ARTICLE
Received 5 Nov 2014 | Accepted 6 Feb 2015 | Published 17 Mar 2015

DOI: 10.1038/ncomms7539

Aqueous proton transfer across single-layer graphene

Jennifer L. Achtyl, Raymond R. Unocic, Lijun Xu, Yu Cai, Muralikrishna Raju, Weiwei Zhang, Robert L. Sacci, Ivan V. Vlassiouk, Pasquale F. Fulvio, Panchapakesan Ganesh, David J. Wesolowski, Sheng Dai, Adri C.T. van Duin, Matthew Neurock & Franz M. Geiger

Proton transfer across single-layer graphene proceeds with large computed energy barriers and is therefore thought to be unfavourable at room temperature unless nanoscale holes or dopants are introduced, or a potential bias is applied. Here we subject single-layer graphene supported on fused silica to cycles of high and low pH, and show that protons transfer reversibly from the aqueous phase through the graphene to the other side where they undergo acid-base chemistry with the silica hydroxyl groups. After ruling out diffusion through macroscopic pinholes, the protons are found to transfer through rare, naturally occurring atomic defects. Computer simulations reveal low energy barriers of 0.61–0.75 eV for aqueous proton transfer across hydroxyl-terminated atomic defects that participate in a Grotthuss-type relay, while pyrylium-like ether terminations shut down proton exchange. Unfavourable energy barriers to helium and hydrogen transfer indicate the process is selective for aqueous protons.
brick-and-mortar networks of stacked graphene oxide nanosheets can act as effective membranes, while single-layer graphene exhibits dramatically lower permeabilities towards gases. In fact, graphene is thought to be unfit even for proton transfer, which is associated with computed gas-phase energy barriers exceeding 1.4 eV (ref. 10) unless dopants or nanoscale openings are externally introduced, or an external potential bias is applied. To determine whether graphene is indeed impermeable to protons, we place well-characterized single-layer graphene on top of a fused silica substrate and cycle, at room temperature and constant ionic strength, the bulk pH of an aqueous solution above the graphene layer between basic and acidic. We test for proton exchange through graphene by probing the underlying silica surface with an interfacial potential-dependent version of second harmonic generation (SHG) using 120 fs input pulses at energies well below the graphene damage threshold. With a detection limit of 10^{-5} to 10^{-6} V (ref. 16), the method is sensitive enough to follow protonation or deprotonation of as little as 1% of the available silanol groups present in the area probed by SHG. The interfacial potential vanishes at the point of zero charge (PZC of fused silica ~ 2.5) (ref. 17), and the SHG signal intensity is small (14,18,19). Increasing the pH at constant ionic strength shifts the relevant interfacial acid–base equilibria SiOH^+ + OH^- ⇄ SiOH + H_2O and SiOH + OH^- ⇄ SiO^- + H_2O (pKa ~ 4.5 and ~8.5, respectively) to the right, and the resulting interfacial potential polarizes the interfacial water molecules such that the SHG signal intensity increases (14,18).

Intuitively, the close proximity of the graphene layer and the charged fused silica surface, combined with the sensitivity of the method, make our approach akin to an A-scale voltmeter for detecting even rare occurrences of proton exchange. We find no significant difference between the SHG versus time traces recorded in the presence and absence of graphene. After ruling out diffusion through macroscopic pinholes, the protons are found to transfer through rare, naturally occurring atomic defect sites in the graphene layer. Computer simulations reveal low energy processes for water-mediated proton transfer across hydroxyl-terminated atomic defect sites that participate in a Grothuss-type relay, while defects terminated by pyrylum-like ether bridges shut down proton exchange.

Results
Silanol protonation and deprotonation unimpeded by graphene.

Using a dual-pump flow system (Fig. 1a) at a flow rate of ~0.9 ml s^{-1}, we varied the bulk solution pH between 3 and 10 while maintaining constant 1 mM ionic strength (see Methods). As shown in Fig. 1b, we find no significant difference between the SHG versus time traces recorded in the presence and absence of graphene, and no statistically significant differences in the kinetic rates and jump durations (Supplementary Note 1, Supplementary Figs 1–2 and Supplementary Tables 1–2). The SHG responses to pH changes are consistent with the acid–base equilibria of the fused silica/water interface, yielding effective pK_a values of 3.5(1) and 8.3(2), which fall within the reported literature values (Supplementary Note 2 and Supplementary Fig. 3). This finding indicates that the SHG experiments do not track merely adsorption to the graphene/water interface but acid–base chemistry at the fused silica surface underneath it, for which proton transfer across the membrane is a necessary condition. As expected from refs 1–5, porous graphene multilayers do not inhibit proton transfer either (Supplementary Note 3 and Supplementary Figs 4–5). On the basis of these results we conclude that the fused silica/water interface does not behave differently in terms of relative surface charge density, in the duration of the jumps or in the rates of the jumps when single-layer graphene is present. These findings indicate that the acid–base chemistry at the fused silica/water interface occurs in an unimpeded fashion in the presence of single-layer graphene.

Importance of macroscopic defects ruled out.

Scanning electron microscopy (SEM, Methods) images of graphene single layers deposited on fused silica windows show a low density of macroscopic pinholes and that the graphene is free of cracks or folds (Fig. 1c). Two-dimensional (2D) diffusion from those locations to the location of the laser beam is considered by calculating, for a given proton diffusion coefficient D, the mean-square displacement, ⟨Δr^2⟩, according to 〈Δr^2⟩ = z · t · D, where t is time and z is the number of neighbouring sites to which the proton can hop (six in for the case of the hexagonal graphene lattice). In the literature, reported theoretically and experimentally determined proton surface diffusion coefficients range between 1.01 × 10^{-7} and 9.00 × 10^{-5} cm^2 s^{-1} (refs 24–39). While the bulk diffusion coefficient for a proton in water is accepted to range between 8 × 10^{-5} and 9 × 10^{-5} cm^2 s^{-1}, there are disagreements in the literature about whether the proton diffusion coefficient is similar to the bulk coefficient or slower than the bulk coefficient on hydrophobic and hydrophilic surfaces for a variety of different systems (24,28,38). Reactivity is expected to substantially slow down the 2D diffusion of the proton (approximately magnitude × 20 reduction) when it moves across an amphoteric oxide whose protonation effectively terminates the diffusion path. Reactive proton diffusion coefficients reported for Nafion are similarly low. Indeed, our own reactive force field calculations containing partially hydroxylated quartz surfaces show the proton diffusion is quickly terminated by protonation of the surface SiO^- groups (Supplementary Note 4 and Supplementary Fig. 6).

This result indicates that proton diffusion is significantly slower in the presence of surface anionic species due to proton trapping at these sites.

In our experiments, the continuous proton supply from the aqueous bulk is expected to form a propagating reaction front: our calculations show a drastically increased proton diffusion coefficient of 4.944 × 10^{-2} cm^2 s^{-1}, or just half of that of bulk water, once protons arriving through any opening within the graphene sheet interact with the hydroxylated portion of the surface that is located behind the reaction front. To conservatively assess an upper bound limit for our estimations, we calculated the proton mean-square displacement using a D-value of 1 × 10^{-6} cm^2 s^{-1}. The probability of placing our laser beam within the propagating reaction front emanating from a given macroscopic pinhole was then estimated to be 4% and 21% for 1 and 10 s SHG jump times, respectively (Supplementary Note 5, Supplementary Figs 7–10 and Supplementary Table 3). Given that the pH jumps were repeated on at least 18 different days with eight different graphene samples and delays in changes of the SHG response were not observed with statistical significance; so we conclude that the diffusion of protons from the few macroscopic pinholes that are present in our samples, or, alternatively, from the sample edge, to the area probed by the laser cannot explain our observations of proton transfer through graphene.

Imaging rare atomic defects.

Scanning transmission electron microscopy (STEM) was then used to search for atomic defects using annular dark field (ADF) STEM imaging at 60 kV (see Methods). The majority of the images show perfect six-fold symmetry in the position of the carbon atoms and vast areas that lack grain boundaries and atomic, or vacancy, defects (Fig. 1d). Nevertheless, similar to prior reports of atomic-scale vacancy
point defects\textsuperscript{44,45}, we find, albeit rarely, atomic defects (Fig. 1e). Unless hydrocarbons or heavy metal atoms\textsuperscript{46} are present in graphene, defect formation due to electron beam-induced etching (as opposed to ion bombardment or oxidative etching)\textsuperscript{47} of pristine chemical vapour deposition (CVD) graphene at the energies employed here is unlikely. Rather, the rare defects we observe on occasion are more likely to originate from the synthesis process or cosmic rays, as the STEM experiments are carried out below the knock-on damage threshold for graphene\textsuperscript{48}, and the femtosecond laser pulses are attenuated below the onset of processes other than SHG\textsuperscript{13}. Given a lower limit to the estimated defect-to-defect distance of ~0.1 \textmu m (ref. 49) (while difficult to determine accurately from Raman spectroscopy, the actual distance is likely to be longer), we assess the probability of placing our laser beam within the propagating reaction front emanating from a given atomic defect to be 100%.

**Discussion**

To elucidate the mechanisms for proton transfer, we discuss findings from density functional theory (DFT) calculations (Fig. 2) and ReaxFF reactive force field molecular dynamics (Fig. 3)\textsuperscript{50,51} simulations (Methods). DFT simulations track the detailed changes in the electronic structure and quantify the corresponding activation barriers as protons transfer from the water layer above the surface through the graphene interface and exit into solution on the opposite side of the surface. The ReaxFF simulations provide a larger scale representation of the interfaces and explicitly include dynamics.

We find that the main restriction for aqueous proton transfer through pristine, defect-free graphene is the energy required to push the proton through the center of an aromatic ring in the hydrophobic graphene layer as shown in Supplementary Fig. 11. While the protons readily migrate in the solution phase above and below the graphene surface via proton shuttling, they are unable to pass through the hydrophobic graphene layer. The energy costs to desolvate the proton from the aqueous layer and drive it through the center of an intact aromatic ring within the graphene layer are quite high and result in an activation barrier, that is, over 3.8 eV.

The basal planes of pristine graphene can, and do, contain rare atomic-scale defect sites comprised of carbon atom vacancies, as shown in Fig. 1e. Our calculations indicate that while the activation barrier for proton transfer through a single-vacancy site is over 1.9 eV lower than that for transfer through the pristine graphene surface, it is still nearly 2.0 eV due to the small size of the vacancy and the hydrophobicity of the surface. The formation of di- and tri-vacancy sites increases the diameter of the opening in the graphene layer and reduces the barrier further to ~1.5 eV, but this barrier is still too high to permit aqueous proton transfer at room temperature.

All of the defect terminations considered are energetically favourable as compared with the bare quad-vacancy system (Supplementary Note 6 and Supplementary Fig. 12). The removal of four carbon atoms in a central aromatic ring in the graphene layer leads to the formation of the quad-vacancy site as shown in Supplementary Fig. 13. This site is comprised of six coordin-
three oxygen atoms in epoxide-like arrangements reminiscent of pyrylium cations (different from the crown ethers recently reported by Guo et al.\textsuperscript{52}, or with six hydroxide groups. Proton transfer through the pyrylium-terminated quad-vacancy site requires 1.7 eV (Fig. 2a), attributed to the protophobicity of pyrylium cations and their in-plane localization, which leaves a 3.4 Å gap between water and the graphene substrate that prevents proton transfer. The hydroxyl-terminated site (Fig. 2b), however, provides hydrogen-bonding networks (Fig. 2d) that interconnect the graphene surface to the water layers above and below it. DFT and ReaxFF simulations indicate that these hydrogen-bonding networks serve as conduits that facilitate proton transfer from the solution phase to the surface through the center of the defect site and into the solution on the opposite side of the membrane via a Grotthuss mechanism\textsuperscript{53} involving proton shuttling. This proton transfer mechanism identified here involves relaying the proton from one of the top three defect hydroxyl groups to the next hydroxyl group and the next, subsequent transfer to one of the bottom three defect hydroxyl groups on the other side, and finally release into the aqueous phase. While solution-phase proton shuttling occurs with activation barriers \(< 0.2\) eV, the barrier for transferring the proton through the defect sites in graphene via the proton relay mechanism is just 0.68 eV (DFT, Fig. 2b, well reproduced by ReaxFF (0.61 eV)), indicating proton transfer will occur at room temperature.

Additional ReaxFF simulations show that a proton transfer channel, consisting of water molecules that transfer the protons through Grotthuss-type reactions, thins and finally vanishes when the pairs of OH groups terminating the defect site are successively replaced with oxygen atoms (Fig. 3a–d). These transfer paths are selective to aqueous protons as helium and H\textsubscript{2} transfer requires barriers exceeding 1.9 eV (Supplementary Note 7 and Supplementary Fig. 14). Table 1 gives the comparison of activation barriers for proton transfer through graphene in water calculated by ReaxFF and DFT. The barriers given by DFT for the pristine and single-vacancy case are high (3.9 and 2.0 eV, respectively) and insurmountable during molecular dynamics (MD) simulations at 300 K. ReaxFF overpredicts the barriers for proton transfer in the pristine and single vacancy case. Yet, the barriers for the relevant quad-vacancy cases given by ReaxFF are in good agreement with DFT. Note that ReaxFF was not specifically trained against any of these barriers.

We conclude that aqueous protons transfer through single-layer graphene via rare, OH-terminated atomic defects at room temperature. While the rarity of the atomic defect sites would make it challenging to follow proton exchange across graphene using the pH-sensitive electrodes, the close proximity of the graphene layer and the charged fused silica surface, where the experimental observation of surface protonation and deprotonation is made by SHG, allows for the experimental observation of proton exchange across these rare defects. The associated energy

**Figure 2 | Density functional theory calculations.** Side and top views of oxygen- (a) and OH- (b) terminated defect models used in the DFT calculations. Snapshots (c,d) and energetics (e,f) from the nudged elastic band calculations for proton transfer through the oxygen- and OH-terminated defect sites marking (region I) release of proton from H\textsubscript{3}O\textsuperscript{+} to oxygen and OH groups, respectively; (region II) relay of proton between oxygen and OH groups, respectively; (region III) release of proton from oxygen and OH groups to H\textsubscript{3}O\textsuperscript{+}, respectively. Denotations of spheres: grey = carbon; red = oxygen; white = hydrogen atoms.

**Figure 3 | Reactive force field calculations.** Proton channel formation from ReaxFF calculations of water-mediated proton transfer through atomic defects terminated in six OH groups (a), four OH groups and one oxygen atom (b), two OH groups and two oxygen atoms (c), and three oxygen atoms (d). Denotations of spheres: grey = carbon; red = oxygen; white = hydrogen atoms.
barriers are comparable to recent experimentally determined activation energy barriers for proton transfer through graphene subjected to an externally applied potential. From the SHG signal jump rates and the time required for 2D proton diffusion, we estimate that the presence of as few as a handful of atomic defects in a 1 μm² area sample of single-layer graphene is sufficient to allow for the apparent unimpeded protonation and deprotonation of the interfacial silanol groups within 10 s (Supplementary Note 8 and Supplementary Fig. 15). Yet, we caution that given the limited accuracy with which the defect density can be determined in large (mm)-scale graphene, aqueous protons may transfer across single-layer graphene not only along the path discussed here but also along others as well. The identification of low barriers specifically for water-assisted transfer of protons through OH-terminated atomic defects in graphene, and high barriers for oxygen-terminated defects could be an important step towards the preparation of zero-crossover proton-selective membranes.

Methods

CVD graphene synthesis. We used graphene having a grain size of ~100 μm (ref. 54) grown on copper foils by atmospheric pressure CVD. The graphene was transferred using spin coating of poly(methyl methacrylate) (PMMA) followed by copper etching in a FeCl₃ solution and PMMA removal in acetone. The transfer was made onto clean fused silica substrates (ISP Optics, 1” diameter, QI-W-25-1), flatness 1 wave per inch at 633 nm) to fill charging effects. Individual images were taken at 120 fs pulse width using variable flow peristaltic pumps as previously reported in vacuum. Using the flow system depicted in Fig. 1a, the pumps were switched to pull solutions from two different reservoirs. For the experiments reported here (clean fused silica substrates) for 1 h, rinsing at 110 °C oven for 30 min, oxygen plasma cleaned (Harrick Plasma) on high for 30 s, and then stored in Millipore water until the experiment. The graphene samples were not cleaned with this procedure, but were instead cleaned by flushing with ~21 of Millipore water before each experiment. Supplementary Note 9 describes the graphene characterization and analysis by Raman and ultraviolet–visible spectroscopy (Supplementary Fig. 16) prior to and after the pH-jump experiments.

Flow system and flow cell. As shown in Fig. 1a, the graphene-on-fused silica sample or the silica window were clamped face down against a Viton O-ring on the Teflon flow cell13,56 so that the surface of the interconnected aqueous phases was in contact below a 99% NaCl solution. Throughout the duration of the experiment, we also had to maintain a minimum of 300 s. After the system reached the steady state at pH 7, the flow was collected until it reached a steady state. It is assumed that the steady-state index between the phases and to avoid the use of an index-matching fluid.

Laser and detection system. A detailed description of our SHG setup has been described previously. Briefly, we use a regeneratively amplified Ti:sapphire system (Hercules, Spectra Physics) that operates at a kHz repetition rate to produce 120 fs pulses to pump an optical parametric amplifier (OPA-CF, Spectra Physics) tuned to produce 600 nm light. After exiting the OPA, the beam is then directed through a variable density filter to attenuate the pulse energy to either 3 ± 0.05 μJ per pulse for bare silica studies or 0.1 ± 0.05 μJ per pulse for graphene studies. The pulse energy used for the graphene films equates to a power density of 2.17(±0.002) μW cm⁻² per pulse with a 30 μm focal spot, which is well below the damage threshold of graphene as previously reported. At an angle just below...
total internal reflection, the p-polarized attenuated fundamental light is then directed through a fused silica hemisphere and focused at the graphene/water or silica/graphene interface. The reflected fundamental and second harmonic lights are directed through a Schott filter and a monochromator to remove any contributions at the fundamental frequency before amplification with a photomultiplier tube and detection using a gated single-photon counting system. Correct power dependencies and spectral responses are verified regularly, the SHG responses are well positioned, and photodamage does not occur. Given that the SHG jump is independent of the mean stream velocity (Supplementary Note 1), we are confident that the acid–base reactions occurring at the fused silica surface are not mass transfer limited. Ultraviolet–visible and Raman spectra indicate that the samples are resistant to acid-base cycling under the conditions employed here.

Computer simulations. First-principles periodic DFT calculations were carried out to determine the lowest energy interfacial water/graphene, water/graphene/water/silica structures and the activation barriers for proton diffusion through these interfaces using the Vienna Ab Initio Simulation Packages (VASP). In the DFT calculations, the reaction systems were modelled by optimizing a water phase above and below a single-graphene sheet. The simulations were carried out in a 5 × 5 supercell comprised of 50 carbon atoms, extended infinitively in the x and y dimensions. A 15 Å gap was inserted between the graphene layer perpendicular to the surface. The gap was subsequently filled with enough water molecules to match the overall density of water at 1.0 × 10^10 kg m^-3. The initial simulations were carried out with water on both sides of the graphene layer. The lower SiO2 substrate was initially simplified by using additional water. Subsequent calculations were carried out with more realistic slabs comprised of water/graphene/water/SiO2 substrates. The reaction rates and mechanisms of proton transfer through the graphene were described in the framework of transition state theory and within the harmonic approximation, which is robust for systems of high densities.

The gap was subsequently filled with enough water molecules to match the overall density of water at 1.0 × 10^10 kg m^-3. The initial simulations were carried out with water on both sides of the graphene layer. The lower SiO2 substrate was initially simplified by using additional water. Subsequent calculations were carried out with more realistic slabs comprised of water/graphene/water/SiO2 substrates. The reaction rates and mechanisms of proton transfer through the graphene were described in the framework of transition state theory and within the harmonic approximation, which is robust for systems of high densities.

All of the calculations were carried out within the generalized gradient approximation using Perdew–Burke–Erzerhöfer functional to treat exchange and correlation effects. Gradient corrections and projector augmented wave pseudopotentials to describe the electron–ion interactions. Plane wave basis sets with a cutoff energy of 400 eV were used to solve the Kohn–Sham equations for calculations for systems without water. Calculations for systems that include water solvation were carried out with cutoff energies for C and O of 283 eV. The surface Brillouin zone was sampled using a Monkhorst–Pack mesh of 3 × 3 × 1. All electronic energies were converged to within a tolerance of 1 × 10^-5 eV. All of the atoms were allowed to relax in the geometry optimizations until the forces on each atom were <0.03 eV Å^-1. Spin polarization was examined for all of the systems explored and applied when needed. Transition states were isolated using the nudged elastic band method applied when needed. Transition states were isolated using the nudged elastic band method (Supplementary Note 12 and Supplementary Fig. 20). In our simulations, we used a MD to validate predictions of force field in describing water/graphene systems and MD to validate predictions of force field in describing water/graphene systems. The gap was subsequently filled with enough water molecules to match the overall density of water at 1.0 × 10^10 kg m^-3. The initial simulations were carried out with water on both sides of the graphene layer. The lower SiO2 substrate was initially simplified by using additional water. Subsequent calculations were carried out with more realistic slabs comprised of water/graphene/water/SiO2 substrates. The reaction rates and mechanisms of proton transfer through the graphene were described in the framework of transition state theory and within the harmonic approximation, which is robust for systems of high densities.

All of the calculations were carried out within the generalized gradient approximation using Perdew–Burke–Erzerhöfer functional to treat exchange and correlation effects. Gradient corrections and projector augmented wave pseudopotentials to describe the electron–ion interactions. Plane wave basis sets with a cutoff energy of 400 eV were used to solve the Kohn–Sham equations for calculations for systems without water. Calculations for systems that include water solvation were carried out with cutoff energies for C and O of 283 eV. The surface Brillouin zone was sampled using a Monkhorst–Pack mesh of 3 × 3 × 1. All electronic energies were converged to within a tolerance of 1 × 10^-5 eV. All of the atoms were allowed to relax in the geometry optimizations until the forces on each atom were <0.03 eV Å^-1. Spin polarization was examined for all of the systems explored and applied when needed. Transition states were isolated using the nudged elastic band method applied when needed. Transition states were isolated using the nudged elastic band method (Supplementary Note 12 and Supplementary Fig. 20). In our simulations, we used a MD to validate predictions of force field in describing water/graphene systems. The gap was subsequently filled with enough water molecules to match the overall density of water at 1.0 × 10^10 kg m^-3. The initial simulations were carried out with water on both sides of the graphene layer. The lower SiO2 substrate was initially simplified by using additional water. Subsequent calculations were carried out with more realistic slabs comprised of water/graphene/water/SiO2 substrates. The reaction rates and mechanisms of proton transfer through the graphene were described in the framework of transition state theory and within the harmonic approximation, which is robust for systems of high densities.

All of the calculations were carried out within the generalized gradient approximation using Perdew–Burke–Erzerhöfer functional to treat exchange and correlation effects. Gradient corrections and projector augmented wave pseudopotentials to describe the electron–ion interactions. Plane wave basis sets with a cutoff energy of 400 eV were used to solve the Kohn–Sham equations for calculations for systems without water. Calculations for systems that include water solvation were carried out with cutoff energies for C and O of 283 eV. The surface Brillouin zone was sampled using a Monkhorst–Pack mesh of 3 × 3 × 1. All electronic energies were converged to within a tolerance of 1 × 10^-5 eV. All of the atoms were allowed to relax in the geometry optimizations until the forces on each atom were <0.03 eV Å^-1. Spin polarization was examined for all of the systems explored and applied when needed. Transition states were isolated using the nudged elastic band method applied when needed. Transition states were isolated using the nudged elastic band method (Supplementary Note 12 and Supplementary Fig. 20). In our simulations, we used a MD to validate predictions of force field in describing water/graphene systems. The gap was subsequently filled with enough water molecules to match the overall density of water at 1.0 × 10^10 kg m^-3. The initial simulations were carried out with water on both sides of the graphene layer. The lower SiO2 substrate was initially simplified by using additional water. Subsequent calculations were carried out with more realistic slabs comprised of water/graphene/water/SiO2 substrates. The reaction rates and mechanisms of proton transfer through the graphene were described in the framework of transition state theory and within the harmonic approximation, which is robust for systems of high densities.

The gap was subsequently filled with enough water molecules to match the overall density of water at 1.0 × 10^10 kg m^-3. The initial simulations were carried out with water on both sides of the graphene layer. The lower SiO2 substrate was initially simplified by using additional water. Subsequent calculations were carried out with more realistic slabs comprised of water/graphene/water/SiO2 substrates. The reaction rates and mechanisms of proton transfer through the graphene were described in the framework of transition state theory and within the harmonic approximation, which is robust for systems of high densities.
34. Smondyrev, A. M. & Voth, G. A. Molecular dynamics simulation of proton transport near the surface of a phospholipid membrane. *Biochim. Biophys. Acta* **1774**, 1136–1155 (2008).

35. van Duin, A. C., Dasgupta, S., Lorant, F. & Goddard, W. A. ReaxFF: a reactive force field for hydrocarbons. *J. Phys. Chem. A* **105**, 9396–9409 (2001).

36. Guo, J. et al. Crown ethers in graphene. *Nat. Commun.* **5**, 5389 (2014).

37. de Groot, J. C. T. Sur la décomposition de l'eau et des corps qu'elle tient en solution à l'aide de l'électricité galvanique. *Ann. Chim.* **58**, 54–73 (1806).

38. Vlassiouk, I. et al. Graphene nucleation density on copper: fundamental role of background pressure. *J. Phys. Chem. C* **117**, 18919–18926 (2013).

39. Huang, P. et al. Grains and grain boundaries in single-layer graphene atomic patchwork quilts. *Nature* **469**, 389–392 (2010).

40. Achtyl, J. L. et al. Interaction of magnesium ions with pristine single-layer and defective graphene/water interfaces studied by second harmonic generation. *J. Phys. Chem. B* **118**, 7739–7749 (2014).

41. Xu, K., Cao, P. & Heath, J. R. Graphene visualizes the first water adlayers on mica at ambient conditions. *Science* **329**, 1188–1191 (2010).

42. Krivanek, O. L. et al. An electron microscope for the aberration-corrected era. *Ultramicroscopy* **108**, 179–195 (2008).

43. Iuchi, S., Chen, H., Paesani, F. & Voth, G. A. Hydrated excess proton at water—hydrophobic interfaces. *J. Phys. Chem. B* **113**, 4017–4030 (2009).

44. Smondyrev, A. M. & Voth, G. A. Molecular dynamics simulation of proton transport near the surface of a phospholipid membrane. *Biochim. Biophys. Acta* **182**, 1460–1468 (2002).

45. Kudin, K. N. & Car, R. Why are water—hydrophobic interfaces charged? *J. Am. Chem. Soc.* **130**, 3915–3919 (2008).

46. Zhang, J. & Unwin, P. R. Scanning electrochemical microscopy (SECM) feedback approach for measuring lateral proton diffusion in langmuir monolayers: theory and application. *Phys. Chem. Chem. Phys.* **4**, 3814–3819 (2002).

47. Tuckerman, M. E., Chandra, A. & Marx, D. Structure and dynamics of OH-(aq). *Acc. Chem. Res.* **39**, 151–158 (2006).

48. Yamashita, T. & Voth, G. A. Properties of hydrated excess protons near phospholipid bilayers. *J. Phys. Chem. B* **114**, 592–603 (2009).

49. Springer, A., Hagen, V., Cherepanov, D. A., Antonenko, Y. N. & Pohl, P. Protons migrate along interfacial water without significant contributions from jumps between ionizable groups on the membrane surface. *Proc. Natl Acad. Sci. U.S.A.* **108**, 14461–14466 (2011).

50. Junge, W. M. S. The role of fixed and mobile buffers in the kinetics of proton movement. *Biochim. Biophys. Acta* **890**, 1–5 (1987).

51. Eikerling, M., Kornyshev, A. A., Kuznetsov, A. M., Ustrnul, J. & Walbran, S. Mechanisms of proton conductance in polymer electrolyte membranes. *J. Phys. Chem. B* **105**, 3646–3662 (2001).

52. Choi, P., Jalani, N. H. & Datta, R. Thermodynamics and proton transport in phospholipid bilayers. *J. Phys. Chem. B* **109**, 152, 3915–3919 (2008).

53. Perdew, J. P., Burke, K. & Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **5**, 3865–3868 (1996).

54. Hammouchi, M. et al. Acoustic waves in finite superlattices: influence of buffer layers. *Phys. Rev. B* **59**, 1999–2010 (1999).

55. Henkelman, G. & Jónsson, H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.* **113**, 9798–9805 (2000).

56. Buettner, M., Choudhury, P., Johnson, J. K. & Yates, J. T. Vacancy clusters as entry ports for cesium intercalation in graphite. *Carborn* **49**, 3937–3952 (2011).