in aqueous solution on the carrier conductivity in graphene, we study four different metal chloride solutions with various cation sizes: KCl, NaCl, LiCl, and CaCl_2 . To quantitatively study the effect of cations on the Fermi level, we fix the anion to Cl^- and the solvent to H_2O , thus focusing on the effect of cations. First, we investigate the effect of ionic concentration on the pump-induced THz conductivity (referred to as “THz photoconductivity” below) of graphene for the four different electrolytes. The electrolyte solutions do not absorb the excitation light and therefore show no differential terahertz

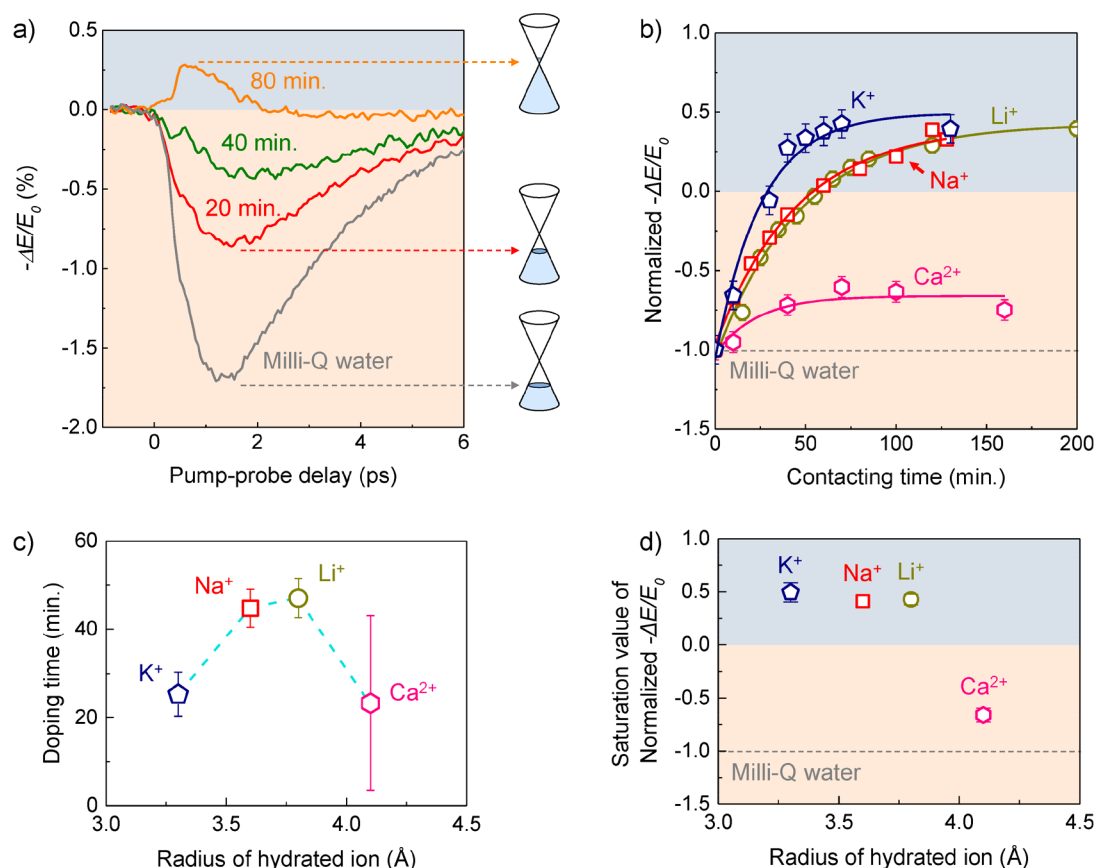


Figure 3. Time evolution of the cation-induced Fermi level shift in graphene. (a) Kinetic sodium ion (Na^+)-induced Fermi level shift in graphene, as revealed by monitoring the pump-induced change in THz transmission depending on the contacting time of sodium ion solution, 0.5 M NaCl aqueous solution. All measurements are conducted in the same spot of a graphene sample. (b) Peak value of the pump-induced THz change, $-\Delta E/E_0$, as a function of contacting time for metal cations including K^+ , Na^+ , Li^+ , and Ca^{2+} . All data points are normalized to the same starting point for a better comparison. (c) Doping time is plotted as the function of the radius of the hydrated ion. (d) Archived final Fermi levels (representing by the cation-induced THz conductivity changes in graphene) vs the hydrated cation radius.

response. We show typical results for NaCl in Figure 2a: the electrolyte gives rise to a decrease in the magnitude of the negative conductivity in graphene, using the THz photoconductivity of graphene in contact with Milli-Q water as a reference. At sufficiently high concentrations, the sign of the photoconductivity becomes positive (>0.1 M for NaCl, as presented in Figure 2a). Following the discussion related to Figure 1b, and given the fact that the initial doping of our graphene is p-type (~ 220 – 280 meV below the Dirac point), we conclude that the NaCl electrolyte induces a shift of the Fermi level toward the Dirac point (i.e., less hole doping) by an amount $\Delta E_F \sim 200$ meV.

As an independent verification of the observations using OPTP measurements, we perform Raman measurements, which allow for extracting the change of Fermi level in graphene. As shown in Figure 2c, we observe a shift of the G band from 1598.2 cm^{-1} for graphene in contact with 0.01 M NaCl electrolyte to 1592.1 cm^{-1} for graphene in contact with Milli-Q water, corresponding to a shift of Fermi level of ~ 150 meV toward the Dirac point, in agreement with our OPTP results (~ 200 meV upshift of the Fermi level in graphene by 0.5 M NaCl electrolyte).

In the following, we vary the cation concentration and study how this affects the THz photoconductivity with respect to that of graphene in contact with Milli-Q water as a reference. We summarize the cation-induced effect on the THz

photoconductivity of graphene (by taking the peak values charge carrier dynamics shown in Figure 2a) for a series of cations with varying ionic concentration, as shown in Figure 2b. Whereas all electrolytes show qualitatively the same effect (less negative photoconductivity and thus a Fermi energy shift toward the Dirac point), the achieved final Fermi level in graphene displays an obvious cation size effect with a trend from the largest shift for K^+ (with the smallest solvation radius of ~ 3.3 Å among all cations studied here³⁵) to the smallest change for Ca^{2+} (with the largest solvation radius of ~ 4.1 Å for the cations used³⁵). Sodium and lithium ions with similar size of hydrated radius have comparable effects at high concentration. In our study, we use the hydrated ion (solvation) radius (defined as the radius of the hydration sphere of the ions) rather than the ion radius because the solvation radius is relevant for transport in an aqueous solution.

Tracking the Cation Induced Doping Kinetics in Graphene. To further investigate the underlying mechanism for the observed size-dependent cation effect on the Fermi level, we monitor in situ the kinetics of the Fermi level changes by tracking the THz photoconductivity as a function of graphene–electrolyte contacting time. In Figure 3a for graphene in contact with a 0.5 M sodium chloride solution, the ion-induced Fermi level shift is not an instantaneous process. Instead, it takes ~ 80 min for the THz conductivity of graphene to gradually turn from negative to positive

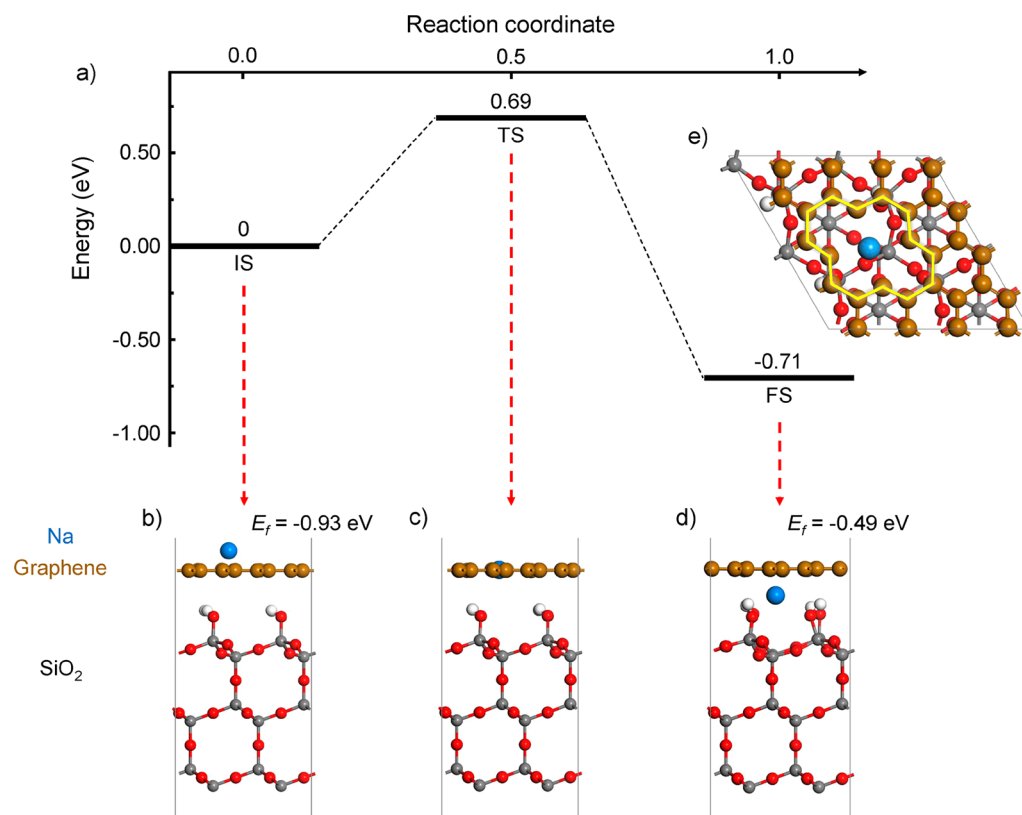


Figure 4. Simulation of cation effect at the graphene/SiO₂ interface. (a) System energetics for Na adsorbing at graphene's top surface, the energy barrier for Na permeation through a graphene double vacancy defect, and Na residing at the graphene–SiO₂ substrate interfaces. (b–d) Modeled atomic structures in cross-sectional views corresponding to the three energy states in (a). When Na is at graphene's top surface and at SiO₂'s surface beneath graphene, the calculated Fermi energies of the system are -0.93 and -0.49 eV, respectively (details in Figure S6). (e) Na residing at graphene–SiO₂ substrate interfaces after it permeates through a double vacancy defect (highlighted as a yellow polygon).

(corresponding to a change from hole-doped graphene to graphene with a Fermi energy in the vicinity of the Dirac point). We also study these cation-induced dynamics for graphene in contact with cations of different concentrations and sizes. First, we measure the ionic effect induced by 10^{-2} and 0.5 M NaCl electrolyte at the same sample spot of a graphene sample, as demonstrated in Figure S2a. The time required for reaching the final Fermi energy is much shorter for increased concentrations (~ 80 min vs 150 min to change the THz conductivity sign from negative to positive for 0.5 M in comparison to 10^{-2} M NaCl, respectively). Second, we compare concentration-dependent THz conductivity measurements for K⁺, Li⁺, and Ca²⁺. For a reliable comparison, we conduct all the THz measurements in a single spot of a graphene sample and fix the cationic concentration to be 0.5 M for all cases (for all original data, see Figure S2b in the Supporting Information). We describe the normalized time-dependent dynamics of the photoconductivity change by a single-exponential process, as indicated by the solid lines in Figure 3b. We plot the inferred exponential time scales and the final photoconductivity as a function of the solvation radius of the cations in Figure 3c,d. It appears that all three small cations (Li⁺, Na⁺, K⁺) used here can effectively modify the carrier density of graphene. However, cations with a larger ionic solvation radius (K⁺ < Na⁺ < Li⁺) require an increasingly longer time to achieve the Fermi level shift. For the largest hydrated ions, Ca²⁺, we observe a rather slight change in graphene's conductivity and, thus, Fermi energy. Finally, it is worth commenting that although the trend of the size-

dependent kinetics and degree of Fermi energy shift induced by cations (as shown in Figure 3c,d) is highly reproducible for all samples, we find that the absolute changes (e.g., doping time and magnitude) vary from sample to sample, presumably due to the variations in initial doping and defect densities of graphene in different samples (see the extended discussion in the next section).

Ionic Permeation and Interfacial Doping of Supported Graphene. The observed cation-induced change in Fermi energy (more specifically, the reduced hole density) challenges the intuitive and straightforward view that the cations are located on the top surface of graphene (which would not give rise to the observed slow, size- and time-dependent doping processes), and that they act only passively as scattering centers, solely modifying the carrier mobility. Instead, our results here can be explained by an ionic process that involves concentration-, size-, and time-dependent permeation of metal cations through atomic defects in graphene.^{17–19} The intercalated cations between the graphene and substrate surfaces then electrostatically screen the p-doping effect of the SiO₂ substrate, thus resulting in graphene with reduced p-doping. In principle, an atomically perfect graphene lattice is impermeable for all ions except for protons (H⁺), thus acting as an ideal sieve to protons from other cations.²⁰ This picture, however, does not hold for large-area graphene with inevitable atomic defects, such as missing carbon atoms resulting in nanopores. Indeed, permeation of ions and water molecules through graphene atomic defects has previously been reported,^{17–19} and selective cation transport through graphene

nanopores has also been demonstrated.^{17–19,36–38} Moreover, based on atomic force microscopy measurements of the CVD graphene used here (see Figure S3), we find grain boundaries and holes in the size range of up to several micrometers, which can be the initial sites for cation intercalation. As such, cation permeation is kinetically possible in our CVD graphene and is thermodynamically favorable (which is further supported by the simulation discussion in Figure 4). The cations tend to move to the supported silica surfaces and remain intercalated between graphene and the silica substrate, due to the negative surface potential of silica at neutral pH. The permeated cations can subsequently diffuse in-plane, away from the defect centers, along the graphene–SiO₂ interface.

For a certain size and amount of atomic defects in graphene, ionic permeation, as well as the subsequent diffusion of ions intercalated between graphene and SiO₂, depends critically on the size of the hydrated ions.^{18,19,36–38} Therefore, we expect cationic permeation and in-plane diffusion to speed up with smaller solvated ion size, as we indeed observe. When the size of hydrated cations or a hydrated cation complex (as for the case of Ca²⁺³⁹) further increases to be comparable or larger than the defects or nanopore size in graphene, ionic blockade can take place,³⁶ also in accordance with our experiment.

To further support our explanation and model of ionic permeation and the resultant shift of the Fermi energy of graphene by the intercalated cations, we highlight two additional experimental observations. First, following the equilibration of the graphene/silica system with a specific electrolyte solution, we exchange that solution with pure water and investigate the reverse process of the Fermi level shift (“redoping”) (Figure S2c). We find that substrate-induced hole doping is recovered after rinsing away the solutions containing the cations Li⁺, Na⁺, and K⁺. The recovery of the doping level in the absence of ions exhibits distinct size-dependent kinetics (detailed discussion in Figure S2). If the cations would not intercalate between SiO₂ and graphene, we would expect the ions to dissolve very quickly back into the water when the graphene is contacted with pure water. Instead, we observe a time scale on the order of tens of minutes and a clear dependence on ion hydration size, thus corroborating our picture of intercalated cations. Second, we find that the relative change in THz conductivity (and thus Fermi level shift) for a given ionic composition and concentration is much more pronounced when the graphene contains fewer polymer residues (by comparing two sets of graphene samples using different post-transfer treatments; details in Figure S4). We rationalize that the Fermi level shift depends crucially on the sample cleanliness; that is, when the cation permeation pathway is blocked by the polymer residuals, a smaller change in carrier density in graphene is achieved.

Simulations. We now present first-principles calculations by which we explore the interaction between SiO₂-supported graphene and electrolyte solutions. The simulations are based on spin-polarized density functional theory calculations as implemented in the Vienna ab initio simulation package,^{40,41} using Perdew–Burke–Ernzerhof⁴² functionals and the plane-wave projector augmented wave⁴³ method with van der Waals interactions.

In the optimized structure of supported graphene, the Si–O bond lengths are in the range of 1.60–1.62 Å, in good agreement with those in previous studies.^{44,45} The binding energy of –0.84 eV for a unit cell of the complex system is calculated as the energy difference between the bonded system

and the isolated parts, suggesting high stability. We then add a Na atom (consisting of Na⁺ ion plus an electron) into the model system to investigate the cation effect on graphene. To simplify the calculation, here, only Na⁺ is included in the simulation, and charge neutralization is realized by adding an electron instead of a Cl[–] anion. Despite the simplicity of our model, it captures the essence of the cation–graphene interaction and explains our experimental data well (as shown below). First, we investigate the energetics for two configurations of Na⁺ either on top of graphene or residing between graphene and the SiO₂ support. As shown in Figure 4a, our results clearly illustrate that it is energetically more favorable for the cation to reside between graphene and SiO₂ than to be adsorbed at the top surface of graphene, in good agreement with the conclusions from the experiments. Furthermore, we explore the kinetic Na⁺ permeation processes for graphene with (e.g., single vacancies and double vacancies) and without atomic defects (detailed in the Supporting Information). The permeation of Na⁺ through a perfect graphene layer is associated with a prohibitively high energetic barrier (>10 eV). The presence of a double vacancy reduces the barrier to 0.69 eV (3.22 eV with a single vacancy, as shown in Figure S5), which is comparable to the penetration barrier of 1.2–1.6 eV for a proton to migrate through the perfect graphene monolayer.²⁰ Finally, to investigate the impact of intercalating cations on graphene, we compute the density of states (DOS) of the complex with and without Na⁺ (Figure S6). The Fermi level appreciably shifts toward less negative values (from –0.93 to –0.49 eV) when Na⁺ is included in the complex. Figure S7 shows the partial DOS of the C atoms around Na⁺. Substantial p-orbitals of these carbon atoms emerge in the vicinity of the up-shifted Fermi level, suggesting that the new filled state originates from electrons in the p-orbitals of the C atoms in the vicinity of interfacial Na⁺. The shift of Fermi level in the complex system induced by Na⁺ is in line with the experimental results.

Summary. To summarize, employing optical pump–THz probe spectroscopy as a contact-free, all-optical conductivity measurement, we investigate the role of a series of cations with various solvation radii (based on chloride salt XCl and YCl₂ with X = Li⁺, Na⁺, K⁺, and Y = Ca²⁺) on the electrical conductivity of graphene. We observe a cation-induced shift of the Fermi level in excess of 200 meV toward the Dirac point in graphene. Combined with theoretical calculations, such an ionic effect in graphene appears to involve cationic permeation through defects in graphene, which is kinetically controlled by the interplay of the hydration radius of cations and the size of atomic defects in graphene.

These findings not only provide a new tool to monitor the ionic dynamics at graphene and potentially other materials interfaces but also offer new insights into the role of cation permeability through graphene and the influence of ion interfacial dynamics on electronic properties. Finally, these results are of interest for electrochemical charge and energy storage, graphene device processing (where, for example, etching chemical or electrolytes are extensively in use), desalination membranes, and ionic-sensing devices. Regarding the last case, controlling the size and density of atomic defects in graphene, as well as the nature of surface charges in supporting substrates, can serve as effective and novel approaches to enhance the ionic sensitivity and specificity.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.nanolett.9b04053>.

Optical pump–THz probe spectroscopy; graphene transfer; electrolyte contacting; computational methods and details; stability of graphene in laser excitation; evolution of the cation doping dynamics on graphene; surface characterization of graphene on SiO₂; comparison between less-clean graphene and clean graphene on fused silica; energy landscape and modeled structures for Na⁺ ion penetrating vacancies; density of state calculation result of graphene–SiO₂ interface; calculated PDOS of the C atom around Na⁺ (PDF)

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Author Contributions

H.I.W. and X.J. conceived the research and wrote the paper with input from all authors. H.I.W., K.-J.T., and M.B. supervised the project and interpreted the data. K.S., X.J., and F.H.L.K. prepared and characterized the graphene samples. Z.L., Z.C., A.N., and K.M. helped with the graphene sample preparation. X.J. obtained and analyzed the Raman and OPTP spectroscopy data. X.Y. helped with OPTP spectroscopy measurements. M.H. and J.J. performed the first-principles simulations.

Notes

The authors declare no competing financial interest.

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