## Peer Review File

# Molecular-scale insights into the electrical double layer at oxide-electrolyte interfaces

Corresponding Author: Professor Annabella Selloni

**This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.**

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

The group of authors has applied the DPLR method to make a machine learning potential to simulate TiO2 anatase (101) in the neutral pH electrolyte solution (0.4 M NaCl), the acidic electrolyte solution (0.4 M NaCl + 0.2 M HCl) and the basic electrolyte solution (0.4 M NaCl + 0.2 M NaOH) with the level of accuracy of AIMD simulations. Based on these simulations, they have investigated the double-layer charging, the point of zero charge, and the capacitance asymmetry. The results agree with experimental values and theoretical studies reported previously. It is a very appealing study with state-of-the-art techniques. However, the manuscript cannot be accepted in its current form and the following points need to be addressed during the revision.

Major points:

1) The most striking observation made in this set of simulations was the specific adsorption of Na+ at the anatase (101) surface. This leads to the formation of a double layer between adsorbed Na+ and counterion Cl- even in the neutral pH electrolyte solution. Is there any experimental evidence (besides Ref. 40) supporting this theoretical claim? In addition, what's the effective surface charge density due to the specific adsorption of Na+? Can the authors show the cumulative charge density profile(s) of ions based on Figure 2b or Figure S5 and put these new analyses in the Supporting Information? This will help the readers appreciate both the magnitude and the spread of this EDL at neutral pH due to specific ion adsorption.

2) If there are specific adsorptions of Na+, this will ramp up the point of zero charge (PZC). I think the discussion of PZC from simulations needs to be revised and expanded in light of this. In this scenario, the PZC is no longer just determined by reaction 1 and reaction 2 shown in Section 4 in the Supporting Information but is also affected by the surface charge density of adsorbed Na+.

3) On Page 4, Line 96, the authors commented that they cannot do other (surface) charge densities in the simulations because their nominal pHs are already 1.6 and 12.4. I don't think that is the case. Just inspecting Figure 1 and Figure 2 together in Ref. 40, it is clear that the surface charge density at the TiO2 surface will go from +8 uC/cm^2 to -8 uC/cm^2 when the solution pH changes from pH 4 to pH 7 (just by 3 units!). Given that the surface charge densities reported by the authors are comparable in magnitude (7.7 uC/cm^2 and -7.5 uC/cm^2) to the experiments, their nominal pH shift (11 units) calculated from the chemical composition does not reflect the true pH (shift) in the system. Therefore, the hands of the authors are not really tied because of the limitation of pH range and it would be much more impressive if they could use DPLR to do a full computational titration curve and therefore generate a differential capacitance curve.

4) The asymmetry in the Helmholtz capacitance on oxide surfaces has been reported and discussed in previous AIMD. In fact, the authors of Ref 24 and 25 provided different molecular explanations. Ref. 24 explained the capacitance asymmetry in terms of the extent of the water fluctuations at the interface, while Ref. 25 explained the phenomena with the orientation of chemisorbed water. In their most recent follow-up (https://doi.org/10.26434/chemrxiv-2024-bs1rr), a positive correlation between the water adsorption energy and the capacitance asymmetry has been established. These points need to be clarified when the authors introduce previous studies and discuss their results.

5) The authors' rationale for the capacitance asymmetry goes to the width of the double layer. It seems straightforward given their system already shows a specific adsorption of Na+ even at neutral pH. However, the specific ion adsorption was not seen in Ref. 24 for TiO2 rutile (110) despite that the capacitance value and its asymmetry are very similar to what was reported by the authors. This suggests that both the capacitance value and its asymmetry have little to do with the ion positions. It would be interesting to expand the discussion and include this point of view in the section "Differential capacitance".

6) The experimental data (Ref. 40) that the authors used to compare their simulations are meant for rutile rather than anatase. Ref. 19 and 24 were AIMD modelling of protonic double-layer at TiO2 rutile surface. Therefore, it would be fair to compare the capacitance values obtained from DPLR with these previous works from AIMD simulations and to mention them in the revised Text.

7) In Ref. 23, the degree of water dissociation was reported by the same authors to be 5.6% for the anatase (101)/water system. This value increases to 14% for the anatase(101)/0.4 M NaCl (sol) system reported in this work. Therefore, the specific adsorption of Na+ increases the degree of water dissociation. It would be interesting to mention this point in the revision. Then, the authors observed that the degree of water dissociation goes down to 9% with H+ adsorption in the acidic electrolyte solution. Figure 1 in Ref. 25 already reported this observation and it would be fair to mention it in the revised Text.

Minor points:

1) How were the WCs in Cl- and Na+ in DPLR represented? Were they simply neglected? What about their treatments in computing the electrostatic potential? Were they treated as a point dipole as in the case of Ti4+?

2) How does the adsorption of Na+ change the total surface charge density in acidic and basic electrolyte solutions as compared to the case in the neutral electrolyte solution? It would be very informative if the authors could replot Figure 1c including adsorbed Na+, i.e. $\sigma = e(NH+ - NOH- + NNa+)/S$, and add it to the Supporting Information.


Reviewer #2

(Remarks to the Author)
The manuscript of Car, Selloni and co-workers reports a computational study of the electrical double layer on TiO2 in contact with 0.4 M NaCl. To charge the surface, 0.2 M of HCl or NaOH is added. As such, the ionic strength of the medium is not constant, which could induce a first bias.
The major issue, however, is that "all additional H+ (or OH-) ions were gradually adsorbed on the surface within 3 ns". In other words, the interface and solution are not in equilibrium in terms of pH, making the corresponding results difficult to interpret in terms of described physics.
Unfortunately, the manuscript is, overall, quite technical and not focused on chemical insight: It is only on page 9 that the authors start to discuss actual chemistry. However, (a) the current discussion is very succinct (the last two paragraphs before the conclusion are the most interesting ones, but the results are poorly analysed/discussed, which is a pity. (b) some of the claims, such as "This allows Na+ to screen the surface charge more effectively than Cl-" is supposed to be highly cation/anion specific, as it depends on the (de-)solvation energies. In view of the absence of relative trends as a function of cations/anions and the validation of solvation energies, it is very difficult to judge whether this is meaningful, obvious or an artifact.
In summary, it a manuscript that is based on a large amount of simulations, but its chemical insight and conclusions are weak in its current form.

On a technical level, I think the authors should also report relative errors (not only eV/atoms), as this is most meaningful for assessing the accuracy for configurational sampling. Furthermore, unless I understood something wrong in their methodology, the authors should make it explicit that their approach to retrieve the electrostatic potential is only "relative". In other words, for example it cannot be used to compute the (absolute) potential of zero charge of metals.


Reviewer #3

(Remarks to the Author)
Zhang et al report a study of the water/anatase interface using machine learning potentials. The aim of the work is to understand how microscopic nature of the electronic double layer.

This is an excellent paper in all respects. It was a joy to read. The simulations are impressive and the figures are writing are impeccable. We congratulate the authors on such a well executed and presented study and only wish that all papers were as clear and easy to follow as this!

The main results are i) cations have a higher affinity to the surface which explains the difference between capacitance between basic and acid conditions, and ii) this difference it is attributed to a difference in the charge mechanisms.

Point i) has been suggested in the literature (this is acknowledged). Point ii) seems to be a new observation for which one requires the highly sophisticated simulations reported.

Publication in Nature Comms is recommended. However, we would like the authors to take the following points into consideration as addressing them will strengthen the paper.

We think the authors should explain better:

What causes the Na+ double peak in the density profiles. This result is counterintuitive since one would expect a Cl- layer to follow the (first) Na+ one. Does this play any relevant role? The authors use this point to argue that ML potentials are required.
What causes the different charging mechanisms? That section is rather descriptive, finding a clear explanation would support that it is not an artefact of the simulations, either deficiency of the ML potential, lack of convergence or finite size problems. (See also the first technical point below)

Technical details:

• page 5: 'All additional H+ (or OH−) ions were gradually adsorbed on the surface within 3 ns, leading to a positively (or negatively) charged surface' Does this mean that there are no protons/OH- in the bulk region? The appropriate way to define pH for this setup is to compute the H+/OH- concentration in the bulk region, if aqueous ions aren't present in the bulk region, it is unclear at which pH the simulations are being made. Also some evidence that the protocol for "adding HCL … NaOH at random positions" is robust would be helpful.
• It would be nice if they can show density profiles for the production system, as this is the key (raw) outcome of the simulations. The text mentions systems with a 67 A aqueous electrolyte yet the water density profiles for these systems are not shown (In Fig S3 it looks like the water region is <30 A). In addition, does the ion profile in the diffuse layer follow the mean-field approximations?
• Looking at Figures S3 and S4, the short-range models perform equally well than the long-range one. However, the authors argue otherwise in the methods section of the main document. In Fig. S5 there are differences but these simulations were run at 600 K. This raises a separate question about whether the simulations are fully conveyed. It would be very helpful for building confidence in these results if a convergence plot of ion and water density profiles as a function of simulation time (at the production temperature) was included in the SI.

Reviewer #4

(Remarks to the Author)
In this work, the authors have applied ab initio based machine learning potential (MLP) to simulate TiO2/NaCl electrolyte interface under different pH conditions. One of the highlights is they incorporate the long range electrostatics in the MLP, as implemented in the state-of-the-art DPLR, which is absolutely crucial for modelling electric double layers (EDL) at oxide interfaces. The efficiency and accuracy of the DPLR enable the authors to not only reliably calculate the microscopic structures of EDL, but also the EDL capacitances. More interestingly, the simulations show that that Na+ ions can lose partial solvation shell and specifically adsorb on anatase 101 surface directly coordinating with the surface oxygen. This finding would have direct implications on and point of zero charge (PZC) and flat band potential (FBP), contributing to the asymmetry of differential capacitance, if it is proven to be correct. The work overall is well structured, and I would recommend its publication provided the following issues have been satisfactorily addressed.

The above mentioned new finding is certainly interesting, but I have slight concern on the accuracy of the trained MLP and sufficiency of timescale achieving adsorption equilibrium. I would suggest that the authors provided some further evidence showing the accuracy of MLP, in particular for the structures with specific adsorption. For example, RMSEs of energies and forces for these structures in comparison with DFT. Also, calculate free energy profile for specific adsorption of Na+ to check the adsorption barrier and energy.

The reason I have this concern is that one of the implications of this finding is that the FBP of anatase 101 would be dependent of not only pH, but also the concentration of Na+ as adsorption thermodynamics, and thus ion concentration, determines the coverage of specifically adsorbed Na+ and further interfacial dipole due to the ordered ion pairs. This can in principle be observed in experiment – Is there any literature work showing this?

A related question is that would a similar behaviour occur on other surfaces, such as also well studied rutile 110. Of course, the difference is that bridge oxygen on rutile 110 is less exposed compared to anatase 101. Again, is there any experimental evidence that may indicate this difference?

Regarding the definitions of IMHP2 for Na+ and OHP for Cl- in Figure 2, I have a different opinion. Cations and anions have different sizes, and we don't usually expect that the positions of OHPs of cations and anions should line up. The definition of OHP should base on the criterion that the ions having full solvation shells approach the surface to the closest positions. In this sense, IMHP2 for Na+ should be defined as OHP for Na+, even though its position is different from that for Cl-. Similarly, IMHP1 for Cl- can be considered as IHP for Cl-.

Finally, I find that the section "microscopic surface charging mechanism" is less clear compared to the rest of the manuscript, which is worthy of improvement. The authors haven't explained the origin why the total number of surface charges would have such influences on the fraction of water dissociation. If these two quantities are positively correlated, why does the case under basic conditions with the higher total number of surface charges take almost the same water dissociation fraction as those under neutral conditions? It is also not clear how the specific adsorption of Na+ would affect the adsorption of water ions, as well as surface water dissociation.

Reviewer #5

(Remarks to the Author)
I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have thoroughly replied to the referees' comments and revised the manuscript accordingly. Although I don't agree with all the interpretations, it is fair to say that the authors have done a very good job. Therefore, I recommend it for publication.


Reviewer #2

(Remarks to the Author)
The authors have done all that could be expected with a reasonable additional effort, addressing the comments of the reviewers carefully and honestly.
Also, they have clarified important aspects, so that the manuscript is overall improved.
As such, I recommend publication of the manuscript.

Reviewer #3

(Remarks to the Author)
The authors have responded well to my queries. Publication is recommended.

Reviewer #4

(Remarks to the Author)
The authors have addressed the issues I raised and I am happy to recommend its publication as it is. I have also read through the comments from other reviewers as well as the authors' responses. I believe that the authors have done well in responses and corresponding revisions.

Reviewer #5

(Remarks to the Author)
I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

**NCOMMS-24-32405-T: Molecular-scale insights into the electrical double layer at oxide-electrolyte interfaces**

Reviewer Comments: Blue

Author Responses: Black

Revisions: Red

## Comments from Reviewer #1 and our detailed responses

**General Comments:** The group of authors has applied the DPLR method to make a machine learning potential to simulate TiO2 anatase (101) in the neutral pH electrolyte solution (0.4 M NaCl), the acidic electrolyte solution (0.4 M NaCl + 0.2 M HCl) and the basic electrolyte solution (0.4 M NaCl + 0.2 M NaOH) with the level of accuracy of AIMD simulations. Based on these simulations, they have investigated the double-layer charging, the point of zero charge, and the capacitance asymmetry. The results agree with experimental values and theoretical studies reported previously. It is a very appealing study with state-of-the-art techniques. However, the manuscript cannot be accepted in its current form and the following points need to be addressed during the revision.

**Authors' response:** We are grateful to Reviewer #1 for providing valuable feedback and comments, which are very helpful for further improving the quality of our manuscript.

**Major points:**

**Comment 1.1**: 1) The most striking observation made in this set of simulations was the specific adsorption of Na+ at the anatase (101) surface. This leads to the formation of a double layer between adsorbed Na+ and counterion Cl- even in the neutral pH electrolyte solution. Is there any experimental evidence (besides Ref. 40) supporting this theoretical claim?

**Authors' response:** There is substantial experimental evidence supporting the specific adsorption of cations at oxide surfaces even in neutral pH electrolyte solutions. For instance, Ref. 15 [*Langmuir* 20, 4954-4969 (2004)] utilized X-ray Reflectivity and X-ray Standing Waves experiments to investigate the rutile $TiO_2(110)$- solution interfacial structure and observed that $Rb^+$, $Sr^{2+}$, $Zn^{2+}$, and $Y^{3+}$ specifically adsorb on the rutile surface (pH ~6 to 11). These cations, with large atomic numbers, can be easily detected by X-ray techniques, whereas $Na^+$ could not, due to its small atomic number (Z=11). For $Na^+$, Ref. 15 reported molecular dynamics simulations suggesting that this ion is adsorbed at the surface. In addition, subsequent DFT calculations for anatase (101) in Ref.13 [*Langmuir* 29, 8572-8583 (2013)] found that $Na^+$ ions adsorb specifically at the surface $O_{2C}$ sites. In fact, this DFT study reported that "the most favorable coordination environment for $Na^+$ on the (101) anatase surface is an inner-sphere bidentate surface species, with the $Na^+$ ion coordinated to two bridging oxygen surface sites". This agrees with our finding that the adsorbed $Na^+$ is, on average, coordinated to two $O_{2c}$ atoms as shown in Fig. 2c of our main manuscript.

Note that both Refs. 13 and 15 were already cited in the original version of our manuscript.

**Changes in revised manuscript:** We added the text in red to page 7

"The Na$^+$ ions forming the first peak are, on average, coordinated to two surface O$_{2C}$ atoms (Fig. 2c), consistent with previous DFT results[13]."

**Comment 1.2:** "In addition, what's the effective surface charge density due to the specific adsorption of Na+? Can the authors show the cumulative charge density profile(s) of ions based on Figure 2b or Figure S5 and put these new analyses in the Supporting Information? This will help the readers appreciate both the magnitude and the spread of this EDL at neutral pH due to specific ion adsorption.

**Authors' response:** We thank the reviewer for this comment, which made us realize that the term "specific adsorption" may be confusing and induce the readers to consider the adsorbed Na$^+$ ions as a part of the surface charge. The specifically adsorbed Na$^+$ ions are part of the electrical double layer (EDL) rather than the surface charge, as indicated by the following remarks:

(1) As described in a widely used electrochemistry textbook (see, e.g., section 1.2.3, pages 12-14, of Bard *et al* "Electrochemical methods: fundamentals and applications", J. Wiley & Sons, 2022), the EDL is composed of an *inner layer* with total charge density $\sigma^i$, which is contributed by ions specifically adsorbed, and a *diffuse layer* with total charge density $\sigma^d$. The charge density at the solid surface $\sigma^M$ is balanced by the charge density in the EDL, which is expressed as $-\sigma^M = \sigma^i + \sigma^d$. Therefore, $\sigma^i$, i.e., the charge density contributed by the adsorbed Na$^+$ ions, is a part of the EDL rather than a part of the surface charge, and the latter should not include the contribution from Na$^+$ ions.

(2) As shown in Figure R1 below, the bond distance between Na$^+$ and O$_{2C}$ atoms, $r_{Na-O2c}$, is approximately 2.3 Å, which is almost the same as the distance between a Na$^+$ and a water molecule of its first hydration shell in the bulk solution. This distance is sufficiently large to exclude the Na$^+$ ions from being considered part of the surface charge.

Since the surface charge is determined solely by the H$^+$ and OH$^-$ ions that are adsorbed at the surface, we have defined the surface charge density $\sigma$ as $\sigma = e(N_{H+} - N_{OH-})/S$ rather than $\sigma = e(N_{H+} - N_{OH-} + N_{Na+})/S$ in our manuscript.
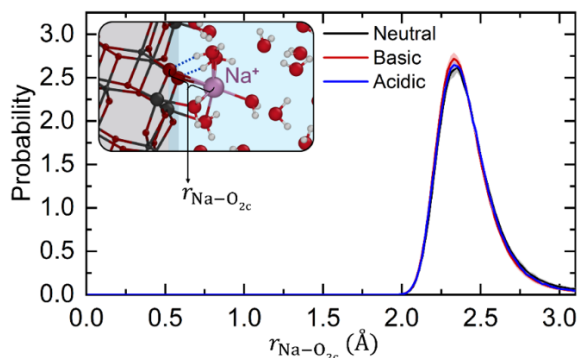


**Fig. R1** Normalized probability distribution of the distance between the Na$^+$ in the IHP and O$_{2C}$ atoms at TiO$_2$ surface, which is denoted as $r_{Na-O2c}$. The inset schematically shows the definition of $r_{Na-O2c}$.

**Changes in the revised manuscript**: we added Fig. R1 to the Supplementary Material (as Supplementary Figure 17) and the following text to page 7

"The distance, $r_{Na-O2c}$, between $Na^+$ and $O_{2C}$ fluctuates around 2.3 Å (Supplementary Figure 17), a value similar to the average distance between $Na^+$ and the water molecules in its first hydration shell in the bulk solution. With the $O_{2C}$ atoms substituting hydration water molecules, these $Na^+$ ions exhibit incomplete hydration shells (Fig. 2c) and can thus be identified as inner-sphere surface complexes…"

**Comment 2:** 2) If there are specific adsorptions of Na+, this will ramp up the point of zero charge (PZC). I think the discussion of PZC from simulations needs to be revised and expanded in light of this. In this scenario, the PZC is no longer just determined by reaction 1 and reaction 2 shown in Section 4 in the Supporting Information but is also affected by the surface charge density of adsorbed Na+."

**Authors' response:** The effect of adsorbed $Na^+$ on the pH point of zero charge (pH$_{pzc}$) has been discussed in previous literature. According to a widely cited paper by Sverjensky [*Geochimica et Cosmochimica Acta*, *69*, pp.225-257 (2005)], pH$_{pzc}$ is defined to "reflect only the protonation reactions". This paper also states that "electrolyte ion adsorption at the surface" can influence "the intersection point of surface titration curves corresponding to different ionic strengths". This intersection point is referred to as "the point-of-zero-salt effect (pH$_{pzse}$)", which "can be expected to differ from the pH$_{pzc}$. Values of the pH$_{pzse}$ for a given solid can depend on the ionic strengths and on the electrolyte type used in the experiments." In this work, we consider the pH$_{pzc}$ , for which only reaction 1 and reaction 2 are relevant. Furthermore, even for pH$_{pzse}$, the effect of the adsorbed ions is small. As shown by the titration curves for anatase in *Langmuir* 29, 8572-8583 (2013), the intersection points of different salt concentrations almost overlap. Therefore, the specific adsorption of $Na^+$ has a minimal effect on the pH$_{pzse}$ and does not influence the pH$_{pzc}$ reported in our study.

**Changes in the revised manuscript**: We added the text in red to page 4

"To support this inference, we performed enhanced sampling DPLR simulations to explicitly evaluate the pH$_{PZC}$ of the anatase (101)-neat water interface (Supplementary Section 4). We focused on neat water in this simulation because pH$_{pzc}$ is defined to reflect only the protonation reaction[43], unaffected by the presence of salt ions."

**Comment 3:** 3) On Page 4, Line 96, the authors commented that they cannot do other (surface) charge densities in the simulations because their nominal pHs are already 1.6 and 12.4. I don't think that is the case. Just inspecting Figure 1 and Figure 2 together in Ref. 40, it is clear that the surface charge density at the TiO2 surface will go from +8 uC/cm^2 to -8 uC/cm^2 when the solution pH changes from pH 4 to pH 7 (just by 3 units!). Given that the surface charge densities reported by the authors are comparable in magnitude (7.7 uC/cm^2 and -7.5 uC/cm^2) to the experiments, their nominal pH shift (11 units) calculated from the chemical composition does not reflect the true pH (shift) in the system. Therefore, the hands of the authors are not really tied because of the limitation of pH range and it would be much more impressive if they could use DPLR to do a full computational titration curve and therefore generate a differential capacitance curve."

**Authors' response:** We thank the reviewer for this comment. First, we would like to clarify that our statement on page 4, line 96 ("We note that with 2376 water molecules, adding a single $H^+$ or $OH^-$ ion yields a pH of 1.6 or 12.4, so pH values 1.6 < pH < 12.4 are not accessible to our simulations.") did not imply that we are unable to simulate other surface charge densities. Instead, our intention was just to point

out that the bulk region of our simulation cell cannot achieve pH values between 1.6 and 12.4 due to the limited cell size. **To avoid misunderstanding, we have deleted that sentence in the revised manuscript.**

In addition, we agree with the reviewer that conducting simulations with other surface charge densities would enhance the reliability and significance of our work. However, our DPLR simulations on large systems are computationally quite expensive and it is too demanding to obtain a full computational titration curve. Following the reviewer's suggestion, we have conducted two additional DPLR simulations with higher surface charge densities. Specifically, we increased the number of HCl and NaOH ion pairs in the electrolyte from 10 to 18, achieving higher surface charge densities of $\sigma_{a\prime} = 12.99 \pm 0.21 \ \mu C/cm^2$ and $\sigma_{b\prime} = -13.62 \pm 0.14 \ \mu C/cm^2$, respectively. The results of these new calculations are found to be fully consistent with our previous results (see Fig. R2 below), providing a more comprehensive understanding of the interface and increasing the robustness of our findings.

**Changes in revised manuscript:**

**(i)** We added Fig. R2a as Supplementary Fig. 18 and Fig. R2b as Fig. 3c of the main text. We also added the following discussion to Supplementary Section 10

"The ion density distributions of these two higher concentration systems (Supplementary Figure 18) exhibit the same features as the system presented in Fig. 2b of the main manuscript, but with large differences between the neutral, basic, and acidic systems due to the increased surface charge densities. Specifically, in the higher concentration basic system, more Na$^+$ ions are drawn close to the surface to screen the higher negative surface charge density, resulting in a first Na$^+$ peak with intensity as high as 25 M. This leads to a large capacitance of $C_{b\prime} = 130.9 \pm 14.4 \ \mu F/cm^2$. In contrast, for the higher concentration acidic system, there is only a modest increase in the Cl$^-$ peak intensity due to the repulsion between the negatively charged Cl$^-$ ion and the electronegative O$_{2c}$ atoms. Consequently, the capacitance of the higher concentration acidic system increases only slightly, viz. $C_{a\prime} = 63.1 \pm 2.8 \ \mu F/cm^2$. These calculated capacitances agree well with the experimental results as shown in Fig. 3c of the main manuscript."

**(ii)** The new results are mentioned on page 4

"Additional results for TiO$_2$ interfaces with electrolytes containing higher concentrations of NaOH and HCl are reported in Supplementary Section 10 and Fig. 3c."
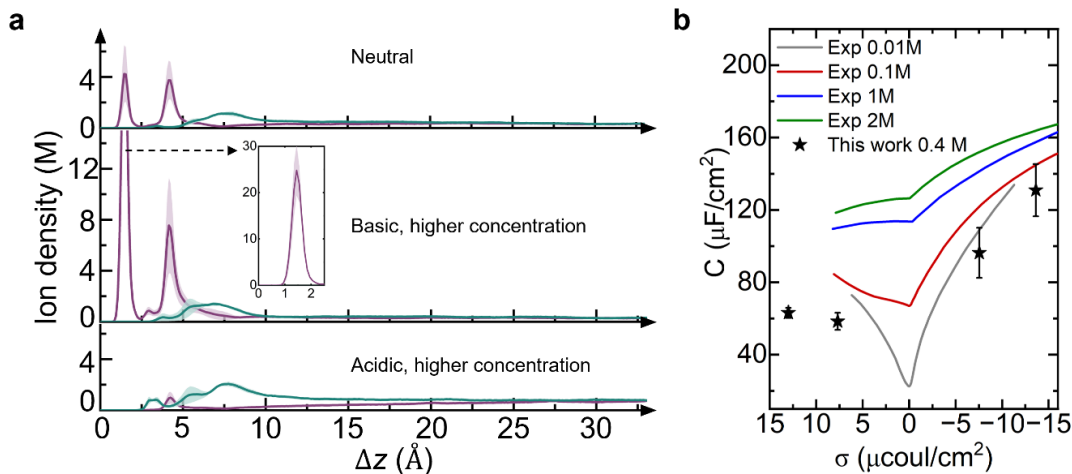


**Fig. R2 a,** Ion density distributions as functions of distance, $\Delta z$, from the solid surface, obtained from DPLR simulations of anatase (101) in contact with higher concentration acidic (0.4 M NaCl + 0.4 M HCl)

4

and basic (0.4 M NaCl + 0.4 M NaOH) solutions, compared to that of the neural 0.4 M NaCl solution. **b,** Comparison between our computed interfacial capacitance (star symbols) and experiments [40,51] for rutile TiO$_2$- aqueous NaNO$_3$ interfaces (solid lines). Different colors of the experimental curves represent different concentrations of the background NaNO$_3$ salt.

**Comment 4**: 4) The asymmetry in the Helmholtz capacitance on oxide surfaces has been reported and discussed in previous AIMD. In fact, the authors of Ref 24 and 25 provided different molecular explanations. Ref. 24 explained the capacitance asymmetry in terms of the extent of the water fluctuations at the interface, while Ref. 25 explained the phenomena with the orientation of chemisorbed water. In their most recent follow-up (https://doi.org/10.26434/chemrxiv-2024-bs1rr), a positive correlation between the water adsorption energy and the capacitance asymmetry has been established. These points need to be clarified when the authors introduce previous studies and discuss their results.

**Authors' response:** We appreciate the insights provided by Refs. 24, 25 and the most recent follow-up and have included a brief discussion of that work into our revised manuscript.

**Changes in revised manuscript:** We added the following sentences on pages 8-9:
"However, the underlying reason for this phenomenon remains a topic of active debate. Some studies attributed the larger capacitance under basic conditions to the high affinity of cations to the oxide[12,40]. In contrast, recent AIMD studies proposed that the difference is due to the distinct properties of water under basic and acidic conditions[24,25,49]. For example, Ref. 24 attributed it to the larger interfacial water fluctuations under basic conditions, Ref. 25 explained it in terms of the orientation of chemisorbed water, and Ref. 49 attributed it to the water adsorption energy."

**Comment 5**: 5) The authors' rationale for the capacitance asymmetry goes to the width of the double layer. It seems straightforward given their system already shows a specific adsorption of Na+ even at neutral pH. However, the specific ion adsorption was not seen in Ref. 24 for TiO2 rutile (110) despite that the capacitance value and its asymmetry are very similar to what was reported by the authors. This suggests that both the capacitance value and its asymmetry have little to do with the ion positions. It would be interesting to expand the discussion and include this point of view in the section "Differential capacitance".

**Authors' response:** We agree with the Reviewer that Ref. 24 did not report specific ion adsorption. It should be noted, however, that many details of those AIMD simulations were very different from ours. In particular, the ion concentration in Ref. 24 was much higher than ours while the simulation time was too short to allow for ion equilibration. Moreover, Ref. 24 only focused on the Helmholtz capacitance, $C_H$, whereas we calculate the full EDL capacitance $C$, with $\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_D}$, $C_D$ being the capacitance of the diffuse layer.

**Changes in revised manuscript:**
**(i)** We added the following text on page 8
"The microscopic structure of the EDL determines the differential capacitance $C$ of the interface, which is composed of contributions from the capacitance of the Stern layer ($C_H$, also called Helmholtz

capacitance) and the diffuse layer ($C_D$)[46], with $\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_D}$. While $C_H$ has been studied previously by AIMD simulations[19,24,25], the calculation of $C$ with *ab initio* accuracy has been a long-standing challenge due to the long simulation times and large simulation cells needed to equilibrate the EDL."

**(ii)** We made the following changes/additions on page 11

"Therefore, our simulations agree with the suggestion that the larger capacitance under basic conditions is primarily due to the higher affinity of cations to the oxide. Differences between our findings and previous AIMD simulations[19,24] are likely related to the higher ion concentrations used in the latter, their short equilibration times and their focus on the Helmholtz part only of the differential capacitance."

**Comment 6**: 6) The experimental data (Ref. 40) that the authors used to compare their simulations are meant for rutile rather than anatase. Ref. 19 and 24 were AIMD modelling of protonic double-layer at TiO2 rutile surface. Therefore, it would be fair to compare the capacitance values obtained from DPLR with these previous works from AIMD simulations and to mention them in the revised Text.

**Authors' response:** We thank the reviewer for pointing this out. Ref. 24 found that "$C_H^-$ is about 50% higher than $C_H^+$", which agrees well with our finding that the capacitance under basic conditions, $C_b$, is larger than that under acidic conditions, $C_a$, with $C_b/C_a = 1.6 \pm 0.3$. Ref. 19 found that the "inner sphere complexes have a slightly larger capacitance (0.4 F m$^{-2}$) compared to outer sphere complexes (0.3 F m$^{-2}$).", which also agrees with our results that the inner-sphere surface complexes of Na$^+$ results in a larger capacitance than the outer-sphere surface complexes of Cl$^-$.

**Changes in revised manuscript:** We added the comparison of the capacitance obtained from our DPLR simulations and previous AIMD works on page 9

"In particular, our calculated ratio of $C_b/C_a = 1.6 \pm 0.3$ agrees well with previous DFT[19,24] and experimental[40] results showing $C_b/C_a \approx 1.5$ at similar oxide/electrolyte interfaces".

**Comment 7**: In Ref. 23, the degree of water dissociation was reported by the same authors to be 5.6% for the anatase (101)/water system. This value increases to 14% for the anatase(101)/0.4 M NaCl (sol) system reported in this work. Therefore, the specific adsorption of Na+ increases the degree of water dissociation. It would be interesting to mention this point in the revision. Then, the authors observed that the degree of water dissociation goes down to 9% with H+ adsorption in the acidic electrolyte solution. Figure 1 in Ref. 25 already reported this observation and it would be fair to mention it in the revised Text.

**Authors' response:** The increase in the degree of water dissociation from 5.6% to 14% is not due to the addition of NaCl, but rather the result of transitioning from deep potential short-range (DPSR) to deep potential long-range (DPLR) simulations. As shown in Supplementary Figure 7 (already included in the original version of our manuscript), we computed the work required to move an H$^+$ from a surface O$_{2C}$ to an OH$^-$ adsorbed on an adjacent Ti$_{5c}$ at the anatase (101)-water interface. DPLR is in closer agreement with DFT than DPSR. The higher energy of undissociated water predicted by DPLR in comparison to DPSR is in accordance with the larger water dissociation fraction observed in DPLR simulations ($14.1 \pm 2.0\%$) relative to that reported by previous DPSR simulations ($5.6 \pm 0.5\%$) in Ref. 23.

To further clarify this point, we conducted DPLR molecular dynamics simulations of the TiO$_2$-water interface, using the same simulation cell size and simulation conditions as the TiO$_2$-NaCl$_{(aq)}$ interface.

As shown in Fig. R3 (see below), the averaged water dissociation fraction at the TiO$_2$-water interface after equilibrium is 13.6 ± 2.1%, which agrees with the water dissociation fraction of 14.1 ± 2.0% observed at the TiO$_2$-NaCl(aq) interface. Therefore, the specific adsorption of Na$^+$ does not significantly affect the water dissociation.

**Changes in revised manuscript:**

**(i)** We added Fig. R3 as Supplementary Fig. 8 and the following text to Supplementary Section 2.5.3.

We note that the increase in water dissociation fraction from 5.6% in a previous study[19] to 14% in this work is not due to the addition of NaCl, but rather the result of transitioning from DPSR to DPLR simulations. To further clarify this, we conducted DPLR molecular dynamics simulations of the TiO$_2$-neat water interface, using the same simulation cell size and simulation conditions as the TiO$_2$-NaCl$_{(aq)}$ interface. As shown in Supplementary Fig. 8, the averaged water dissociation fraction of the TiO$_2$-water interface after equilibrium is 13.6 ± 2.1%, which agrees with the water dissociation fraction of 14.1 ± 2.0% observed at the TiO$_2$-NaCl(aq) interface. 8
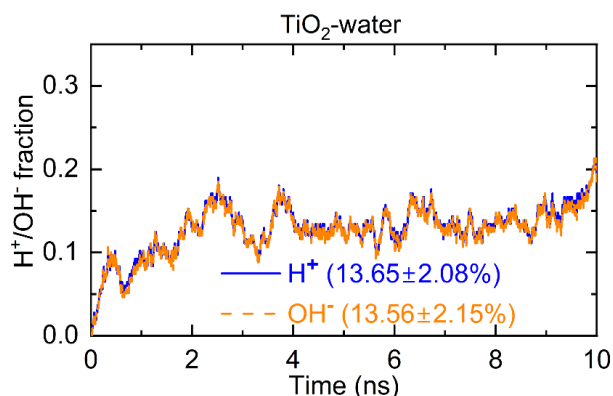


**Fig. R3** Time evolution of the surface H$^+$ and OH$^-$ coverage at TiO$_2$-water interface. The legends list the surface ion coverages averaged between 3-10 ns.

**(ii)** We mentioned Ref. 25, by adding the following sentence on page 12

"…, consistent with the increase of water dissociation fraction with the pH reported in a previous AIMD study[25]".

**Minor points:**

**Comment 8**: 1) How were the WCs in Cl- and Na+ in DPLR represented? Were they simply neglected? What about their treatments in computing the electrostatic potential? Were they treated as a point dipole as in the case of Ti4+?

**Authors' response:** In our DPLR simulations, the WCs for Cl$^-$ and Na$^+$ are treated explicitly. Specifically, Na$^+$ has a $+9e$ charge on the ion, counterbalanced by a $-8e$ charge from its WCs, and Cl$^-$ has a $+7e$ charge on the ion, counterbalanced by a $-8e$ charge from its WCs.

**Changes in revised manuscript:** We added the following sentence to Supplementary Section 2.3: "The WCs of O, Na$^+$, and Cl$^-$ are all treated explicitly."

**Comment 9**: 2) How does the adsorption of Na+ change the total surface charge density in acidic and basic electrolyte solutions as compared to the case in the neutral electrolyte solution? It would be very informative if the authors could replot Figure 1c including adsorbed Na+, i.e. \sigma = e(NH+ - NOH- + NNa+)/S, and add it to the Supporting Information.

**Authors' response:** As clarified in our response to Comment 1.2, the adsorbed Na$^+$ ions are part of the EDL rather than the surface charge. Therefore, the surface charge is solely determined by the H$^+$ and OH$^-$ ions adsorbed at the surface. This is why, in our manuscript, the surface charge density $\sigma$ is defined as $\sigma = e(N_{H+} - N_{OH-})/S$ rather than $\sigma = e(N_{H+} - N_{OH-} + N_{Na+})/S$.

**Comments from reviewer #2 and our detailed responses**

**General Comments**: The manuscript of Car, Selloni and co-workers reports a computational study of the electrical double layer on TiO2 in contact with 0.4 M NaCl … In summary, it a manuscript that is based on a large amount of simulations, but its chemical insight and conclusions are weak in its current form.

**Authors' response:** We thank Reviewer #2 for carefully reading our manuscript. Based on their comments, we have made significant revisions to provide further analysis and interpretation of our simulations and strengthen the chemical insights and conclusions of our work. We hope these revisions can address their concerns.

**Comment 1**: To charge the surface, 0.2 M of HCl or NaOH is added. As such, the ionic strength of the medium is not constant, which could induce a first bias.

**Authors' response:** We thank the reviewer for raising this important point. In this work, we considered TiO$_2$ interfaced with three different electrolyte solutions having initial concentrations of 0.4 M NaCl$_{(aq)}$ (neutral), 0.4 M NaCl$_{(aq)}$ + 0.2 M NaOH$_{(aq)}$ (basic), and 0.4 M NaCl$_{(aq)}$ + 0.2 M HCl$_{(aq)}$ (acidic). After equilibration with the electrical double layer, the average Na$^+$ and Cl$^-$ concentrations in the bulk electrolyte region were $0.34 \pm 0.02$, $0.41 \pm 0.02$, and $0.45 \pm 0.08$ M for the neutral, basic, and acidic solutions, respectively. The differences in ionic concentration among these three systems are rather small, with the neutral solution showing a slightly lower ion concentration compared to the basic and acidic systems.

To assess the impact of this small difference, we conducted an additional DPLR molecular dynamics simulation of the TiO$_2$ interfaced with a neutral NaCl electrolyte at a higher initial salt concentration of 0.5 M. After equilibration, the ionic density distribution of the TiO$_2$-0.5 M NaCl$_{(aq)}$ system was very similar to that of the TiO$_2$-0.4 M NaCl$_{(aq)}$ system reported in Fig. 2b of the main manuscript in the region close to the interface (see Fig. R4 below), whereas the average Na$^+$ and Cl$^-$ concentration in the bulk electrolyte region was $0.44 \pm 0.10$ M, which is close to the ion concentrations of the basic, 0.4 M NaCl$_{(aq)}$ + 0.2 M NaOH$_{(aq)}$, and acidic, 0.4 M NaCl$_{(aq)}$ + 0.2 M HCl$_{(aq)}$, solutions. Using the neutral TiO$_2$-0.5 M NaCl$_{(aq)}$ system as a reference, we obtained capacitance values of $C_a = 63.4 \pm 2.6\ \mu F/cm^2$ and $C_b = 87.9 \pm 5.7\ \mu F/cm^2$ under acidic and basic conditions, respectively, yielding a ratio $C_b/C_a = 1.4 \pm 0.1$. These new results agree (within respective error bars) with our previous findings of $C_b/C_a = 1.6 \pm 0.3$, as well as with the experimental results of $C_b/C_a \approx 1.5$. Therefore, the small differences in ionic strength among neutral, basic and acidic solutions do not affect the conclusions of our study.
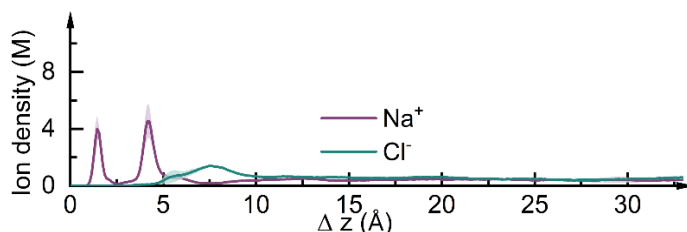


**Fig. R4** Ion density distributions as functions of distance $\Delta z = z - z_{\text{surface}}$ from the solid surface, obtained from DPLR simulations of anatase (101) in contact with 0.5 M NaCl$_{(aq)}$; the position of the solid surface, $z_{\text{surface}}$, corresponds to the average position of the O$_{2c}$ sites. The simulation were conducted for 5 ns at 330

K with the first 3 ns discarded for equilibration purposes. The error bars were derived from simulations using two independent DPLR models.

**Changes in the revised manuscript**: We have added Fig. R4 and the following paragraph to Supplementary Information Section 8.

"Another limitation of the finite cell size is the difference in ion concentration between neutral and acidic or basic systems. To change the pH of the systems, we added 0.2 M HCl or 0.2 M NaOH to 0.4 M NaCl solution. This procedure follows the titration experiment protocol[29,30]. In the experimental setup, the ionic strength remains essentially unchanged due to the large size of the system. Instead, the addition of NaOH and HCl to our finite-sized simulation cell alters the ionic strength. After equilibration with the electrical double layer, the average $Na^+$ and $Cl^-$ concentrations in the bulk electrolyte region for the neutral, basic, and acidic systems are $0.34 \pm 0.02$, $0.41 \pm 0.02$, and $0.45 \pm 0.08$ M, respectively. The differences in ionic concentration among these three systems are relatively small, with the neutral system showing a somewhat lower ion concentration compared to the basic and acidic systems. To assess the impact of this difference in ionic concentration, we conducted an additional DPLR molecular dynamics simulation of the $TiO_2$ interface with a neutral NaCl electrolyte at a higher initial salt concentration of 0.5 M. After equilibration, the ionic density distribution of this $TiO_2$-0.5 M $NaCl_{(aq)}$ system (Supplementary Fig. 16) is very similar to that of the $TiO_2$-0.4 M $NaCl_{(aq)}$ system in Fig. 2b of the main manuscript in the region close to the interface. However, the average $Na^+$ and $Cl^-$ concentration of the 0.5 M $NaCl_{(aq)}$ solution in the bulk electrolyte region was found to be $0.44 \pm 0.10$ M, which is closer to the ion concentrations of the basic and acidic solutions compared to the original 0.4 M $NaCl_{(aq)}$ system. Using the 0.5 M $NaCl_{(aq)}$ system as a reference, we obtained capacitance values under acidic and basic conditions of $C_a = 63.4 \pm 2.6 \, \mu F/cm^2$ and $C_b = 87.9 \pm 5.7 \, \mu F/cm^2$, respectively, yielding a ratio of $C_b/C_a = 1.4 \pm 0.1$, which is comparable to the value of $C_b/C_a = 1.6 \pm 0.3$ obtained using the 0.4 M $NaCl_{(aq)}$ reference, and aligns well with the experimental estimate of $C_b/C_a \approx 1.5$. This indicates that the small differences in ionic strength among neutral, basic and acidic solutions do not affect the conclusions of our study."

**Comment 2**: The major issue, however, is that "all additional H+ (or OH-) ions were gradually adsorbed on the surface within 3 ns". In other words, the interface and solution are not in equilibrium in terms of pH, making the corresponding results difficult to interpret in terms of described physics.

**Authors' response:** We thank the reviewer for bringing up this important issue. Our simulations indeed result in a surface charge density of $\sigma_a \approx 7.7 \, \mu C/cm^2$ and $\sigma_b \approx -7.5 \, \mu C/cm^2$ for acidic and basic systems, respectively, with no water ions in the bulk region of the electrolyte. In the experiment, values of $\sigma_a$ and $\sigma_b$ very similar to those we obtained equilibrate with bulk solutions that have pHs of $\approx$ 4.4 and 7.4, respectively [*Langmuir* 29, 8572-8583 (2013)]. For our simulation cell size (2376 water molecules), a pH value of 4.4 (or 7.4) corresponds to a negligible amount of $\sim 2 \times 10^{-3}$ $H^+$ (or $1 \times 10^{-5}$ $OH^-$) ions in the electrolyte solution. This aligns with our finding that there are no $H^+$ or $OH^-$ ions left in the bulk region after equilibrium. Achieving a pH of 4.4 (or 7.4) would require simulating a cell with one million (or two hundred million) water molecules, which is beyond our current capabilities. We thus believe that our system is essentially in equilibrium in terms of pH.

**Changes in revised manuscript:** We have added the following discussion on page 5

"Averaging over 3-10 ns, we obtained surface charge densities $\sigma_a = 7.69 \pm 0.04\ \mu C/cm^2$ and $\sigma_b = -7.54 \pm 0.13\ \mu C/cm^2$ at the interfaces with the acidic and basic electrolyte, respectively. In experiments[13], such values of $\sigma_a$ and $\sigma_b$ equilibrate with bulk solutions that have pHs of $\approx$ 4.4 and 7.4, respectively. For our simulation cell size (2376 water molecules), a pH value of 4.4 (or 7.4) corresponds to a negligible amount of $\sim 2 \times 10^{-3}$ H$^+$ (or $1 \times 10^{-5}$ OH$^-$) ions in the electrolyte solution. This is consistent with the fact that there are no H$^+$ or OH$^-$ ions left in the bulk region of our electrolyte solution."

**Comment 3**: Unfortunately, the manuscript is, overall, quite technical and not focused on chemical insight: It is only on page 9 that the authors start to discuss actual chemistry. However, (a) the current discussion is very succinct (the last two paragraphs before the conclusion are the most interesting ones, but the results are poorly analysed/discussed, which is a pity.

**Authors' response:** We thank the reviewer for pointing out this important problem and for recognizing the importance of our findings concerning the different microscopic surface charging mechanisms under basic and acidic conditions (last two paragraphs before the conclusion). To obtain more chemical insights into the origin of these distinct mechanisms, we analyzed the in-plane salt ion distribution (see Fig. R5 below). We found that the distinct mechanisms are caused by the different capacitances under basic and acidic conditions. The large capacitance under basic conditions indicates a strong ability of the EDL to screen the OH$^-$ surface charge. This is evidenced by the high probability of Na$^+$ ions surrounding an OH$^-$ surface ion in Fig. R5a. Consequently, the surface can accommodate more OH$^-$ ions in-plane, making the second path favorable under basic conditions. In contrast, the small capacitance under acidic conditions reflects a weak ability of the EDL to screen the H$^+$ surface charge. This is demonstrated by the low probability of Cl$^-$ ions surrounding an H$^+$ surface ion, as shown in Fig. R5b. Consequently, the surface cannot accommodate more H$^+$ ions in-plane, making the first pathway favorable under acidic conditions.
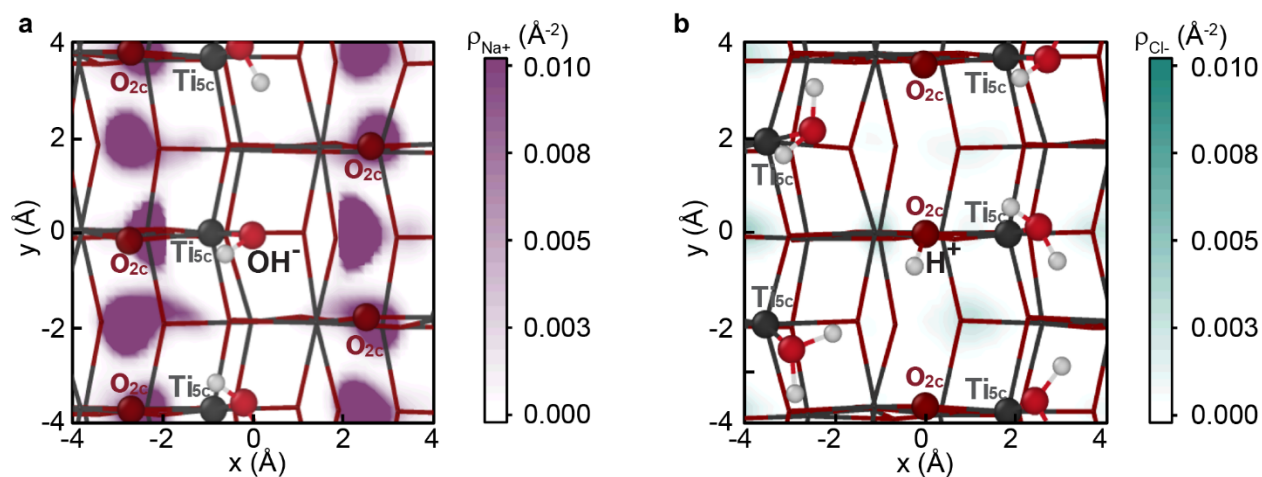


**Fig. R5** Top view of the anatase TiO$_2$ surface, with the $x$ and $y$ axes representing the $[\bar{1}01]$ and $[010]$ directions, respectively. **a,** The purple contour shows the 2D projected number density of IHP Na$^+$ ion around a surface OH$^-$ ion for the TiO$_2$-NaCl$_{(aq)}$+NaOH$_{(aq)}$ interface. **b,** The green contour shows the 2D projected number density of IMHP1 Cl$^-$ ion around a surface H$^+$ ion for the TiO$_2$-NaCl$_{(aq)}$+HCl$_{(aq)}$ interface.

**Changes in revised manuscript:** To provide more chemical insights, we made extensive changes in different parts of the manuscript

(I)     We added Fig. R5 as new Figure 5 in the main text and rewritten most of the section "Microscopic surface charging mechanism". The revised section reads (new text in red):

"The distinct interfacial capacitances resulting from the higher affinity of cations to the oxide surface, compared to anions, is found to give rise to distinct microscopic charging mechanisms on negative and positive surfaces. As shown in Fig. 4a, for the charge-neutral $TiO_2$-$NaCl_{(aq)}$ interface, $14 \pm 2\%$ water molecules adsorbed at $Ti_{5c}$ sites are dissociated into adsorbed $H^+$ at $O_{2c}$ and $OH^-$ at $Ti_{5c}$, with zero net surface charge. Starting with an equilibrated $TiO_2$-$NaCl_{(aq)}$ configuration, when we add bases or acids into the electrolyte, the $OH^-$ or $H_3O^+$ ions have two potential pathways to be adsorbed at the surface. For an electrolyte $OH^-$ (Fig. 4b), one pathway is to recombine with a surface $H^+$ ion at the $O_{2c}$ site to form a water molecule in the liquid, which decreases the surface's $H^+$ population. Another pathway is to recombine with an $H^+$ from an adsorbed $H_2O$, which results in an additional $OH^-$ ion adsorbed at the surface $Ti_{5c}$ site. Similarly, an electrolyte $H^+$ can either recombine with a surface terminal $OH^-$ into a water molecule or occupy an empty $O_{2c}$ site (Fig. 4c). Although both pathways result in the same net surface charge $\sigma$, the total number of surface charges, $N_{SC}= N_{H+}+ N_{OH-}$, is different. The first pathway reduces $N_{SC}$, whereas the second increases it.

The averaged ion coverages in Fig. 4 suggest that $OH^-$ ions prefer the second pathway (increasing $N_{SC}$), whereas protons slightly prefer the first (decreasing $N_{SC}$). As a result, if we define water dissociation fraction as the smaller value between the fraction of surface $H^+$ ions and the fraction of surface $OH^-$ ions, the average water dissociation fraction decreases significantly (to ~ 9%) with the acidic electrolyte whereas it remains approximately the same as that of the neutral interface under basic conditions, consistent with the increase of water dissociation fraction with the pH reported in a previous AIMD study[25]. These trends can be related to the different capacitances under basic and acidic conditions. The large capacitance under basic conditions indicates a strong ability of the EDL to screen the $OH^-$ surface charge. This is evidenced by the high probability of $Na^+$ ions surrounding an $OH^-$ surface ion, as shown in Fig. 5a. Consequently, the surface can accommodate more $OH^-$ ions in-plane, making the second pathway favorable under the basic condition. In contrast, the small capacitance under acidic conditions reflects a weak ability of the EDL to screen the $H^+$ surface charge. This is demonstrated by the low probability of $Cl^-$ ions surrounding an $H^+$ surface ion, as shown in Fig. 5b. As a result, the surface cannot accommodate more $H^+$ ions in-plane, making the first pathway favorable under acidic conditions.

The fact that negatively charged surfaces allow a larger density of surface hydroxyl groups is important in photocatalysis because these groups can trap photo-generated holes and form hydroxyl radicals[38,50], which are key intermediates of many photo-oxidation reactions. The photooxidation of water is indeed known to be faster at high pH[51]."

(II)     We revised the discussion on page 7

"Specifically, within the Stern layer, we identify not just a single ionic peak, but three distinct peaks: a first $Na^+$ peak at 1.5 Å from the surface, followed by a small $Cl^-$ peak at 3.4 Å of low intensity due to the repulsion between the $Cl^-$ and the electronegative $O_{2c}$ atoms, and another $Na^+$ peak at 4.2 Å. The $Na^+$ ions forming the first peak are, on average, coordinated to two surface $O_{2C}$ atoms (Fig. 2c), consistent with previous DFT results[13]. The distance, $r_{Na-O2c}$, between $Na^+$ and $O_{2C}$ fluctuates around 2.3 Å (Supplementary Figure 16), a value similar to the distance between $Na^+$ ions and water molecules in their

first hydration shell in bulk solution. With the $O_{2c}$ atoms substituting hydration water molecules, these $Na^+$ ions exhibit incomplete hydration shells (Fig. 2c) and can thus be identified as inner-sphere surface complexes[15,18] and the corresponding peak as the IHP. Instead, the $Cl^-$ ions forming the second peak (Fig. 2 d) and the $Na^+$ ions contributing to the third peak (Fig. 2 e) exhibit complete hydration shells. While this characteristic is consistent with the definition of outer-sphere surface complexes[43], these ions do not satisfy the OHP criterion that their interactions with the surface involve only long-range electrostatic forces[44]. As shown in Fig. 2d and Fig. 2e, some water molecules in the hydration shell of these ions are either adsorbed on $Ti_{5c}$ atoms or form strong hydrogen bonds with surface $O_{2c}$ atoms. Since these surface water molecules have a diffusion coefficient 1~2 orders of magnitude smaller than that of bulk water[45], these ions can be considered as semi-adsorbed on the surface via surface water molecules. Consequently, these two ionic peaks cannot be classified as either IHP or OHP. In this work, we designate the corresponding layers as intermediate Helmholtz planes (IMHPs), since their peaks fall between the IHP and the OHP. We also find that the ions within the Stern layer are not fixed but can exchange with other ions of the same type in the electrolyte. Specifically, $Na^+$ ions in the IHP have a residence time on the order of nanoseconds, while ions in IMHPs have a residence time of tens to hundreds of picoseconds (Supplementary Information Section 5). "

(III)     We largely rewrote the section "Differential capacitance":

"The microscopic structure of the EDL determines the differential capacitance $C$ of the interface, which is composed of contributions from the capacitance of the Stern layer ($C_H$, also called Helmholtz capacitance) and the diffuse layer ($C_D$)[46], with $\frac{1}{C} = \frac{1}{C_H} + \frac{1}{C_D}$. While $C_H$ has been studied previously by AIMD simulations[19,24,25], the calculation of $C$ with *ab initio* accuracy has been a long-standing challenge due to the long simulation times and large cells needed to equilibrate the EDL. Interestingly, experiments found that, at equivalent magnitudes of charge densities, negatively charged oxide interfaces have a higher capacitance than their positively charged counterparts for metal oxides such as anatase[40], rutile[40], and zinc oxide[47]. This is in contrast with the symmetric capacitance predicted by the GCS model, suggesting that the EDL at these oxide surfaces can screen negative surface charges more effectively than positive ones. However, the underlying reason for this phenomenon remains a topic of active debate. Some studies attributed the larger capacitance under basic conditions to the high affinity of cations to the oxide[12,40]. In contrast, recent AIMD studies proposed that the difference is due to the distinct properties of water under basic and acidic conditions[24,25,49]. For example, Ref. 24 attributed it to the larger interfacial water fluctuations under basic conditions, Ref. 25 explained it by the orientation of chemisorbed water, and Ref. 49 attributed it to the water adsorption energy.

To obtain insight into the observed asymmetry of $C$, we calculated this quantity with *ab initio* accuracy using our DPLR method. Specifically, starting from the definition of $C$ as the first-order derivative of the surface charge density $\sigma$ with respect to the electrostatic potential drop $\psi$, $C = \frac{d\sigma}{d\psi}$, we used the finite difference expression $C \approx \frac{\Delta\sigma}{\Delta\psi}$, where $\Delta$ represents the deviation of a charged interface from a neutral reference interface. While $\sigma$ is readily available in simulations (Fig. 1c), $\psi$ depends not only on the distribution of the ions but also on that of valence electrons, which is generally not available in simulations based on force fields. In our DPLR approach[35], however, $\psi$ can be explicitly calculated (see Methods for details). The average potential profile calculated in this way for the $TiO_2$-$NaCl_{(aq)}$ interface is displayed by the green line in Fig. 3a. Within the $TiO_2$ region, the potential exhibits pronounced oscillations, while the

homogeneous and isotropic nature of the liquid electrolyte results in a more uniform profile. Macroscopic averaging[49] of $\phi(z)$ yields the black line in Fig. 3a, from which the potential drop $\psi$, defined as the potential difference between solid and liquid phases, is extracted. At this point, the capacitance can be calculated. Taking the neutral TiO$_2$-NaCl$_{(aq)}$ interface as the reference and using the results in Fig. 1c, we have $\Delta\sigma_b = -7.54 \pm 0.13\ \mu C/cm^2$ for the TiO$_2$-NaCl+NaOH basic solution interface, and $\Delta\sigma_a = 7.69 \pm 0.04\ \mu C/cm^2$ for the TiO$_2$-NaCl+HCl acidic solution interface. By comparing the macroscopically averaged[49] electrostatic potential at the acidic and basic solution interfaces with the neutral reference (Fig. 3b), we determine the potential drop differences $\Delta\psi_a = 131.6 \pm 10.6\ mV$ and $\Delta\psi_b = -78.3 \pm 11.2\ mV$, respectively. Consequently, the differential capacitances are $C_a = 58.4 \pm 4.7\ \mu F/cm^2$ and $C_b = 96.2 \pm 13.8\ \mu F/cm^2$ under acidic and basic conditions, respectively. As shown in Fig. 3c, our results (which include the computed capacitances at higher HCl and NaOH concentrations reported in Supplementary Section 10) reproduce the experimental trends[40,51] quite satisfactorily. In particular, our calculated ratio of $C_b/C_a = 1.6 \pm 0.3$ agrees well with previous DFT[19,24] and experimental[40] results showing $C_b/C_a \approx 1.5$ at similar oxide/electrolyte interfaces.

.

Based on our simulations, the larger capacitance observed under basic conditions in comparison to acidic ones can be understood as follows. For the negative (positive) surface, the positive Na$^+$ (negative Cl$^-$) ions are drawn towards the surface to screen the surface charge. However, the abilities of Na$^+$ and Cl$^-$ to screen the surface charge differ. Fig. 2b shows that Na$^+$ can approach the surface more closely than Cl$^-$ ions because the outermost layer of TiO$_2$ surface is composed of electronegative O$_{2c}$ atoms. This allows Na$^+$ to screen the surface charge more effectively than Cl$^-$. In more detail, when the system is negatively charged under basic conditions, the affinity of Na$^+$ ions to the electronegative surface O$_{2c}$ atoms draws them close to the surface, effectively screening the surface OH$^-$ ions. This effect is evidenced by Fig. 2b, which shows a significant amplification of the Na$^+$ peak intensity when transitioning from a neutral to a basic system. In contrast, when the system is positively charged under acidic conditions, a substantial proportion of O$_{2c}$ atoms (82% in our acidic system) do not bind H$^+$ ions (Fig. 2d). These electronegative O$_{2c}$ atoms repel Cl$^-$ ions, preventing them from moving close to the surface to screen the surface H$^+$ ions. Consequently, the transition from a neutral to an acidic system induces a modest increase in the Cl$^-$ peak intensity as shown in Fig. 2b. This leads to a smaller absolute value of $\Delta\psi_b$ than $\Delta\psi_a$, and consequently a larger $C_b$ than $C_a$. Compared to the significant changes of ion distributions at different pHs, the water distribution and orientation undergo smaller changes (Supplementary Section 6). Therefore, our simulations agree with the suggestion that the larger capacitance under basic conditions is primarily due to the higher affinity of cations to the oxide. Differences between our findings and previous AIMD simulations[19,24] are likely related to the higher ion concentrations used in the latter, their short equilibration times, and their focus on the Helmholtz part only of the differential capacitance."

**Comment 4**: (b) some of the claims, such as "This allows Na+ to screen the surface charge more effectively than Cl-" is supposed to be highly cation/anion specific, as it depends on the (de-)solvation energies. In view of the absence of relative trends as a function of cations/anions and the validation of solvation energies, it is very difficult to judge whether this is meaningful, obvious or an artifact.

**Authors' response:** We agree with the reviewer that different cation/anion pairs will have different (de-)solvation energies which can affect their interactions with the surface. However, in this work we

focused on Na$^+$ and Cl$^-$ because these are prototypical and widely studied ions in both simulations and experiments. We thus expect the main qualitative features of this work to hold for other electrolytes as well. In fact, titration experiments [*Journal of Colloid and Interface Science*, 27, 305-318 (1968) and 28, 92-105 (1968)] have observed larger capacitances under basic conditions also at the TiO$_2$ interfaces with NaNO$_3$, CsNO$_3$, LiNO$_3$, NaClO$_4$, and NaI solutions. To address the Reviewer's concerns about the validity of our work, we have however conducted additional simulations of the TiO$_2$ interface with higher concentrations of acidic and basic electrolytes (see Supplementary Section 10). The new results agree well both with our previous findings in the original manuscript and with experiments, confirming that our results are neither obvious nor an artifact, but meaningful and insightful.

**Changes in revised manuscript:**
**(i)** We added the following details to page 10.
"This allows Na$^+$ to screen the surface charge more effectively than Cl$^-$. In more detail, when the system is negatively charged under basic conditions, the affinity of Na$^+$ ions to the electronegative surface O$_{2c}$ atoms draws them close to the surface, effectively screening the surface OH$^-$ ions. This effect is evidenced by Fig. 2b, which shows a significant amplification of the Na$^+$ peak intensity when transitioning from a neutral to a basic system. In contrast, when the system is positively charged under acidic conditions, a substantial proportion of O$_{2c}$ atoms (82% in our acidic system) do not bind H$^+$ ions (Fig. 2d). These electronegative O$_{2c}$ atoms repel Cl$^-$ ions, preventing them from moving close to the surface to screen the surface H$^+$ ions. Consequently, the transition from a neutral to an acidic system induces a modest increase in the Cl$^-$ peak intensity as shown in Fig. 2b."

**(ii)** The results of the new simulations are reported in the new Fig. 3c, Supplementary Section 10 and mentioned on page 4
"Additional results for TiO$_2$ interfaces with electrolytes containing higher concentrations of NaOH and HCl are reported in Supplementary Section 10 and Fig. 3c."

**Comment 5**: On a technical level, I think the authors should also report relative errors (not only eV/atoms), as this is most meaningful for assessing the accuracy for configurational sampling.

**Authors' response:** Following the reviewer's suggestion, we calculated the coefficient of determination ($R^2$) to evaluate the relative errors of the results predicted by our deep neural network (DNN) with respect to those obtained from DFT calculations. An $R^2$ value of 1 indicates perfect prediction, while a value closer to 0 indicates a poor fit. For our DNN models, the $R^2$ value for energy, force, and Wannier centroids (WC) are 0.96, 0.99, and 0.99, respectively. The high $R^2$ values demonstrate that the predictions made by our DNN are in excellent agreement with the DFT results, thus validating the accuracy of our model.

**Changes in revised manuscript:** We added $R^2$ values to Supplementary Section 2.5.1
"The coefficient of determination, $R^2$, for energy, force, and WC are 0.96, 0.99, and 0.99, respectively, indicating that our DNN models can accurately reproduce DFT results."

**Authors' response:** Our approach to retrieve the electrostatic potential can be used to calculate the difference between the average electrostatic potentials in the solid and the solution, which is the quantity of interest in our study. However, it is well known that computing absolute potentials requires the use of appropriate strategies when using periodic boundary conditions. This issue has been discussed extensively in the literature, see, e.g., Le et al, *Phys. Rev. Letters* **119**, 016801 (2017) and references therein. The integration of such strategies with our approach is an interesting possibility that we may explore in future studies.

**Changes in revised manuscript:** We added the following paragraph to Supplementary Section 7
"Our approach to retrieve the electrostatic potential can be used to calculate the difference between the average electrostatic potentials in the solid and the solution, which is the quantity of interest in our study. However, it is well known that computing absolute potentials requires the use of appropriate strategies when using periodic boundary conditions. This issue has been discussed extensively in the literature[28]. The integration of such strategies with our approach is an interesting topic to explore in future studies."

## Comments from reviewer #3 and our detailed responses

**General Comments**: Zhang et al report a study of the water/anatase interface using machine learning potentials. The aim of the work is to understand how microscopic nature of the electronic double layer. This is an excellent paper in all respects. It was a joy to read. The simulations are impressive and the figures are writing are impeccable. We congratulate the authors on such a well executed and presented study and only wish that all papers were as clear and easy to follow as this!

The main results are i) cations have a higher affinity to the surface which explains the difference between capacitance between basic and acid conditions, and ii) this difference it is attributed to a difference in the charge mechanisms.

Point i) has been suggested in the literature (this is acknowledged). Point ii) seems to be a new observation for which one requires the highly sophisticated simulations reported. Publication in Nature Comms is recommended. However, we would like the authors to take the following points into consideration as addressing them will strengthen the paper.

**Authors' response:** We appreciate Reviewer #3's recognition of the importance of our work and thank them for their insightful comments, which are very helpful for further improving the quality of our manuscript. Below, we address the specific points raised by the reviewer.

**Comment 1**: We think the authors should explain better: What causes the Na+ double peak in the density profiles. This result is counterintuitive since one would expect a Cl- layer to follow the (first) Na+ one. Does this play any relevant role? The authors use this point to argue that ML potentials are required.

**Authors' response:** The $Na^+$ double peak arises from the fact that this ion can adsorb in two different states on the anatase surface, either as a partially hydrated (inner-sphere) complex or as a fully hydrated (adsorbed outer-sphere) species (see Fig. 2c and 2e of our manuscript). This is a phenomenon that is not unusual at mineral-aqueous solution interfaces and originates from a subtle balance between the ion hydration and adsorption free energies, which in turn are affected by various factors including ion concentration, pH, specific oxide surface etc. (see, e.g., Lee et al, *Geochimica et Cosmochimica Acta* 123 (2013) 416–426).

The reviewers are correct that one would expect a $Cl^-$ layer to follow the first $Na^+$ one. Actually, we do observe a $Cl^-$ peak following the first $Na^+$ peak in the ion density distribution, but it has a very small intensity. The small intensity is because the outmost layer of the $TiO_2$ surface is formed by the electronegative $O_{2c}$ atoms, which repel the negatively charged $Cl^-$ ions (see Fig. 2d).

**Changes in revised manuscript:** We added an inset in Fig. 2b to show a blowup of the first $Cl^-$ peak. We also added the following text on page 7**.**

"Specifically, within the Stern layer, we identify not just a single ionic peak, but three distinct peaks: a first $Na^+$ peak at 1.5 Å from the surface, followed by a $Cl^-$ peak at 3.4 Å of low intensity due to the repulsion between the $Cl^-$ and the electronegative $O_{2c}$ atoms, and another $Na^+$ peak at 4.2 Å."

**Authors' response:** To provide a clearer explanation of the different charging mechanisms under basic and acid conditions, we have analyzed the in-plane salt ion distribution, which is now reported in the newly added Fig. 5 of the revised manuscript. We found a high probability for $Na^+$ ions to be surrounding an $OH^-$ surface ion (Fig. 5a), which indicates a strong ability of the EDL to screen the $OH^-$ surface charge. Consequently, the surface can accommodate more $OH^-$ ions in-plane, making the second pathway favorable under basic conditions. In contrast, we found a low probability for $Cl^-$ ions to be surrounding an $H^+$ surface ion (Fig. 5b). Consequently, the surface cannot accommodate more $H^+$ ions in-plane, making the first pathway favorable under acidic conditions.

**Changes in revised manuscript:** We added a new figure (Fig. 5) to the main text and extensively revised the section on "Microscopic surface charging mechanism". The revised section reads:

"The distinct interfacial capacitances resulting from the higher affinity of cations to the oxide surface, compared to anions, is found to give rise to distinct microscopic charging mechanisms on negative and positive surfaces. As shown in Fig. 4a, for the charge-neutral $TiO_2$-$NaCl_{(aq)}$ interface, $14 \pm 2\%$ water molecules adsorbed at $Ti_{5c}$ sites are dissociated into adsorbed $H^+$ at $O_{2c}$ and $OH^-$ at $Ti_{5c}$, with zero net surface charge. Starting with an equilibrated $TiO_2$-$NaCl_{(aq)}$ configuration, when we add bases or acids into the electrolyte, the $OH^-$ or $H_3O^+$ ions have two potential pathways to be adsorbed at the surface. For an electrolyte $OH^-$ (Fig. 4b), one pathway is to recombine with a surface $H^+$ ion at the $O_{2c}$ site to form a water molecule in the liquid, which decreases the surface's $H^+$ population. Another pathway is to recombine with an $H^+$ from an adsorbed $H_2O$, which results in an additional $OH^-$ ion adsorbed at the surface $Ti_{5c}$ site. Similarly, an electrolyte $H^+$ can either recombine with a surface terminal $OH^-$ into a water molecule or occupy an empty $O_{2c}$ site (Fig. 4c). Although both pathways result in the same net surface charge $\sigma$, the total number of surface charges, $N_{SC} = N_{H^+} + N_{OH^-}$, is different. The first pathway reduces $N_{SC}$, whereas the second increases it.

The averaged ion coverages in Fig. 4 suggest that $OH^-$ ions prefer the second pathway (increasing $N_{SC}$), whereas protons slightly prefer the first (decreasing $N_{SC}$). As a result, if we define water dissociation fraction as the smaller value between the fraction of surface $H^+$ ions and the fraction of surface $OH^-$ ions, the average water dissociation fraction decreases significantly (to $\sim 9\%$) with the acidic electrolyte whereas it remains approximately the same as that of the neutral interface under basic conditions, consistent with the increase of water dissociation fraction with the pH reported in a previous AIMD study[25]. These trends can be related to the different capacitances under basic and acidic conditions. The large capacitance under basic conditions indicates a strong ability of the EDL to screen the $OH^-$ surface charge. This is evidenced by the high probability of $Na^+$ ions surrounding an $OH^-$ surface ion, as shown in Fig. 5a. Consequently, the surface can accommodate more $OH^-$ ions in-plane, making the second pathway favorable under the basic condition. In contrast, the small capacitance under acidic conditions reflects a weak ability of the EDL to screen the $H^+$ surface charge. This is demonstrated by the low probability of $Cl^-$ ions surrounding an $H^+$ surface ion, as shown in Fig. 5b. As a result, the surface cannot accommodate more $H^+$ ions in-plane, making the first pathway favorable under acidic conditions.

The fact that negatively charged surfaces allow a larger density of surface hydroxyl groups is important in photocatalysis because these groups can trap photo-generated holes and form hydroxyl

radicals[38,50], which are key intermediates of many photo-oxidation reactions. The photooxidation of water is indeed known to be faster at high pH[51]."

**Comment 3**: page 5: 'All additional H+ (or OH−) ions were gradually adsorbed on the surface within 3 ns, leading to a positively (or negatively) charged surface' Does this mean that there are no protons/OH- in the bulk region? The appropriate way to define pH for this setup is to compute the H+/OH- concentration in the bulk region, if aqueous ions aren't present in the bulk region, it is unclear at which pH the simulations are being made. Also some evidence that the protocol for "adding HCL … NaOH at random positions" is robust would be helpful.

**Authors' response:** We thank the reviewers for bringing up this important issue. The pH values mentioned in the original version of the manuscript refer only to the initial conditions. After all H+ (or OH-) ions are adsorbed on the surface, there is a surface charge density of $\sigma_a \approx 7.7\ \mu C/cm^2$ and $\sigma_b \approx -7.5\ \mu C/cm^2$ for the acidic and basic systems respectively, with no water ions in the bulk region of the electrolyte. In the experiment, values of $\sigma_a$ and $\sigma_b$ very similar to those we obtained equilibrate with bulk solutions have pHs of $\approx 4.4$ and 7.4, respectively [*Langmuir* 29, 8572-8583 (2013)]. For our simulation cell size (2376 water molecules), a pH value of 4.4 (or 7.4) corresponds to a negligible amount of $\sim 2 \times 10^{-3}$ H$^+$ (or $1 \times 10^{-5}$ OH$^-$) ions in the electrolyte solution. This aligns with our finding that there are no H$^+$ or OH$^-$ ions left in the bulk region after equilibrium. Achieving a pH of 4.4 (or 7.4) would require simulating a cell with one million (or two hundred million) water molecules, which is beyond our current capabilities. We thus believe that our system is essentially in equilibrium in terms of pH.

Regarding the protocol for "adding HCl … NaOH at random positions", we performed two additional simulations at higher HCl and NaOH concentrations, where we still added the ions at random positions in the initial configuration. The results of the new simulations are fully consistent with those at lower concentration, demonstrating the robustness of our protocol.

**Changes in revised manuscript:**
(i)        We added the following clarification on page 4 of the revised manuscript:
"In the electrolyte, NaCl serves as a background salt, and adding 0.2 M NaOH or HCl changes the pH of the initial configuration from a nominal value of 7 to 13.3 or 0.7.

(ii)        We also added the following discussion on page 5:
"Averaging over 3-10 ns, we obtained surface charge densities $\sigma_a = 7.69 \pm 0.04\ \mu C/cm^2$ and $\sigma_b = -7.54 \pm 0.13\ \mu C/cm^2$ at the interfaces with the acidic and basic electrolyte, respectively. In experiments[13], such values of $\sigma_a$ and $\sigma_b$ equilibrate with bulk solutions that have pHs of $\approx 4.4$ and 7.4, respectively. For our simulation cell size (2376 water molecules), a pH value of 4.4 (or 7.4) corresponds to a negligible amount of $\sim 2 \times 10^{-3}$ H$^+$ (or $1 \times 10^{-5}$ OH$^-$) ions in the electrolyte solution. This is consistent with the fact that there are no H$^+$ or OH$^-$ ions left in the bulk region of our electrolyte solution."

(iii)        The results of the new simulations at higher NaOH and HCl concentration have been included in the new Fig. 3c and Supplementary Section 10.

**Comment 4**: It would be nice if they can show density profiles for the production system, as this is the key (raw) outcome of the simulations. The text mentions systems with a 67 A aqueous electrolyte yet the water density profiles for these systems are not shown (In Fig S3 it looks like the water region is <30 A).

**Authors' response:** Fig. S3 indeed used a small cell to enable comparison with AIMD, while the production simulations were carried out on a large system with a 67 Å thick aqueous electrolyte. The ion and water density profiles of the production system are shown in Fig. 2b of the main text and Supplementary Figure 13 (Figure S8 in the original version of our manuscript), respectively. Note that both figures were already provided in the original version of our manuscript. Our simulation cell has two symmetric surfaces. To make the figure more concise, Fig. 2b in the manuscript averages the data over the two symmetric surfaces. Similarly, the water density in Supplementary Fig. 13 is also averaged over the two symmetric surfaces.

**Changes in revised manuscript:** We have plotted the full range of the water density profile of our production system in the updated Supplementary Fig. 13.

**Comment 5**: In addition, does the ion profile in the diffuse layer follow the mean-field approximations?

**Authors' response:** As already reported on page 7 of the original manuscript: "The structure of the diffuse layer agrees with that given by the GCS model, i.e., the $Cl^-$/$Na^+$ density decreases/increases with increasing distance from the OHP until the two densities become identical within the error bars of the simulation."

**Comment 6**: Looking at Figures S3 and S4, the short-range models perform equally well than the long-range one. However, the authors argue otherwise in the methods section of the main document. In Fig. S5 there are differences but these simulations were run at 600 K. This raises a separate question about whether the simulations are fully conveyed. It would be very helpful for building confidence in these results if a convergence plot of ion and water density profiles as a function of simulation time (at the production temperature) was included in the SI.

**Authors' response:** Figures S3 and S4 of the original version of our manuscript refer to the $TiO_2$ interface with pure water. In this system, long-range electrostatic interactions are less critical compared to systems containing ions, which explains why the short-range models appear to perform equally well as the long-range ones. However, for the $TiO_2$ interface with electrolyte solutions, accurately capturing the long-range electrostatic interactions is essential, as illustrated in Fig. S5 (Supplementary Figure 10 in the revised manuscript).

The reason why the simulation in the latter figure was performed at 600 K instead of 330 K is as follows. It is well-established that all effects from the solid surface can be completely screened by the electrical double layer (EDL). Therefore, outside the EDL, the electrolyte should recover its bulk properties. A key property of the bulk electrolyte is that the densities of positive and negative ions should be equal. However, as shown in Fig. S5a of the original manuscript, DPSR simulations predict an approximately 0.06 M higher density of $Cl^-$ ions compared to $Na^+$ ions in the central region of the solution. Although this 0.06 M difference is small, it indicates that the short-range model is qualitatively incorrect. To accurately capture

this 0.06 M difference, we need to increase the simulation temperature to 600 K to reduce the error bar in ion density to less than 0.06 M. While a 10 ns simulation at 330 K cannot achieve an error bar less than 0.06 M, it does not imply that the simulation is not converged: The ion density in the double layer is on the order of 6 M, which is two orders of magnitude larger than 0.06 M. Therefore, an error bar larger than 0.06 M at 330 K will not affect our conclusions.

Following the reviewer's suggestion, we further checked the convergence of ion and water density with respect to simulation time. In Figs. R6 and R7, we show the ion and water density averaged over the periods from 3 to 6.5 ns and from 6.5 to 10 ns, respectively. The results averaged over 3 to 6.5 ns agree well with those averaged over 6.5 to 10 ns, indicating good convergence of the 10 ns simulation at the production temperature.

**Changes in revised manuscript:** We added the above discussion and Figs. R6 and R7 below to Supplementary Section 2.4
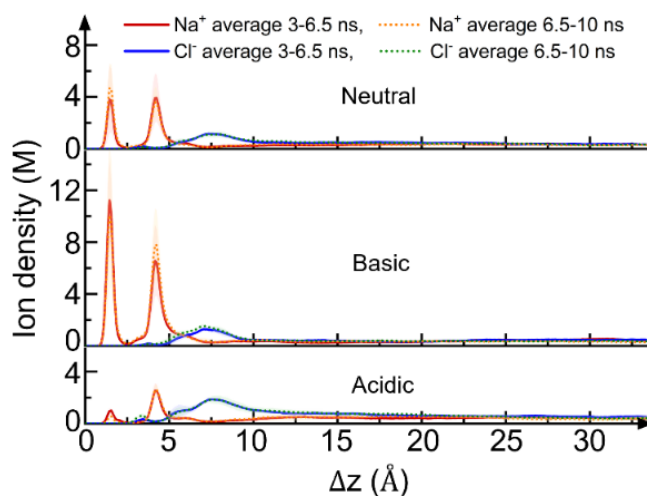


**Fig. R6** Ion density distributions as a function of distance, $\Delta z = z - z_{\text{surface}}$, from the solid surface, obtained from 330 K DPLR simulations of anatase (101) in contact with different electrolytes. The solid lines represent averages over the period from 3 to 6.5 ns, while the dashed lines represent averages over the period from 6.5 to 10 ns.



**Fig. R7** Water density distributions as a function of distance, $\Delta z = z - z_{\text{surface}}$, from the solid surface, obtained from 330 K DPLR simulations of anatase (101) in contact with different electrolytes. The solid

lines represent averages over the period from 3 to 6.5 ns, while the dashed lines represent averages over the period from 6.5 to 10 ns.
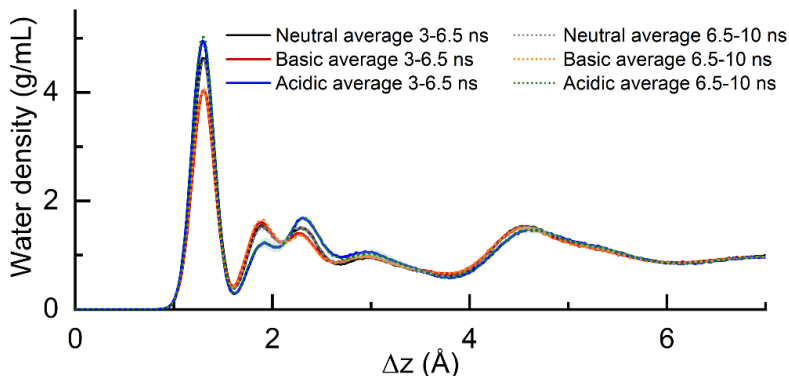
**Comments from reviewer #4 and our detailed responses**

**General Comments**: In this work, the authors have applied ab initio based machine learning potential (MLP) to simulate TiO2/NaCl electrolyte interface under different pH conditions. One of the highlights is they incorporate the long range electrostatics in the MLP, as implemented in the state-of-the-art DPLR, which is absolutely crucial for modelling electric double layers (EDL) at oxide interfaces. The efficiency and accuracy of the DPLR enable the authors to not only reliably calculate the microscopic structures of EDL, but also the EDL capacitances. More interestingly, the simulations show that that Na+ ions can lose partial solvation shell and specifically adsorb on anatase 101 surface directly coordinating with the surface oxygen. This finding would have direct implications on and point of zero charge (PZC) and flat band potential (FBP), contributing to the asymmetry of differential capacitance, if it is proven to be correct. The work overall is well structured, and I would recommend its publication provided the following issues have been satisfactorily addressed.

**Authors' response:** We thank Reviewer #4's for recognizing the importance of our work and for their insightful comments, which are very helpful for further improving the quality of our manuscript.

**Comment 1**: The above mentioned new finding is certainly interesting, but I have slight concern on the accuracy of the trained MLP and sufficiency of timescale achieving adsorption equilibrium. I would suggest that the authors provided some further evidence showing the accuracy of MLP, in particular for the structures with specific adsorption. For example, RMSEs of energies and forces for these structures in comparison with DFT. Also, calculate free energy profile for specific adsorption of Na+ to check the adsorption barrier and energy.

**Authors' response:** Following the reviewer's suggestion, we have conducted additional benchmark calculations to check both the accuracy of the MLP and the timescale convergence of the simulation. In particular: (1) We calculated the RMSEs of energies, forces, and Wannier Centroids (WCs) for structures with specific adsorption and found that our deep neural network models well reproduce the DFT results; (2) We calculated the work required to move a specifically adsorbed Na$^+$ ion from the surface to the bulk solution and found that our deep neural network models well reproduce the DFT results; (3) We checked that the timescale was sufficient for achieving adsorption equilibrium

**Changes in revised manuscript:**
(1) We added Fig. R8 below as Supplementary Figure 5 and the following discussions to Supplementary Section 2.5.1

To further validate the accuracy of the DNN models for the specific adsorption of Na$^+$ ions at the TiO$_2$ surface, we compared energies, forces, and WCs from DNN models and DFT for configurations with specific adsorption. In detail, we conducted DPLR molecular dynamics simulation of a relatively small model of the TiO$_2$-NaOH$_{(aq)}$ interface, comprising a five-layer (1×3) anatase (101) slab with 81 H$_2$O molecules and 1 NaOH ion pair. The simulation was conducted within the canonical ensemble at 330 K for 600 ps, with the Na$^+$ ion adsorbed at the surface. The initial 100 ps of the simulation was discarded for equilibration purposes. From the subsequent 500 ps, 50 configurations were uniformly extracted from the trajectory. As shown in Supplementary Fig. 5, the z-distances of the Na$^+$ ion from the solid surface of these 50 configurations fluctuate around 1.5 Å, which corresponds to the first Na$^+$ peak of ion density distribution (see Fig. 2b of the main manuscript), indicating that the Na$^+$ ion is adsorbed at the TiO$_2$ surface in these configurations. Supplementary Fig. 5b-d compares the energies, atomic forces, and WCs predicted by our

DNN models with the results from DFT-SCAN calculations, for these 50 configurations with specific adsorption. It can be seen that the DNN models accurately reproduce the DFT results, with root-mean-squared errors of 0.38 meV/atom for energies, 0.095 eV/Å for atomic forces, and 0.003 Å for WCs.
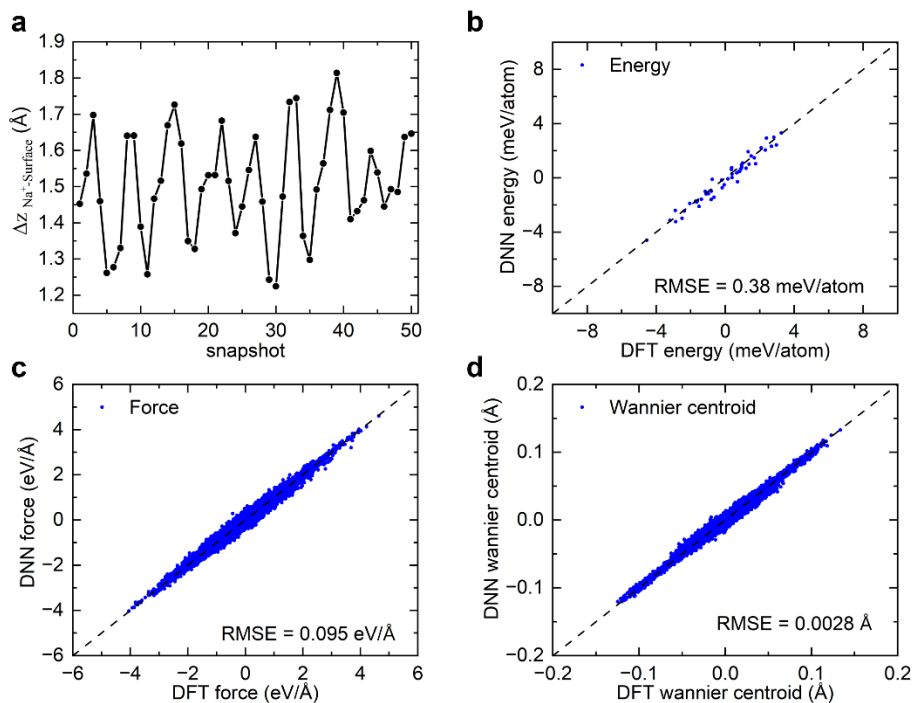


**Fig. R8 a,** Distance of the $Na^+$ ion from the solid surface, $\Delta z_{Na+-surface} = z_{Na+} - z_{surface}$, in the $z$-direction for the 50 selected snapshots. The position of the solid surface, $z_{surface}$, corresponds to the average position of the $O_{2c}$ sites. **b-d,** Comparison between the energies, atomic forces, and Wannier centroids predicted by the DNN models and DFT-SCAN calculations for the 50 snapshots in **a**. The average value of the energy was shifted to zero for better visualization.

(2) We added Fig. R9 below as Supplementary Figure 9 and the following discussions to Supplementary Section 2.5.4.

To calculate the potential of mean force for the specific adsorption of $Na^+$ ion, we conducted ten DPLR molecular dynamics simulations of the $TiO_2$-$NaOH_{(aq)}$ interface, where we used a five-layer (1×3) anatase (101) slab with 81 $H_2O$ molecules and 1 NaOH ion pair. Each simulation was conducted within the canonical ensemble at 330 K for 2 ns using our DPLR model1. We extracted 330 atomic configurations with different distances of the $Na^+$ ion from the solid surface, $\Delta z_{Na+-surface} = z_{Na+} - z_{surface}$. The force along $z$ on the $Na^+$ ion was calculated using two DPLR models ($f_{DPLR\,model\,j}$, $j$=1, 2) and DFT ($f_{DFT}$). Since the configurational space was explored using DPLR model1, a reweighting process was performed using Eq. (1). The potential of mean force was then computed as the integral of reweighted forces. As shown in Supplementary Fig. 9, the potential of mean force for the specific adsorption of a $Na^+$ ion calculated by DPLR agrees well with the DFT result, with both DPLR and DFT results showing a minimum at around 1.5 Å, which is the position of the first $Na^+$ peak in the ion density distribution (see Fig. 2b of the main manuscript) and corresponds to the adsorbed $Na^+$ ion. This indicates that our DPLR model can well reproduce the DFT results for the adsorption of $Na^+$ at the $TiO_2$ surface.
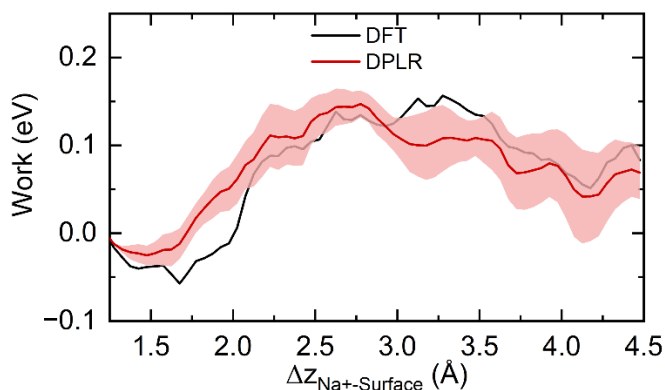
24

**Fig. R9** Potential of mean force for the specific adsorption of a Na$^+$ ion. The black and red lines represent the results obtained from DFT and DPLR, respectively. Shaded areas indicate the standard deviation obtained from two independent DPLR models.

(3) We added two new figures (Supplementary Figures 2 and 3) and the following text to Supplementary Section 2.4

To check the convergence of ion and water densities with respect to simulation time, we plotted the ion and water density averaged over the periods from 3 to 6.5 ns and from 6.5 to 10 ns, respectively, in Supplementary Figs. 2 and 3. The results averaged over 3 to 6.5 ns agree well with those averaged over 6.5 to 10 ns, indicating the 10 ns simulation is well converged.

**Comment 2**: The reason I have this concern is that one of the implications of this finding is that the FBP of anatase 101 would be dependent of not only pH, but also the concentration of Na+ as adsorption thermodynamics, and thus ion concentration, determines the coverage of specifically adsorbed Na+ and further interfacial dipole due to the ordered ion pairs. This can in principle be observed in experiment – Is there any literature work showing this?

**Authors' response:** We appreciate the reviewer's insightful comment. Indeed, the effect of ion concentration on the flat band potential (FBP) has been discussed in existing literature, see, e.g. Xu and Schoonen, *American Mineralogist*, 85, pp.543-556 (2000). As pointed out in this paper, however, the flatband potential at the point of zero charge "is the only meaningful flatband potential". In this respect, the real concern is whether there is an effect of ion concentration on the pH point of zero charge (pH$_{pzc}$). According to a widely cited paper by Sverjensky [*Geochimica et Cosmochimica Acta*, 69(2), pp.225-257 (2005)], pH$_{pzc}$ is defined to "reflect only the protonation reactions". While electrolyte ion adsorption at the surface can influence the "point-of-zero-salt (pH$_{pzse}$) effect", even for pH$_{pzse}$ the effect of the adsorbed ions is found to be small (see, e.g., *Langmuir* 29, 8572-8583 (2013)). Therefore, the specific adsorption of Na$^+$ has a minimal effect on the pH$_{pzse}$ and does not influence the pH$_{pzc}$.

On the other hand, away from the pH$_{pzc}$, the flatband potential can indeed depend on the ion concentration. For example, a recent experiment [*ACS omega*, 5(7), 3522-3532 (2020)] measured the flat band potential of the TiO$_2$/KOH solution interface using Mott-Schottky analysis and found that the KOH results in a "more negative flat-band potential". They further conducted molecular dynamics simulations to understand this effect and found that this effect is related to "K$^+$ ions prefer to adsorb onto the TiO$_2$ surface and bond to O$_{2c}$."

**Changes in the revised manuscript**: We added the text in red to page 4

"To support this inference, we performed enhanced sampling DPLR simulations to explicitly evaluate the $pH_{PZC}$ of the anatase (101)-neat water interface (Supplementary Section 4). We focused on neat water in this simulation because $pH_{pzc}$ is defined to reflect only the protonation reaction[43], unaffected by the presence of salt ions."

**Comment 3**: A related question is that would a similar behaviour occur on other surfaces, such as also well studied rutile 110. Of course, the difference is that bridge oxygen on rutile 110 is less exposed compared to anatase 101. Again, is there any experimental evidence that may indicate this difference?

**Authors' response:** Experimentally, the larger capacitance under basic conditions compared to the acidic conditions has been observed on several other oxide surfaces, such as rutile TiO2 [*Journal of Colloid and Interface Science* 28, 92-105 (1968)] and ZnO [*Journal of Colloid and Interface Science*, 32, pp.533-538 (1970)]. However, to the best of our knowledge, no experimental or theoretical studies have investigated the capacitance differences between anatase and rutile. This is an interesting topic that deserves further study.

**Changes in revised manuscript:**  We added the following text on page 8
"Interestingly, experiments found that, at equivalent magnitudes of charge densities, negatively charged oxide interfaces have a higher capacitance than their positively charged counterparts for metal oxides such as anatase[40], rutile[40] and zinc oxide[45]. This is in contrast to the symmetric capacitance predicted by the GCS model, suggesting that the EDL at these oxide surfaces can screen negative surface charges more effectively than positive ones."

**Comment 4**: Regarding the definitions of IMHP2 for Na+ and OHP for Cl- in Figure 2, I have a different opinion. Cations and anions have different sizes, and we don't usually expect that the positions of OHPs of cations and anions should line up. The definition of OHP should base on the criterion that the ions having full solvation shells approach the surface to the closest positions. In this sense, IMHP2 for Na+ should be defined as OHP for Na+, even though its position is different from that for Cl-. Similarly, IMHP1 for Cl- can be considered as IHP for Cl-.

**Authors' response:** We thank the reviewer for this comment. We believe that the IMHP1 $Cl^-$ cannot be considered as either IHP or OHP for the following reasons:
1. These $Cl^-$ ions have a full solvation shell, as shown in Fig. 2d of our manuscript, meaning they cannot be considered as the IHP.
2. In the hydration shell of these $Cl^-$ ions, some solvation water molecules are adsorbed at the surface $Ti_{5c}$ sites, and some solvation water molecules are hydrogen bonded to surface $O_{2c}$ sites. These two types of solvation water molecules have a diffusion coefficient 1-2 orders of magnitude smaller than that of bulk water, indicating that these $Cl^-$ ions can be considered as semi-adsorbed at the $TiO_2$ surface. According to textbooks [Bard, et al Electrochemical methods: fundamentals and applications], the interaction of the OHP ions with the solid surface "involves only long-range

electrostatic forces". Thus, these semi-adsorbed $Cl^-$ ions cannot be considered as the OHP either. Therefore, in this work, we classify them as "intermediate Helmholtz plane" (IMHP). The same reasoning applies to the $Na^+$ ions in IMHP2 (Fig. 2e).

**Changes in revised manuscript:** We added the following sentences on page 7

"Instead, the $Cl^-$ ions forming the second peak (Fig. 2 d) and the $Na^+$ ions contributing to the third peak (Fig. 2 e) exhibit complete hydration shells. While this characteristic is consistent with the definition of outer-sphere surface complexes[43], these ions do not satisfy the OHP criterion that their interactions with the surface involve only long-range electrostatic forces[44]. As shown in Fig. 2d and Fig. 2e, some water molecules in the hydration shell of these ions are either adsorbed on $Ti_{5c}$ atoms or form strong hydrogen bonds with surface $O_{2c}$ atoms. Since these surface water molecules have a diffusion coefficient 1~2 orders of magnitude smaller than that of bulk water[45], these ions can be considered as semi-adsorbed on the surface via surface water molecules. Consequently, these two ionic peaks cannot be classified as either IHP or OHP. In this work, we designate the corresponding layers as intermediate Helmholtz planes (IMHPs), since their peaks fall between the IHP and the OHP. We also find that the ions within the Stern layer are not fixed but can exchange with other ions of the same type in the electrolyte. Specifically, $Na^+$ ions in the IHP have a residence time on the order of nanoseconds, while ions in IMHPs have a residence time of tens to hundreds of picoseconds (Supplementary Information Section 5)."

**Comment 5**: Finally, I find that the section "microscopic surface charging mechanism" is less clear compared to the rest of the manuscript, which is worthy of improvement. The authors haven't explained the origin why the total number of surface charges would have such influences on the fraction of water dissociation. If these two quantities are positively correlated, why does the case under basic conditions with the higher total number of surface charges take almost the same water dissociation fraction as those under neutral conditions? It is also not clear how the specific adsorption of Na+ would affect the adsorption of water ions, as well as surface water dissociation.

**Authors' response:** We thank the reviewer for this valuable feedback. Below, we provide a detailed explanation to address these points.

*(1) Relationship between total surface charges and fraction of water dissociation:* The fraction of water dissociation in this work is defined as the smaller value between the fraction of surface $H^+$ ions and the fraction of surface $OH^-$ ions. Specifically, for the basic system, the fractions of surface $H^+$ and $OH^-$ ions are 14% and 23%, respectively, resulting in a water dissociation fraction of 14%. For the acidic system, the fractions of surface $H^+$ and $OH^-$ ions are 18% and 9%, respectively, resulting in a water dissociation fraction of 9%.

*(2) Effect of specific adsorption of $Na^+$ on water ion adsorption and surface water dissociation:* Due to the specific adsorption of $Na^+$, the surface $OH^-$ ions can be well screened by these $Na^+$ ions. To illustrate this more clearly, we analyzed the in-plane salt ion distribution. As shown in Fig. 5, a newly added figure in the revised manuscript, there is a high probability to find $Na^+$ ions surrounding an $OH^-$ surface ion. Due to the efficient screening of $OH^-$ by $Na^+$, the surface can accommodate more $OH^-$ ions in-plane. Therefore, the $OH^-$ ions take the second pathway to be adsorbed at the surface, which increases the fraction of surface $OH^-$ ions without changing the fraction of surface $H^+$ ions. In contrast, around a surface $H^+$ ion,

the probability to find Cl$^-$ ions is much smaller, indicating that the H$^+$ ion is not well screened. Consequently, the surface cannot accommodate more H$^+$ ions in-plane, making the first pathway favorable under acidic conditions. According to the relationship between total surface charges and the fraction of water dissociation discussed in point 1, the larger fraction of surface ions under basic conditions results in a larger water dissociation fraction.

**Changes in revised manuscript:** We added a new figure (Fig. 5) to the main text and extensively revised the section on "Microscopic surface charging mechanism". The revised section reads:

"The distinct interfacial capacitances resulting from the higher affinity of cations to the oxide surface, compared to anions, is found to give rise to distinct microscopic charging mechanisms on negative and positive surfaces. As shown in Fig. 4a, for the charge-neutral TiO$_2$-NaCl$_{(aq)}$ interface, $14 \pm 2\%$ water molecules adsorbed at Ti$_{5c}$ sites are dissociated into adsorbed H$^+$ at O$_{2c}$ and OH$^-$ at Ti$_{5c}$, with zero net surface charge. Starting with an equilibrated TiO$_2$-NaCl$_{(aq)}$ configuration, when we add bases or acids into the electrolyte, the OH$^-$ or H$_3$O$^+$ ions have two potential pathways to be adsorbed at the surface. For an electrolyte OH$^-$ (Fig. 4b), one pathway is to recombine with a surface H$^+$ ion at the O$_{2c}$ site to form a water molecule in the liquid, which decreases the surface's H$^+$ population. Another pathway is to recombine with an H$^+$ from an adsorbed H$_2$O, which results in an additional OH$^-$ ion adsorbed at the surface Ti$_{5c}$ site. Similarly, an electrolyte H$^+$ can either recombine with a surface terminal OH$^-$ into a water molecule or occupy an empty O$_{2c}$ site (Fig. 4c). Although both pathways result in the same net surface charge $\sigma$, the total number of surface charges, N$_{SC}$= N$_{H+}$+ N$_{OH-}$, is different. The first pathway reduces N$_{SC}$, whereas the second increases it.

The averaged ion coverages in Fig. 4 suggest that OH$^-$ ions prefer the second pathway (increasing N$_{SC}$), whereas protons slightly prefer the first (decreasing N$_{SC}$). As a result, if we define the water dissociation fraction as the smaller value between the fraction of surface H$^+$ ions and the fraction of surface OH$^-$ ions, the average water dissociation fraction decreases significantly (to $\sim$ 9%) with the acidic electrolyte whereas it remains approximately the same as that of the neutral interface under basic conditions, consistent with the increase of water dissociation fraction with the pH reported in a previous AIMD study[25]. These trends can be related to the different capacitances under basic and acidic conditions. The large capacitance under basic conditions indicates a strong ability of the EDL to screen the OH$^-$ surface charge. This is evidenced by the high probability of Na$^+$ ions surrounding an OH$^-$ surface ion, as shown in Fig. 5a. Consequently, the surface can accommodate more OH$^-$ ions in-plane, making the second pathway favorable under the basic condition. In contrast, the small capacitance under acidic conditions reflects a weak ability of the EDL to screen the H$^+$ surface charge. This is demonstrated by the low probability of Cl$^-$ ions surrounding an H$^+$ surface ion, as shown in Fig. 5b. As a result, the surface cannot accommodate more H$^+$ ions in-plane, making the first pathway favorable under acidic conditions.

The fact that negatively charged surfaces allow a larger density of surface hydroxyl groups is important in photocatalysis because these groups can trap photo-generated holes and form hydroxyl radicals[38,50], which are key intermediates of many photo-oxidation reactions. The photooxidation of water is indeed known to be faster at high pH[51]."

**Comments from reviewer #5 and our detailed responses**

**General Comments**: I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

**Authors' response:** We appreciate Reviewer #5's co-review of our manuscript and thank both reviewers for their insightful and excellent comments, which are very helpful for further improving the quality of our manuscript.