Unconventional interfacial water structure of highly concentrated aqueous electrolytes at negative electrode polarizations

Water-in-salt electrolytes are an appealing option for future electrochemical energy storage devices due to their safety and low toxicity. However, the physicochemical interactions occurring at the interface between the electrode and the water-in-salt electrolyte are not yet fully understood. Here, via in situ Raman spectroscopy and molecular dynamics simulations, we investigate the electrical double-layer structure occurring at the interface between a water-in-salt electrolyte and an Au(111) electrode. We demonstrate that most interfacial water molecules are bound with lithium ions and have zero, one, or two hydrogen bonds to feature three hydroxyl stretching bands. Moreover, the accumulation of lithium ions on the electrode surface at large negative polarizations reduces the interfacial field to induce an unusual “hydrogen-up” structure of interfacial water and blue shift of the hydroxyl stretching frequencies. These physicochemical behaviours are quantitatively different from aqueous electrolyte solutions with lower concentrations. This atomistic understanding of the double-layer structure provides key insights for designing future aqueous electrolytes for electrochemical energy storage devices.

With the rapidly increasing demand for renewable energy and mobile devices, the development of next-generation electrochemical energy storage systems has become a key objective in energy research. In electrochemical energy devices, the electrolyte, sandwiched between the positive and negative electrodes, is an essential component determining the performance. Aqueous electrolytes have safety advantages over aprotic organic electrolytes, such as non-flammability and low toxicity. However, conventional aqueous electrolytes are limited by their narrow electrochemical window of 1.23 V due to the hydrogen/oxygen evolution reactions. This limitation can be overcome in highly concentrated aqueous electrolytes, also known as water-in-salt (WiS) electrolytes, which have been shown to significantly widen the electrochemical stability window to over 3.0 V, delivering enhanced performance in Li-ion batteries, supercapacitors, and CO₂ reduction reactions.

Recent reports on WiS electrolytes have drawn considerable attention to their bulk properties. For example, in 21 molal (m, moles of salt per kg of water) lithium bis(trifluoromethane sulphonyl) imide (LiTFSI) WiS electrolytes, more than 90% of the total mole of water molecules are bound with Li⁺, and both the strong interaction with Li⁺ and small free water concentration (<10% of the total mole of water) have been suggested to contribute to the enhanced electrochemical stability of WiS electrolytes. Furthermore, water molecules form nanoscale channels to facilitate Li⁺ transport despite the large macroscopic viscosity of WiS electrolytes. In addition to bulk properties, the performance of the electrochemical device also depends critically on the interfacial properties, especially the structure and dynamics of interfacial water.
on the electrical double-layer (EDL) structure at the electrode–electrolyte interface, a subnanometer region where electrochemical transformations occur. Molecular dynamics (MD) simulations suggest that the high salt concentration in WiS electrolytes significantly alters the Li$^+$ solvation and EDL structures compared to low-concentration electrolytes$^{14–18}$. However, such modeling results have yet to be supported by detailed experimental characterization of the EDL structure at the electrode/WiS electrolyte interface. Previous studies of low-concentration electrolytes have shown that a thorough characterization of EDL structures is crucial for the mechanistic understanding of device performance$^{22,40}$. Extending such studies to the EDL of WiS electrolytes, especially in high electrode polarization regions (e.g., potentials negative than the onset of hydrogen evolution reaction), remains challenging$^{23,24}$.

Herein, the potential-dependent EDL structure of highly concentrated LiTFSI aqueous electrolytes on an Au(111) electrode was studied at electrode polarizations varying from 0 to $\approx 1.55$ V (vs. potential of zero charge, PZC). Comparing the potential-dependent vibrational spectra of interfacial water and ions obtained by in situ electrochemical shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS)$^{25–27}$ with detailed microstructures obtained by MD simulations provides atomistic insights into the EDL structure in WiS electrolytes. The comparison reveals that the interfacial water molecules show three OH stretching bands due to their different hydrogen-bonded structures dictated by interactions among the water, Li$^+$, and TFSI$^-$. The accumulation of Li$^+$ at the electrode surface at high negative polarizations leads to an unusual hydrogen-up (H-up) interfacial water structure that is not observed in dilute aqueous electrolytes and reduces the electric field strength on the interface to give rise to an unexpected blue shift of the OH stretching vibration.

## Results

### In situ probing interfacial water in highly concentrated aqueous electrolyte

As illustrated in Fig. 1a, to study the EDL structure, an electrochemical SHINERS method was used (details in Supplementary Fig. 1 and Supplementary Information), which has proven to be suitable for the investigations at the electrochemical interface, such as specific adsorption of sulfate ion$^{30}$, pyridine$^{31}$, and hydrogen$^{32}$, and most importantly and relevantly, enables an in situ molecular-level probe of the structures of electrical double layer and interfacial water on single-crystal electrode surfaces$^{22,29,32}$. The Raman signal of the interfacial layer is significantly enhanced in the junction between the Au(111) surface and the core/shell Au/SiO$_2$ nanoparticles due to the enhanced optical field strength. The thin SiO$_2$ layer (2 nm in thickness) is electrochemically inert, which can insulate the Au particles (~57 nm in diameter) from the single-crystal Au electrode while still providing enhancement of the electric field (see Supplementary Fig. 1 for the TEM characterization of Au nanoparticles and their size distribution histogram). MD simulations, as shown in the schematic in Fig. 1b and with details described in the Method section, were utilized to investigate the atomistic structure of the EDL and the water hydrogen-bonded structure at the Au(111) electrode–WiS electrolyte interface.

The vibrational spectra of interfacial water in the OH stretching region and their changes with applied potentials were measured by in situ electrochemical Raman spectroscopy in 21 m LiTFSI aqueous electrolytes. All electrode potentials are relative to the PZC of the Au(111) electrode, which is around $\approx 0.1$ V vs. Ag/AgCl electrode (see Supplementary Figs. 2, 3 for corresponding cyclic voltammogram and PZC measurement of Au(111) in 21 m LiTFSI aqueous electrolyte). The Raman spectra at $+0.5$ and $+0.9$ V show negligible dependence on the applied bias (Supplementary Fig. 4) and agree well with bulk water Raman spectra of WiS electrolyte. Therefore, the spectrum at $+0.9$ V was subtracted from the total Raman signal to reveal the spectra of interfacial water. Shown in Fig. 2a are the Raman spectra of the interfacial water OH stretching mode in the 3200–3600 cm$^{-1}$ region from $+0.5$ to $+1.55$ V. Inspired by the assignments of Raman spectra of water in the low-concentrated aqueous electrolytes$^{22,29,32–34}$, the spectra can be well fitted by the sum of three Gaussian bands, Peak 1, 2, and 3 (with increasing frequencies), suggesting three major types of water molecules in the EDL. As shown in Fig. 2b, c, both the frequencies and intensities of these three bands show a strong dependence on the applied potential, reflecting the bias-dependent change of the interfacial water structure and electric field$^{22}$. The Raman frequencies of Peak 1–3 decrease linearly from $+0.1$ to $\approx 1.15$ V, consistent with Stark effect induced frequency shifts$^{22,27,40}$, which is caused by the monotonically increasing total electric field experienced by interfacial water in the potential region of 0 to $\approx 0.96$ V, as disclosed by MD simulations in Fig. 2d. However, at more negative potentials, from $\approx 1.15$ to $\approx 1.55$ V, the Raman frequencies of these three peaks increase, which is not observed in 7 m LiTFSI aqueous electrolyte (Supplementary Fig. 5) and have not been reported previously$^{32}$. MD simulations reveal an

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**Fig. 1** Probing the electrochemical double-layer structure at the electrode-electrolyte interface. **a** Schematic of in situ probe of the EDL using SHINERS method. Bottom left: schematic structure of the Li$^+$-free water, Li$^+$-bound water molecules, and TFSI$^-$ anion, respectively; Top right: schematic of a spectro-electrochemical cell, where an Au(111) electrode, a Pt wire, and an Ag/AgCl electrode were used as the working electrode (WE), counter electrode (CE), and reference electrode (RE), respectively. The large spheres in the bottom center are the core/shell Au/SiO$_2$ nanospheres. **b** Typical MD simulation snapshot of 21 m WiS electrolyte in contact with Au(111) electrodes under applied bias. The interfacial water molecules on the negative electrode surface are magnified.
unexpected decrease in the total electric field experienced by the interfacial water at the highly negative potential region from −0.96 to −1.51 V (Fig. 2d), which accounts for this blue shift in the water OH stretching mode \(^{38,39}\). The origin of this unexpected change in the interfacial electric field will be further discussed below.

The absolute intensities of Raman bands depend on the population of interfacial species and their Raman enhancement factors, both of which can change with potential, and their relative contributions cannot be easily separated. Thus, only the relative intensities of Raman bands and their potential dependence are analyzed, which will be characterized in the portion of total intensity was used to avoid the variation of plasmonic enhancement during the potential scan.

**Fig. 2** | Vibrational Raman spectra of interfacial water at Au(111)/WiS electrolyte (21 m LiTFSI) interface. **a** In situ electrochemical Raman spectra of the OH stretching mode of interfacial water at the Au(111) surface measured in 21 m LiTFSI aqueous electrolyte (gray curves) and their fits to the sum of three Gaussian bands of increasing frequency: Peak 1 (red), 2 (blue), and 3 (pink). **b** Potential-dependent frequencies of Peak 1 (red squares), 2 (blue circles), and 3 (pink triangles) of interfacial water obtained from spectral fits in panel **a** and their linear fit (solid lines) in regions of +0.1 ~ −1.15 V and −1.15 ~ −1.55 V. **c** Potential dependence of the relative intensities of Peak 1 (red squares), 2 (blue circles), and 3 (pink triangles) obtained from the fits in **a**. Herein, a relative Raman intensity profile representing the change in the portion of total intensity was used to avoid the variation of plasmonic enhancement during the potential scan. **d** Simulated electric field (E) strength (red circles) experienced by the interfacial water and the linear fit (solid red line) in regions of 0 ~ −0.96 V and −0.96 ~ −1.51 V. **e** Schematics of potential-dependent probability of interfacial water with donor numbers of 0 (pink triangles), 1 (blue circles), and 2 (red squares), respectively. As shown in the schematic in Supplementary Fig. 11, H-bond formation was determined based on the geometric criteria of hydrogen bond length \((r_{HB} \leq 0.35\text{ nm})\) and angle \((\alpha_{HB} \leq 30^\circ)\). The error bars in **b–e** present the standard error in experiments or simulations. **f** Schematics of Li\(^+\)-bound interfacial water with donor number changing from (i) 0 to (ii) 1 and (iii) 2, respectively. In the formation of an H-bond with a Li\(^+\)-bound water molecule as a donor, another water molecule or TFSI\(^-\) can act as an acceptor.

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seen by the AFM measurement, indicating the high surface smoothness. In sharp contrast, after holding at −1.5 V, the surface morphology of the electrode became much more roughened with several valley-like regions (Supplementary Fig. 8c, d), suggesting the formation of SEI at this potential.

It has been well established that in aqueous solutions and dilute electrolytes, the frequency of the OH stretching mode of interfacial water is determined by the hydrogen bond (H-bond) environment of water molecules, giving rise to distinct peaks for ice-like water \(13,14\), liquid-like water \(15,16\), and dangling OH bonds \(22,36\). To help the assigned the observed interfacial OH stretching spectra, MD simulations were performed to explore the structure of water molecules and the corresponding H-bond network at the electrode-WiS electrolyte interface. As shown in Supplementary Fig. 9, more than 93% of the total mole of interfacial water molecules are within the first solvation shell of Li\(^+\) (referred to as Li\(^+\)-bound water), and less than 7% of the total mole of water molecules are outside the first solvation shell of Li\(^+\) (Li\(^+\)-free water). This can be attributed to the strong interaction between Li\(^+\) and water molecules under the high salt concentration \(16,17\), forming more than 93% of the total mole of the corresponding H-bond network at the electrode-WiS electrolyte interface.

Further, as shown in Supplementary Fig. 9, more than 93% of the total mole of interfacial water molecules are within the first solvation shell of Li\(^+\) (referred to as Li\(^+\)-bound water), and less than 7% of the total mole of water molecules are outside the first solvation shell of Li\(^+\) (Li\(^+\)-free water). This can be attributed to the strong interaction between Li\(^+\) and water molecules under the high salt concentration \(16,17\). Furthermore, the simulated number density of Li\(^+\)-bound water increases during the cathodic scan, likely induced by the accumulation of Li\(^+\) on the electrode surface, consistent with previous work in dilute aqueous electrolytes \(22\). As the polarization increases to ~1.0 V, water molecules get noticeably reorganized: the H atom distribution shows a new peak at the first layer (~0.17 nm to the surface) and a decrease of the peak height at the second layer (Fig. 3a, b); the distribution of \(\theta_{\text{normal}}\) becomes less ordered (Fig. 3d) and the peak of \(\theta_{\text{dipole}}\) distributions shifts to 115° (Fig. 3e). These changes can be attributed to the reoriented “dipole-down” structure (i.e., the water dipole points towards the electrode surface), in accord with previous reports of water structure on gold electrodes by X-ray absorption spectroscopy \(41\) and Raman spectroscopy \(42\). However, under high polarization, we observe that a shoulder of H atoms grows in at the third layer (~0.35 nm to the surface, see Fig. 3b), and a peak of \(\theta_{\text{dipole}}\) distribution at around 60° gradually increases (Fig. 3e). Such structure could be ascribed to an unusual “dipole-up structure” (i.e., the water dipole points away from the electrode surface). Such an unusual interfacial water structure has never been reported on highly negatively charged surfaces \(22,32\). In order to describe the structure transition of interfacial Li\(^+\)-bound water molecules with the applied potential more accurately, we then calculated the differential 2D angular distribution of two OH groups of Li\(^+\)-bound water relative to the arrangement of water under PZC. Specifically, the OH bond of a water molecule can be classified into “H-up,” parallel, and “H-down” with the angle between the OH bond of water and the normal of the electrode surface ranging in 0–70°, 70–110°, and 110–180°, respectively (Supplementary Fig. 12). As shown in Fig. 3f, the arrangement of Li\(^+\)-bound water molecules adjusts from parallel to “H-down” under low polarization. Nevertheless, under high polarization, though the major Li\(^+\)-bound water molecules transfer from parallel to “H-down”, part of the water molecules transfer into an unusual H-up configuration.

Analysis of the EDL structure suggests that the change of interfacial water orientation is induced by the variation of interfacial Li\(^+\) distribution. As shown in Fig. 3c, at the PZC, most Li\(^+\) ions are located at the third layer (~0.35 nm to the surface), and a small amount of Li\(^+\) ions is located at the second layer, the plane of water (~0.26 nm to the surface). At more negative potentials, Li\(^+\) accumulates in the inner region of the EDL (~0.17 nm to the surface), agreeing with our experimental observation of LiOH deposition on Au(111) at ~1.55 and ~1.83 V (Fig. 2a and Supplementary Fig. 6). The accumulation of Li\(^+\) partially screens the electric field, enabling the H-up structure of interfacial water. As a comparison, the Li\(^+\) distribution in the low concentration (7 m) LiTFSI aqueous electrolyte shows negligible density in the first atomic layer (Supplementary Fig. 13a–c), which inhibits the occurrence of the dipole-up structure of interfacial water (Supplementary Fig. 13d, e).
In addition to the structure of interfacial Li+ and water at negative electrode polarizations, our study also reveals the structure of the counter ion (i.e., TFSI−) within the interfacial region. As shown in Supplementary Fig. 14a, b, the vibrational Raman spectra exhibit multiple bands of TFSI− in the 250 to 1300 cm−1 spectral region. These bands show a similar lack of potential dependence, and only the sharpest peak at 746 cm−1 (S-N-S bending mode, δS−N−S) is discussed. Over the entire potential range (+0.3 to −1.55 V), the δS−N−S peaks show negligible frequency shifts (Supplementary Fig. 14a), while the integrated intensity changes by <10% over the spectral region (Supplementary Fig. 14b). The MD simulations reveal that at the PZC, the TFSI− number density distribution has a prominent peak of their center of mass at 0.4 nm from the electrode surface (Supplementary Fig. 14c), indicating that TFSI− ions sit above the interfacial water layer (−0.26 nm to the surface) and slightly above the Li+ layer (−0.35 nm to the surface). At more negative potentials, the number density of TFSI− at the 0.4 nm peak decreases, suggesting that the increased negative charge of the electrode surface pushes more TFSI− ions further away from the surface by electrostatic repulsion while attracting more Li+ into the inner layer by electrostatic attraction (Fig. 3c). Detailed analysis of the MD simulation results show that at the PZC, the hydrogen bond acceptors of interfacial water are mostly the sulfonyl oxygen of TFSI− (Supplementary Fig. 15), for ~93.9% for water with one H-bond donor and ~92.7% for water with two H-bond donors. At more negative potentials, the percent of H-bonds with TFSI− acceptor decreases as more TFSI− ions are pushed further away from the electrode surface.

The analysis of the combined in situ electrochemical Raman spectroscopy and constant-potential MD simulations results have led us to propose an EDL model in highly concentrated aqueous electrolytes. As depicted schematically in Fig. 4, most interfacial water molecules are within the first solvation shell of Li+ with their O atoms interacting with the Li+ and their H atoms forming 0, 1, and 2 H-bonds, with TFSI− as the principal H-bonding acceptor. The electrolyte in the double layer shows a structural order in the density profile along the normal to electrode surface; with water molecules closest to the electrode surface interacting with the Li+ and TFSI− ion layers above. Under low polarization (from 0 to −0.6 V), the interfacial water molecules adopt parallel and H-down structures (Fig. 4a). However, under high polarization (from −1.5 to −1.9 V), Li+ ions accumulate on the electrode surface, inserting between the electrode and water layer (Fig. 4b). As a result, the amount of interfacial Li+-bound water adopting an “H-up” orientation increases from ~10% (PZC) to ~20% (high polarization); meanwhile, the amount of interfacial Li+-bound water with a parallel orientation decreases from ~43 to ~16% (Supplementary Fig. 16). Specifically, in terms of the “H-up” structure of interfacial Li+-bound water, ~20% of interfacial Li+-bound water molecules form zero H-bond (i.e., two dangling OH bonds), and -55% of interfacial Li+-bound water molecules adopt one H-bond (i.e., one dangling OH bond); meanwhile, the rest -25% of interfacial Li+-bound water molecules form two H-bonds (i.e., zero dangling OH bond, Supplementary Fig. 17).

Molecular insights into the structural transition of interfacial water
As shown in Fig. 2b, d, the potential-dependent OH stretching frequency shifts of interfacial water molecules with different H-bond
numbers correlate well with the average electric field experienced by the interfacial water, indicative of the Stark effect-induced frequency shift. To understand how the potential-dependent double-layer structure change leads to the observed frequency shift, we decompose the total field on the interfacial water (red circles) into contributions from the electrode (H2O-electrode, gray bar), water molecules (H2O-H2O, orange bar), and Li+ and TFSI- ions (H2O-LiTFSI, blue bar), as presented in Fig. 5a. Details can be referred to Methods. It is found that, in the 21 m electrolyte, the strength of the electric field from the electrode increases linearly with the applied potential (Fig. 5a), due to the monotonically increased surface charge density. The peak locations of the Li+ layers are nearly independent of polarization (Supplementary Fig. 18), generating a nearly polarization-independent electric field at ~1.56 V (Supplementary Fig. 5), although the slope of the frequency shift decreases. Unfortunately, measurements at more negative potential are difficult due to the great H2 evolution. Moreover, MD simulations show no discernable Li+ accumulation in the inner layer of the EDL (Supplementary Fig. 13c). It is possible that the interfacial field may also be screened at the negative potential range in the lower concentration electrolyte, but the extent of screening is smaller and does not lead to a blue shift of the Raman frequencies of the OH stretching bands.

Fundamentally, the unique atomic structure of the EDL in highly concentrated aqueous electrolytes can be used to reveal the nature of the water electrosorption in wet ionic liquids and also the mechanism of enhancing/expanding the voltage window stability via adding salt. Recently, an “H-up” water structure was predicted to lower the potential of hydrogen evolution reaction on the negative electrode in humid ionic liquids. Therefore, the unusual “H-up” structure of interfacial water and the H-bond network with TFSI- anions at very negative potentials in this work may be used to tune the onset potential of water-reduction reaction in aqueous electrolytes for electrochemical energy storage devices.

In summary, by combining in situ vibrational spectroscopy and constant-potential MD simulations, we have studied the atomistic structure of the EDL of highly concentrated (21 m LiTFSI) aqueous electrolytes at an Au(111) electrode. The Raman spectra of interfacial water OH stretching modes show three bands with potential-dependent relative intensities and frequencies. MD simulations reveal that >93% of the interfacial water molecules are in the first solvation shell of the Li+. These interfacial water molecules cannot serve as H-bond acceptors but donors because their O atoms are coordinated with the Li+. Their H-bond environments differ in the H-bond donor number, ranging from 0, 1, and 2, corresponding well
to the three observed OH stretching bands with decreasing frequencies. This assignment is supported by the good agreement between the potential dependence of the observed relative Raman intensities of these bands and the simulated probability of water molecules with these donor numbers.

Ascribed to Stark effect induced vibrational frequency shifts, the frequencies of all three OH bands shift to lower values at more negative electrode polarizations from the PZC to $-1.15$ V; while they exhibit an unexpected blue shift from $-1.15$ to $-1.55$ V, which has not been observed in low-concentration electrolytes. MD simulations reveal that over this potential range, Li ions in WiS electrolytes accumulate on the electrode surface, inserted between the electrode and the first layer of water molecules. This reduces the electric field strength experienced by the interfacial water molecules, giving rise to the observed blue shift of their OH stretching frequencies. It also leads to unusual “H-up” interfacial water molecules with the dipole pointing away from the electrode surface despite the negative electrode polarization. Finally, at more negative potentials, the decomposition reaction of the electrolyte is observed to yield a LiOH deposit at Au(111) surface.

Our work uncovers the detailed atomistic structure of the EDL in concentrated WiS electrolytes and identifies unique structural features at high negative electrode polarizations that differ from those in low-concentration electrolytes. These findings provide important insights for the molecular-level understanding of interfacial Li-ion behaviors in WiS electrolyte systems.

**Methods**

**Materials**

Lithium bis(trifluoromethane sulphonyl) imide (LiN(SO$_2$CF$_3$)$_2$, LiTFSI, purity of 99.95%), sodium citrate (99%), sodium silicate solution (reagent grade), and gold(III) chloride hydrate (~50% Au basis) were purchased from Sigma-Aldrich. The (3-aminopropyl)trimethoxysilane (APTMS, 97%) was purchased from Alfa Aesar. All the chemicals were used as received.

In electrochemical experiments, ~ 3 mL of electrolyte was used. An Ag and a Pt wire were used as the quasi-reference and counter electrode, respectively. Both the Ag and Pt wires are 0.5 mm in diameter, ~40 mm in length, and 99.999% in purity.

**Synthesis of Au shell-isolated nanoparticles (SHINs)**

Au core nanospheres with a diameter of ~55 nm were synthesized according to reference[42]. In brief, 1.4 mL of 1 wt% sodium citrate solution was added to 200 mL of boiling 1 wt% HAuCl$_4$ solution (obtained by dissolving the gold(III) chloride hydrate (~50% Au basis) were purchased from Sigma-Aldrich. The (3-aminopropyl)trimethoxysilane (APTMS, 97%) was purchased from Alfa Aesar. All the chemicals were used as received.

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Electrochemical Raman spectroscopic measurements

In situ Raman measurements were performed on a home-built Raman spectrometer with a backscattering configuration (see Supplementary Fig. 1c for the setup). Excitation at 633 nm from a HeNe continuous-wave laser (Thorlabs) was focused through a 50× objective (Mitutoyo), and the signal was collected via an electron-multiplying CCD camera (Andor). The laser power at the sample surface was -10 mW. A halogen lamp (Thorlabs) was used for the white light imaging of the sample surface, which facilitates the data acquisition during spectro-electrochemical measurement. All the spectra were calibrated using a neon spectral calibration lamp (Newport) and a standard silicon (III) wafer. An Au(111) electrode was used as a working electrode throughout the experiment. Meanwhile, a homemade spectroelectrochemical cell with an Ag/AgCl reference electrode and a Pt counter electrode was used in the electrochemical Raman spectroscopic experiments. To extract the signal of interfacial water, a spectrum at the potential where the potential-dependent signal vanished was used as a reference to obtain the difference spectra of interfacial water\(^5\). Herein, the background was removed via Origin 2020 software. Because of the weak Raman intensity of interfacial water in highly concentrated electrolytes at a single-crystal surface, a Savitzky–Golay smoothing method was applied to the Raman spectra of interfacial water for a better signal-to-noise ratio. The ohmic drop in the spectroelectrochemical cell was compensated for each Raman spectrum. All potentials in this work are referenced to the PZC. The electrochemical Raman spectroscopic measurements were carried out at 25 °C without a climatic/environmental chamber.

It is worth noting that the SHINERS method was performed on an atomically flat Au(111) electrode surface, for which the enhancement of the Raman signal is much lower than that in the conventional surface-enhanced Raman spectroscopy (SERS) on a roughened Au electrode\(^43\). At the same time, the amount of water in the highly concentrated electrolyte is lower than that in the dilute electrolyte. Hence, the signal-to-noise ratio of the Raman spectra is lower as compared to the conventional SERS measurements in dilute electrolyte\(^4\).

Electrochemistry measurements

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed in a glass single-chamber electrochemical cell (see Supplementary Fig. 19 for the photograph of the cell) on an electrochemical workstation (AUTOALB). Argon gas was bubbled into the electrolyte for 15 min to remove dissolved oxygen prior to each experiment. A slow argon flow was kept above the electrolyte during the whole experiment process. An Au(111) electrode was used as a working electrode. In the electrochemical polishing process, the Au(111) electrode was electrochemically oxidized in 0.5 M H\(_2\)SO\(_4\) solution and then was immersed in 1 M HCl solution to reduce the gold oxide. Then, the electrode was washed using a great amount of ultra-pure water. These procedures were repeated three times. Finally, the electrode was annealed with an H\(_2\) flame and cooled down in an argon atmosphere before each experiment. A platinum wire was used as the auxiliary electrode and a silver wire was used as a quasi-reference electrode. After each experiment, the potential was calibrated to Ag/AgCl electrode, which was used in situ Raman measurements. The electrochemistry measurements were carried out at 25 °C without a climatic/environmental chamber.

The capacitance curves were obtained by EIS potential scan within the EDL region. The EISs were measured at the potentiostatic mode in a climatic/environmental chamber. Electrochemistry measurements were carried out at 25 °C without a climatic/environmental chamber. The auxiliary electrode and a silver wire was used as a quasi-reference electrode. The electric field was applied in the presence of electrolytes. For each simulation, the MD system was first heated at 500 K for 3 ns and then annealed to 300 K over a period of 2 ns, followed by another 10 ns to reach equilibrium. After that, a 10 ns production was performed for analysis. Each case was repeated three times with different initial configurations to certify the accuracy of the simulation results.

Electric field calculation

The electric field experienced by interfacial water is determined based on MD-obtained trajectories. Instead of the inaccurate cutoff method, the algorithm adopted herein is upgraded by performing the PME method\(^4\), where the long-range electrostatic interactions induced by the electrode, water, and ions have been calculated precisely. Such
analysis has been used in prior simulation work. Technologically, the van der Waals interactions of all particles are turned off first, and then the total electric field ($E_{total}$) experienced by interfacial water is determined based on the rerun of MD-obtained trajectories. Then it is decomposed into contributions from the electrode ($E_{H2O-electrode}$), water molecules ($E_{H2O-H2O}$), and LiTFSI ($E_{LiTFSI}$). To calculate the electric field from water molecules, only the electrostatic interaction of water with water is retained with the van der Waals interaction of all particles and the electrostatic interaction from electrode and LiTFSI being turned off; thus, the electric field ($E_{2}$) experienced by interfacial water is obtained from the rerun of the MD-obtained trajectory, which is referred as $E_{H2O-H2O} - E_{H2O-LiTFSI}$. As for the contribution from LiTFSI, the van der Waals interaction of all particles are turned off, thus the electric field induced by ions is obtained as $E_{H2O-LiTFSI} = E_{2} - E_{H2O-H2O}$. Consequently, the electric field from the electrode is calculated as $E_{H2O-electrode} = E_{total} - E_{H2O-H2O} - E_{H2O-LiTFSI}$.

It is worth noting that the MD-obtained electric field can be used to interpret the experimental findings of this study are available from the corresponding authors upon reasonable request.

**Data availability**

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

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Author contributions
T.L., G.F., C.-Y.L., and M.C. conceived and designed the project, analyzed the results, and drafted the manuscript. C.-Y.L., J.M., and T.L. carried out the electrochemical Raman spectroscopy experiments and analysis. M.C. and G.F. performed the MD simulations. X.L. and H.D.A. prepared and characterized the single-crystal electrode. S.L. and J.Y. conducted the PZC measurement. All authors contributed to the final manuscript.

Competing interests
The authors declare no competing interests.

Additional information

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