Supporting Information for

Kinetic Ionic Permeation and Interfacial Doping of Supported Graphene

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III. References
I. Methods

1. Optical pump-THz probe (OPTP) spectroscopy. We perform photo-conductivity measurements of graphene using optical pump-THz probe (OPTP) spectroscopy. In the setup, the THz generation is based on the optical rectification process in ZnTe non-linear crystals, using 800 nm pulses with duration of ~ 50 fs. The time-dependent electric field strength of THz pulses (~ 1-2 ps duration) transmitted the sample is detected by a second ZnTe crystal using electro-optic sampling. By fixing the sampling delay time to the peak position of the THz pulse, we monitor the THz absorption change by a third laser pulse with a wavelength of 800 nm. By tuning the time delay between the pump and THz probe, we measure the time-dependent THz absorption and therefore, the photo-conductivity of our sample in the time domain. The OPTP setup is kept in an N$_2$ environment to avoid THz absorption in air.

2. Graphene transfer. For transferring CVD grown graphene on the copper foil to fused SiO$_2$ for THz measurements, a layer of PMMA is spin-coated on top of graphene. Subsequently, the copper is first etched in 3 g/100 ml ammonium persulfate ((NH$_4$)$_2$S$_2$O$_8$) aqueous solution which is filtered by a 0.2 $\mu$m Nylon membrane filter in advance. After rinsing the PMMA/graphene in Milli-Q water, we transfer the PMMA/graphene (1 cm $\times$ 1 cm) to fused silica. Then we keep the transferred PMMA/graphene on fused silica in vacuum at 80 °C for 12 hours. Afterward, the PMMA is removed in an acetone bath. Finally, the graphene on fused silica is annealed at 650 °C to remove the PMMA residue. We carry out all steps in dust-free environments.

3. Electrolyte contacting. We control the volume of electrolyte precisely with a micropipette. We sandwich the electrolyte between two pieces of fused silica with the graphene
being transferred on the bottom one and exposed to the electrolyte. The layer thickness of the electrolyte is controlled by a Teflon spacer ~ 10 micrometers (μm). In each measurement, we fix the sample in the OPTP setup to the same position to prevent the doping inhomogeneity of graphene controlled by a translational stage. During the changing of each electrolyte, we use a small piece of absorbent paper to absorb the original electrolyte gently from the edge of fused silica to avoid the damage of graphene, following by Milli-Q water rinsing, to remove the permeated ions at the interface.

4. The computational methods and details. The energy cutoff for the plane-wave basis set is 520 eV. The convergence criteria for structure relaxation are \(10^{-5}\) eV on the energy and 0.01 eV/Å on the residual force of each atom. The Brillouin zone was sampled with a Monkhorst-Pack mesh with \(3 \times 3 \times 1\) k-point grids.

We simulate the interaction between graphene and SiO\(_2\) surfaces using the repeated-slab model of three layers, and we set the vacuum separation to be 15 Å\(^{[1]}\). To model the amorphous SiO\(_2\) (α-SiO\(_2\)) used in the experiment in our periodic DFT calculation, we use the β- cristobalite crystal reported to possess similar structure to α-SiO\(_2\) as an approximation. This approach has been adopted by other authors as well\(^{2-4}\). The cristobalite silica surface contains the (111) and (100) faces mainly\(^{5,6}\). The Bravais-Donnay-Friedel-Harker method shows that β-cristobalite (111) plane is the dominant plane for SiO\(_2\). Therefore, the (111) plane is simulated for the surface of the substrate. For the 1 × 1 surface of β-cristobalite, the 4 × 4 supercell of graphene has a negligible mismatch of lattice constants. For the simulation of the substrate in electrolytes, we employ a fully hydroxylated SiO\(_2\) surface, which has been reported as a good approximation of the substrate\(^{7}\).
II. Supporting figures

Figure S1. The stability of graphene in laser excitation. The photoconductivity signal (peak value of $-\Delta E/E_0$) of graphene as the function of laser excitation time.

Figure S2. Evolution of the cation-induced Fermi level upshift in graphene. a. The peak value of the pump-induced THz change $-\Delta E/E_0$ as a function of Na$^+$ concentration. b, The peak value of $-\Delta E/E_0$ as the function of electrolyte contacting time. c, The reversibility of the cation doping effect on graphene. Here we plot the “re-doping rate $\nu$” (defined in the SI text) vs the hydrated cation size.

Figure S2. Note: We note that, for sufficiently long immersion (up to several hours), the doping
level returns to the initial doping level, indicating that the cation doping effect is thermodynamically reversible. The doping recovery, or reverse doping process, however, can be kinetically controlled by the cation size and Milli-Q water washing or immersion time. In order to quantitatively compare the cation size-dependent reverse doping kinetics, we define here a parameter “re-doping rate $v$” as the relative THz conductivity recovery from the final doping towards the initial doping, after immersing cation treated graphene into Milli-Q water for 10 minutes (see more experiments details in the supplementary information). The re-doping rate $v$ is ranging from 0% (i.e., rinsing is ineffective to remove the cation doping effect) to 100% (i.e., completely back to the initial doping). Remarkably we observe a size-dependent reverse doping kinetics which is inherently connected to the doping kinetics, as discussed in the following: (1) For three small cations K$^+$, Na$^+$, Li$^+$, which give rise to strong electron doping effect, we observe that after 10 minute immersion of graphene into Milli-Q water, none of them go back to the initial doping. Generally, the re-doping rate is very similar as 40-50% for Na$^+$ and K$^+$, and dramatically increase with increasing the hydrated ionic size (80% for Li$^+$) and eventually approached to 100% for the Ca$^{2+}$ (the largest solvated ion used here). This observation is in line with the size-dependent cation doping effect: the larger the ion, the less doping in graphene, and thus the faster the de-doping. The size-dependent reverse doping kinetics discussed here, provide further strong evidence that cation doping and reverse doping processes involve cation permeation though defects in graphene, and interfacial intercalation or diffusion along the graphene-SiO$_2$ interfaces.
Figure S3. Surface characterization of graphene on SiO$_2$. a, AFM image of the graphene on fused silica. b, AFM image of the same fused silica before graphene transfer. The scale bars in a and b (white lines) are 1 µm. c, Line profile along the guided golden lines in a and b. The black curve shows the surface roughness for fused silica which has been used in the experiments with roughness in the range of 1.23 nm. It is clear the roughness (0.54 nm) for graphene covered SiO$_2$ sample is much less than that of fused silica surface.
Figure S4. The comparison between less-clean graphene and clean graphene on fused silica. a, The peak value of the pump-induced THz conductivity for various ions (Na\(^+\), K\(^+\), Ca\(^{2+}\)) as a function of ion concentration, measured on less-clean graphene on fused silica. All data points are normalized to the THz conductivity value in Milli-Q water (shown as a gray dashed line). b, The peak value of the pump-induced THz conductivity for sodium ions (Na\(^+\)) as a function of ion concentration, measured on less-clean graphene (red filled squares) and clean graphene (red open squares) on fused silica. c, AFM images of one typical area of less-clean graphene on fused silica. d, AFM image of one typical area of clean graphene on fused silica.
Figure S5. The energy landscape and modeled structures for Na⁺ ion penetrating vacancies. 

a, The energy landscape for Na adsorbed at graphene top surface, the energy barrier for Na permeation through a vacancy defect, and Na residing at graphene-SiO₂ substrate interfaces for single and double vacancies, respectively. 

b, Na residing at graphene-SiO₂ substrate interfaces after it permeates through a double vacancy defect (highlighted as a yellow polygon). 

c, Na residing at graphene-SiO₂ substrate interfaces after it permeates through a single vacancy defect (highlighted as a yellow polygon).
Figure S6. The density of state (DOS) calculation result of the graphene-SiO$_2$ interface. a, Computed DOS of supported graphene. Inserts are the atomic structures of graphene on SiO$_2$. b, Computed DOS of the system with Na residing at graphene-SiO$_2$ interface. Insert the atomic structure of Na residing at graphene-SiO$_2$ interface.
Figure S7. The calculated PDOS of C atom around Na⁺. 

a, The top view of supported graphene, where yellow C atoms were selected for the PDOS. 
b, The calculated PDOS without Na⁺. 
c, The calculated PDOS with Na⁺.
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