Pinpointing the axial ligand effect on platinum single-atom-catalyst towards efficient alkaline hydrogen evolution reaction

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Developing active single-atom-catalyst (SAC) for alkaline hydrogen evolution reaction (HER) is a promising solution to lower the green hydrogen cost. However, the correlations are not clear between the chemical environments around the active-sites and their desired catalytic activity. Here we study a group of SACs prepared by anchoring platinum atoms on NiFe-layered-double-hydroxide. While maintaining the homogeneity of the Pt-SACs, various axial ligands (−F, −Cl, −Br, −I, −OH) are employed via a facile irradiation-impregnation procedure, enabling us to discover definite chemical-environments/performance correlations. Owing to its high first-electron-affinity, chloride chelated Pt-SAC exhibits optimized bindings with hydrogen and hydroxide, which favor the sluggish water dissociation and further promote the alkaline HER. Specifically, it shows high mass-activity of 30.6 A mgPt−1 and turnover frequency of 30.3 H2 s−1 at 100 mV overpotential, which are significantly higher than those of the state-of-the-art Pt-SACs and commercial Pt/C catalyst. Moreover, high energy efficiency of 80% is obtained for the alkaline water electrolyser assembled using the above catalyst under practical-relevant conditions.

Green hydrogen produced via electrocatalytic hydrogen evolution reaction (HER) has been recognized as a promising alternative to mitigate the pressing carbon emission issues1,2. Thus, HER has been explored extensively through both proton reduction in acidic media, and water reduction in alkaline media3,4. In strong acidic media, noble-metal-based materials are usually needed to catalyse proton reduction for HER to avoid electrode dissolutions5,6. In contrast, abundant materials have shown satisfactory stability for water reduction in alkaline electrolyte7,8. Unfortunately, the HER kinetics is typically one to a few orders of magnitude lower in alkaline electrolyte than in acids, even on the state-of-the-art platinum (Pt)-based electrocatalysts9-13. Besides, HER is also much more sensitive to the catalyst surface-structure in alkaline media than in acids9. Nevertheless, enhancing the sluggish kinetics of water reduction in alkaline electrolyte is crucial to reduce the high overpotential and associated energy loss for green hydrogen production14-17.

Development of highly active single-atom catalysts (SACs) with maximized atomic utilization efficiency is a promising solution to
address the above challenges. The chemical environment of the SACs active-sites, including the ligand identity, coordination number and configuration, can directly influence the electronic state, degrees of freedom and other physicochemical properties of the active-center that are associated to the adsorptions of the reactant/intermediates, and thus further determines the catalytic performance of the SACs. Hence, revealing the chemical environment/catalytic-performance correlations is critical for designing SACs with improved activity. Currently, several methods have been developed to synthesize SACs with relatively controllable chemical-environments around the active-center, including defect engineering, annealing, metal-support interaction, heteroatom tethering, cluster/nanoparticle introduction, etc. While tremendous progress has been made in developing new materials using the above synthetic strategies, the harsh conditions involved inevitably break the homogeneity of the active-centers within SACs, e.g., the metal loading, the coordination number/configuration, and the structure of supports, leading complications and uncertainties in establishing definitive correlations between the chemical-environment of SACs active-centers and their catalytic performance.

Recently, a handful of Pt-SACs have been developed and shown encouraging activity towards alkaline HER, however, systematic explorations on stimulating the HER activity via controllable modifications of the chemical-environment around Pt-single-sites are rare. This motivated us to design Pt-SAC systems in which the chemical-environments around the Pt-sites can be precisely manipulated, so that reliable structure/performance correlations can be determined and utilized for future catalyst design.

Herein, we first introduce Pt-single-sites onto NiFe-layered-double-hydroxide (LDH) nanosheets by electrodeposition, and then develop a facile procedure of irradiation-impregnation to precisely adjust the axial ligand on the Pt-single-sites, based on which we are able to establish robust chemical-environment/HER activity relationship while maintaining the homogeneity of the above Pt-SACs. Note, during the preparation of our manuscript, another Pt-SAC based on NiFe-LDH, however, with different structure owing to different synthetic method, was reported elsewhere, and in which the axial-ligand-effect was not discussed. In this work, the aforementioned irradiation-impregnation procedure allows us to modify the Pt-sites with different axial ligands, e.g., −F, −Cl, −Br, −I, −OH. Through detailed spectroscopic and electrochemical characterizations, we show that the Cl-Pt/LDH exhibits superior HER performance with a low overpotential of 25.2 mV at 10 mA cm$^{-2}$ in 1 M KOH, and a mass activity as high as 30.6 A mgPt$^{-1}$ at the overpotential of 100 mV, which is 5 and 13 times greater than those of the HO-Pt/LDH and commercial 20% Pt/C, respectively. Under the same conditions, the HER activity follows the order of Cl-Pt/LDH > F-Pt/LDH > HO-Pt/LDH > Br-Pt/LDH > I-Pt/LDH, confirming the significant axial-ligand effect on HER activity. Density functional theory (DFT) calculations suggest that, owing to the high first-electron-affinity, Cl chelated Pt-sites show optimized adsorption affinities toward both OH$^-$ and H$, consequently facilitating the sluggish Volmer step (water dissociation) which is typically the kinetic limiting step for alkaline HER. Moreover, a membrane electrode assembly (MEA) based water electrolyser is assembled using Cl-Pt/LDH and pristine NiFe-LDH as the cathodic and anodic catalysts, respectively. Encouragingly, it exhibits decent performance with a modest cell voltage of 1.87 V at 1 A cm$^{-2}$ at 60 $^\circ$C, corresponding to a high energy efficiency of 80%. Overall, our efforts demonstrate the significance of engineering the SAC active-sites with atomic precision, the obtained insights can guide next generation catalyst design.

**Results and discussion**

**Manipulating the axial ligand on Pt-single-sites**

The irradiation-impregnation procedure for adjusting the axial ligand of Pt/LDH is elaborated in Fig. 1a. First, NiFe-LDH nanosheet arrays were synthesized through a hydrothermal method. Then, PtCl$_2$ anion is adsorbed onto the LDH surface through electrodeposition, forming the atomic dispersed Pt-sites. The as-prepared samples show nearly identical X-ray diffraction (XRD) patterns as the NiFe-LDH support (Supplementary Fig. 1, JCPSD No. 40-0215), suggesting that the crystalline structure of the LDH remains. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images show that both the pristine NiFe-LDH and Pt-loaded LDH exhibit plate-like nanosheet array with lateral size of ~500 nm and thickness of ~10 nm (Fig. 1b, e, Supplementary Figs. 2–3), negligible differences in morphology were found. No sub-nanometer clusters or nanoparticles were detected via aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM, Fig. 1c), except discrete bright dots, confirming the atomic dispersion of Pt-atoms in Cl-Pt/LDH. Besides, the uniform distributions of Pt and O on the nanoplates (Fig. 1d, g, and Supplementary Fig. 4) suggest that the Pt-atoms are homogeneously dispersed on the LDH substrate. Meanwhile, the lattice fringe with interplanar spacing of about 2.3 Å corresponds to the (015) planes of NiFe-LDH, in line with the XRD results.

To exchange the Cl ligand, we treated the Cl-Pt/LDH with white light irradiation (3.75 mW cm$^{-2}$; 30 min) in KOH. While the atomic dispersion of Pt-atoms remains unchanged after the irradiation (Fig. 1f), the intensity of Cl signal mostly diminished, suggesting the successful removal of Cl ligand. In addition, the decreased signal at 329 cm$^{-1}$ in the Far-Infrared spectrum after the irradiation further confirms the loss of the coulombic Pt–Cl bonds (Fig. 1h). We tentatively attribute the Cl loss to the anion exchange by hydroxide, yielding the product of HO-Pt/LDH, its structure is later determined by X-ray adsorption spectroscopy. Obvious changes were also observed for the ligand-to-metal charge transfer (LMCT) induced absorption bands (~200–300 nm) in Ultraviolet-visible Diffuse Reflectance spectra (UV-Vis DRS) of Cl-Pt/LDH and HO-Pt/LDH (Fig. 1i), while the metal-to-metal charge transfer (MMCT) remains unchanged, indicating that only ligand exchange occurred after the irradiation. Electron paramagnetic resonance (EPR) measurements were conducted to study the mechanism of Cl removal. As shown in Fig. 1j, profound radical signals were appeared when exposing the Cl-Pt/LDH to light and the radical scavenger 5,5-dimethyl-1-pyrroline N-oxide (DMPO) spontaneously, which can be attributed to the oxidation of the Cl ligand to Cl radicals by photogenerated holes, which then are captured by DMPO to form DMPO$^\bullet$ radicals. In contrast, the absence of radical signals were observed for samples of Cl-Pt/LDH in dark and HO-Pt/LDH under illumination as expected.

Taken together, we conclude that the Cl$^-$ to OH$^-$ ligand exchange is induced by visible light illumination. Later, the HO-Pt/LDH sample was re-immersed into KCl solution, as expected, the −Cl axial ligand can be recovered (denote as R-C1-Pt/LDH) due to the strong binding affinity of halogens on Pt. Worth noting, the loadings of Pt in Cl/Pt-LDH, HO-Pt/LDH and R-X-Pt/LDH (X = F, Cl, Br, or I) are very close based on results of Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) (Supplementary Table 1), suggesting that there are no other detectable structural changes occur besides the axial-ligand exchange. Overall, the facile irradiation-impregnation procedure allows us to precisely manipulate the axial ligand of the Pt-single-sites while maintaining the homogeneity of the Pt-SACs.

**Investigating the coordination and electronic structures**

X-ray photoelectron spectroscopy (XPS) was employed to analyse the detailed chemical composition of Cl-Pt/LDH and HO-Pt/LDH. The loss of Cl 2p signal (Fig. 2a) after light irradiation provides further evidence for the complete ligand exchange. Meanwhile, negligible changes can be found in both Fe 2p and Ni 2p spectra (Supplementary Fig. 5), indicating that the homogeneity of the Pt-SAC is well retained. As shown in Fig. 2b, the 4f$^2$ 8s peaks of Pt-atoms in both Cl-Pt/LDH and HO-Pt/LDH are located between Pt$^{2+}$ (72.7 eV) and Pt$^{4+}$ (74.9 eV), indicating the average valence states of these Pt-atoms are between +2 and +4.
The slightly higher binding energy of the Pt 4f-electrons in Cl-Pt/LDH than that of the HO-Pt/LDH agrees well with previous results where electron transfer was observed from Pt to the Cl ligand\textsuperscript{46}.

X-ray absorption fine structure (XAFS) spectroscopy was performed to investigate the coordination environment and electronic structure of Pt single-sites in Cl-Pt/LDH and HO-Pt/LDH. First, the X-ray absorption near edge structure (XANES) spectra of the above samples and the references of Pt foil, K\textsubscript{2}PtCl\textsubscript{4}, and PtO\textsubscript{2} at the Pt L\textsubscript{3}-edge were analysed. The white line at the Pt L\textsubscript{3}-edge (the intensity of which is a measure of the transition of 2p\textsubscript{3/2} → 5d\textsubscript{3/2} or 5d\textsubscript{5/2}) was recognized as a reliable indicator for the Pt electronic structure, since the unoccupied states above the Fermi level are essentially the 5d character of Pt\textsuperscript{47,48,49}. As shown in Fig. 2c, the white lines of both Cl-Pt/LDH and HO-Pt/LDH locate between those of the K\textsubscript{2}PtCl\textsubscript{4} (Pt\textsuperscript{2+}) and PtO\textsubscript{2} (Pt\textsuperscript{4+}), suggesting that the valence states of Pt-atoms in Cl-Pt/LDH and HO-Pt/LDH are between +2 and +4, in line with the above XPS results. After the curve fitting using standard references, the valence states of Pt in Cl-Pt/LDH and HO-Pt/LDH are estimated as 2.78 and 2.08, respectively (Supplementary Fig. 6a), illustrating the existence of strong ligand effects on the electronic structure of Pt-SACs.

Fourier-transformed (FT) \textit{k}\textsuperscript{2}-weighted extended X-ray absorption fine structure (EXAFS) spectra were employed to further analyse the coordination environment of the Pt-SACs. As shown in Fig. 2d, no Pt-Pt interactions at ~2.50 Å can be detected in both Cl-Pt/LDH and HO-Pt/
LDH, demonstrating the atomic dispersion of Pt-atoms in these samples, which is consistent with the CO chemisorption results from the Fourier-transformed Infrared Spectroscopy (Supplementary Fig. 6b)\(^1\). Besides, two obvious peaks at around 1.60 Å and 2.06 Å are found in Cl-Pt/LDH, which are associated to the Pt-O path in PtO\(_2\) and the Pt-Cl path in K\(_2\)PtCl\(_4\), respectively. In contrast, only one Pt-O like peak at ~1.60 Å can be seen in HO-Pt/LDH, indicating that the Cl ligand is fully replaced after irradiation. Based on the wavelet transform (WT) analysis of the EXAFS spectra (Supplementary Fig. 7), Cl-Pt/LDH displays a higher WT maximum at 5.2 Å\(^{-1}\) than that of HO-Pt/LDH at 4.9 Å\(^{-1}\), suggesting that the average coordination number of the Pt-sites in Cl-Pt/LDH is larger than that in HO-Pt/LDH.

To reveal the chemical environment of the Pt-single-sites, we performed quantitative least-square EXAFS curve-fitting analysis for the Pt-SACs. Several typical structures of LDH based SACs are fitted and modeled (Supplementary Fig. 8). Among them, the Pt-site chelated by three surface O-atoms on the LDH layer and one axial ligand opposite of the Fe-atom is considered to be the most possible structure (Fig. 1a and Supplementary Fig. 8a). The fiducial distances between Pt and coordinated atoms were calculated using standard crystal structures of Pt foil, K\(_2\)PtCl\(_4\), and PtO\(_2\) (Supplementary Fig. 9-11). The best-fitted results of Cl-Pt/LDH (Supplementary Table 2) suggest that the main peak at 1.60 Å in the FT-EXAFS spectra at the Pt L\(_3\)-edge can be attributed to the Pt-O first coordination sphere, whereas the minor peak at 2.06 Å can be attributed to the Pt-Cl first coordination sphere (Fig. 2e and Supplementary Fig. 12). Based on the EXAFS fitting parameters for CI-Pt/LDH at the Pt L\(_3\)-edge, O-atoms within the first coordination sphere is located at 2.02 Å with a coordination number of 3.02, suggesting a tetrahedron geometry for the Pt-sites. Besides, the Cl-atom at 2.29 Å with an estimated coordination number of 0.93 is proposed to be a vertical ligand on Pt. All things considered, we propose the most possible structure of the Cl-Pt/LDH as shown in the inset of Fig. 2e. Similar analysis on HO-Pt/LDH demonstrates that it only has O atoms in the first coordination sphere with a total coordination number of 3.60, affirming that the Cl ligand is replaced by the hydroxide group (Fig. 2f) with no other changes occurred to the Pt-sites.

**Electrocatalytic alkaline HER on Pt-SACs**

The electrocatalytic HER on Cl-Pt/LDH is examined in H\(_2\)-saturated KOH (1.0 M). For comparison, the HER activities of Ni foam, NiFe-LDH, 20% Pt/C deposited on Ni foam (Pt/C\(_{NF}\)) and HO-Pt/LDH are also measured under the same conditions. As shown in Fig. 3a, Cl-Pt/LDH exhibits the superior HER activity and ~100% Faradic efficiency to H\(_2\) among all the Pt-SACs tested here (Supplementary Fig. 13 and Table 3), with modest overpotentials of 25.2 mV, 51.9 mV, and 72.3 mV to achieve the current densities of 10 mA cm\(^{-2}\), 100 mA cm\(^{-2}\), and 200 mA cm\(^{-2}\), respectively, overperforming both Pt/C\(_{NF}\) (27.4 mV, 164.9 mV, and 252.0 mV) and HO-Pt/LDH (41.5 mV, 142.5 mV, and 189.5 mV). The negligible HER activities of pristine Ni foam and the SCN\(^-\) poisoning experiment (Supplementary Fig. 14) both indicate that the high HER activity of Cl-Pt/LDH is originated from the Pt-sites. Further increase in the Pt loading leads to the formation of Pt nanoparticles (Ptnp/LDH) and decrease in activity (Supplementary Fig. 15). The mass activity of Cl-Pt/LDH normalized to the Pt loading at overpotential of 100 mV is estimated as 30.6 A mgPt\(^{-1}\) (Fig. 3b), significantly larger than those of HO-Pt/LDH (6.6 A mgPt\(^{-1}\)), Pt/C\(_{NF}\) (0.2 A mgPt\(^{-1}\)), and the state-of-the-art Pt-SACs reported elsewhere (Pt@DG\(_{37}\), 6.78 A mgPt\(^{-1}\), Ptnp/NiO/Ni\(_{34}\), 20.6 A mgPt\(^{-1}\), and N, Pt-MoS\(_2\), 20.2 A mgPt\(^{-1}\)). Moreover, the turnover frequencies (TOFs) per Pt-site on Cl-Pt/LDH (30.3 H\(_2\) s\(^{-1}\)) at overpotential of 100 mV are 5.9 and 126 times greater than those of HO-Pt/LDH (5.1 H\(_2\) s\(^{-1}\)) and the commercial Pt/C\(_{NF}\) (0.2 H\(_2\) s\(^{-1}\)), respectively (Fig. 3c). Steady-state cyclic voltammetry (CV) in full regions of water splitting is performed to demonstrate the superior performance of Cl-Pt/LDH (Supplementary Figs. 16–17). We then normalized the HER activities by the corresponding ECSAs estimated by measuring...
double-layer capacitance ($C_{dl}$) at non-faradic regions, it turns out that Cl-Pt/LDH remains as the most active catalyst (Supplementary Fig. 18).

Kinetics and intrinsic activities of the Pt-SACs for alkaline HER

*Operando* Raman spectroscopy was performed to probe the surface species and their changes in chemical bonding during HER. As shown in Fig. 3d, only Pt-OH peaks at 1062 cm$^{-1}$ appeared for HER on Pt/CNf 51,52. We therefore propose that the desorption of *OH is slow under the catalytic conditions, which agrees with previous observations suggesting that *OH is not a spectator in alkaline HER 9,53,54. In contrast, such obvious Pt-OH peaks were not observed on Cl-Pt/LDH (Fig. 3e) under the same conditions. Instead, only subtle peaks at ~1630 cm$^{-1}$ were found, which can be attributed to the H–O–H bending mode of the adsorbed water, suggesting the Volmer step and the consequent *OH desorption steps are accelerated, resulting in enhanced HER kinetics 55–57. The subtle peak for adsorbed water exists in the HO-Pt/LDH as well, in line with the enhanced activity compared with that of Pt/C. Note, while minor Pt-OH peaks were also found in HER on HO-Pt/LDH (Fig. 3f), its intensity did not vary along with the changes in overpotential, suggesting the –OH is the axial ligand instead of coming from the water reduction. Overall, we conclude that the improved HER activity on the Pt-SACs is likely originated from the accelerated Volmer step. However, we note that due to the limitations of the operando spectroscopy, we do not exclude the effect of mass transportation during the measurements.

Tafel analysis was carried out to investigate the reaction kinetics of HER. As shown in Supplementary Fig. 19, Cl-Pt/LDH exhibits a low apparent Tafel slope of 24.33 mV dec$^{-1}$, corresponding to a Tafel step limited HER kinetics. This is counterintuitive since Volmer step is usually determined as the rate-determine-step (RDS) for alkaline HER 58,59. We thus believe that the HER on Cl-Pt-LDH is largely limited by the mass transportation of H$_2$ leaving the electrode surface in the above measurements, resulting uncertainties for investigating its intrinsic activities 60. Note, the Pt-SACs may be affected by the H$_2$ mass diffusion to a different extent due to their different gas affinities (Supplementary Fig. 20). To evaluate the intrinsic HER activities of the above catalysts, powder-based catalysts (X-Pt/LDHp) were prepared and tested on a rotating disk electrode (RDE, Supplementary Fig. 21) to eliminate the influence of the H$_2$ mass transportation, at least to the time for the Cl-Pt/LDH and commercial Pt/C at a constant cathodic current density of 50 mA cm$^{-2}$. (inset is chronoamperometry stability tests of Cl-Pt/LDH under the condition with or without the light irradiation.) The Pt loading amount of Cl-Pt/LDH, HO-Pt/LDH, Pt/CNF, Cl-Pt/LDHp, HO-Pt/LDHp, and Pt/C is 1.01 × 10$^{-2}$, 1.01 × 10$^{-2}$, 0.4, 2.88 × 10$^{-4}$, 2.88 × 10$^{-4}$ and 8.00 × 10$^{-3}$ mgPt cm$^{-2}$, respectively.
Moreover, extended stability tests were conducted for both Cl-Pt/LDH and Cl-Pt/HOP, showing a significant lower adsorption resistance ($R_2 = 28.45$ ohm) compared to those of HO-Pt/LDH ($R_2 = 99.8$ mV dec$^{-1}$) and Pt/C ($120.0$ mV dec$^{-1}$), indicating that the sluggish Volmer step is significantly boosted on Cl-Pt/LDH, and the RDS is likely the mixture of Volmer and Heyrovsky steps (Fig. 3g). Note that, the difference in the symmetry of the log/$i$ vs. $E$ curves between Cl-Pt/LDH and HO-Pt/LDH suggest that “OH is an active participant in the hydrogen reactions via Volmer-Heyrovsky mechanism.

Electrochemical impedance spectroscopy (EIS) was also employed to investigate the HER kinetics. As shown in Fig. 3h, the first semicircle at medium frequency is believed to be associated to the kinetics of Volmer step (Supplementary Fig. 23). Apparently, Cl-Pt/LDH shows a significantly lower adsorption resistance ($R_2 = 21.15$ ohm) than HO-Pt/LDH ($R_2 = 28.45$ ohm), indicating that the water dissociation step is more favored on Pt-sites with Cl as axial ligand. In addition, from EIS, characteristic frequencies were conducted to reveal the importance of the axial Cl-ligand to the HER activity. As shown in Supplementary Fig. 24, along with the increase of irradiation period, the Cl: Pt mole-ratio decreased from 1.08 to 0.05 accompanied by the decline of HER activity, suggesting that –Cl is replaced by hydroxide, consistent with the above XAFS results. The ligand exchange occurred quickly under the catalytic conditions. As shown in the inset of Fig. 3i, the HER activity of Cl-Pt/LDH dropped and reached to a plateau within the first half-hour under illumination, suggesting the completion of the ligand exchange within this short period. In contrast, Cl-Pt/LDH retained its activity when light was blocked from the catalytic system, indicating that the –Cl axial ligand on Pt is relatively stable under the HER conditions. Physical characterizations also suggest that its morphological and electronic structures were retained (Supplementary Figs. 25–26).

Moreover, extended stability tests were conducted for both Cl-Pt/LDH and Pt/C at current densities of $50$ mA cm$^{-2}$ (Fig. 3i) and $500$ mA cm$^{-2}$ (Supplementary Fig. 27) under the same conditions. Over the 100-hour testing period, Cl-Pt/LDH exhibited improved durability compared to the commercial Pt/C catalyst, demonstrating the robust chemical structure of the Pt-single-sites under alkaline HER conditions.

Exploring the origin of the axial-ligand effect

We extended the axial-ligand identity using the above irradiation-impregnation procedure to prepare R-F-Pt/LDH, R-Br-Pt/LDH, and R-Cl-Pt/LDH. HAADF-STEM images and the corresponding elemental mappings (Supplementary Figs. 28–31) confirmed the desired axial-ligand exchange on Pt-sites. XPS spectra (Supplementary Fig. 32) indicate that the valence state changes only occur to the Pt-atoms instead of the NiFe-LDH supports. All in all, we believe the homogeneity of the chemical environment around the Pt-sites of these catalysts remain after the ligand exchange. Note, at first glance (Fig. 4a and Supplementary Figs. 33–34), the alkaline HER activities of the Pt-SACs with different axial-ligands scale with the first-electron-affinity of the halogen-atoms. In the following we tried to explore the physical insights of this axial-ligand effect.

First, EIS measurements were carried out to investigate the detailed HER kinetics on these catalysts. Based on the equivalent circuit (Supplementary Fig. 23), $R_2$ and $R_1$ are associated to the Volmer step and Heyrovsky step, respectively. On Pt/C, the phase angle of the Heyrovsky step decreased rapidly while the phase angle of the Volmer step remain largely unchanged when increasing the overpotential for HER (Supplementary Fig. 35). In addition, $R_2$ remains larger than $R_1$ at all overpotentials, indicating the RDS for HER on Pt/C is always the Volmer step under the testing condition (Supplementary Fig. 36). On a contrary, phase angles of both the Volmer and Heyrovsky steps on Pt-SACs decrease along with the increase of overpotential, and $R_2$ is mostly smaller than $R_1$, suggesting that the Volmer step has been accelerated on the Pt-SACs consisting with the previous results (Supplementary Fig. 37 and Supplementary Tables 4–9).

First principal simulations were also performed to rationalize the axial-ligand effect on Pt-SACs for alkaline HER. The computational models for X-Pt/LDH (X = Cl, Br, I, and OH) were built based on the EXAFS fitting results. As shown in Fig. 4b, c and Supplementary Figs. 38, 39, significant charge redistributions were observed at the Pt-X bonding regions, which is likely the origin of the enhanced HER activity. Stepwise reaction barriers for alkaline HER on Pt-SACs were modeled, including the Volmer step of water dissociation, “OH desorption, and the subsequent conversion of $H^+$ to $H_2$. For the Volmer step (Fig. 4d), all the halogen-coordinated Pt-LDHs show stronger H$_2$O adsorption ability and larger formation of enthalpy for water dissociation than those on Pt (111), leading to accelerated Volmer step. Among them, Cl-Pt/LDH exhibits the smallest energy barrier ($0.073$ ev) for the Volmer step. On another hand, the Cl-Pt-sites also exhibit the most optimized H binding energy among the Pt-SACs, leading to the most favored kinetics for the conversion of $H^+$ to $H_2$ (Fig. 4e). Note, while Pt (111) shows slightly more optimized H binding energy compared to that of Cl-Pt/LDH, its water dissociation step is expected to be slower (Fig. 4e), leading to a slower overall HER kinetics. The combined results indicate that the H binding energy is not the sole descriptor for alkaline HER, OH binding energy also plays significant role as it is likely not a spectator for the reaction. The projected density of states (PDOS) of the d-orbitals of the Pt-SACs were calculated as well (Supplementary Fig. 40). Subsequently, the average energy levels of the narrow Pt 5d orbitals occupied by isolated electrons ($E_d^{iso}$) were calculated for Cl-Pt, F-Pt, HO-Pt, Br-Pt, Pt and H* as $0.901$, $0.919$, $0.977$, $1.005$, and $1.052$ ev, respectively (Fig. 4f). This is in good agreement with the above XANES results, where the highest Pt valence state was observed for Pt in Cl-Pt/LDH owing to the largest first-electron-affinity of Cl ligand. According to the d-band theory, the adsorption properties of the surface intermediates are directly associated to the electronic structure of catalysts. Increased first-electron-affinity of the ligands on Pt-single-atoms is expected to increase the $E_d^{iso}$, and further weaken the hydrogen adsorption. Cl-Pt with the highest $E_d^{iso}$ should yield the weakest interaction with H* intermediate, consequently H* is more readily to desorb and form $H_2$ (Fig. 4g). Overall, the computational results agree with our experimental observations, demonstrating that modifying the electronic structure of the Pt-single-sites with axial ligand is an effective strategy in tuning the HER activity.

We further conducted CO stripping experiments to evaluate the “OH binding strength on Pt-SACs, since one could expect that strong Pt-OH bond strength will facilitate the removal of $CO$ owing to the adsorbate-adsorbate interactions. As shown in Supplementary Figs. 41–42, a volcano-type relationship between alkaline HER activity and Pt-OH strength was observed, indicating both “OH adsorption and desorption are important for alkaline HER. Taken together, we show that the alkaline HER activity of X-Pt/SACs increase monotonically with the ligand-first-electron-affinity, as both $H$ and “OH are the dominant descriptors during alkaline HER (Fig. 4h).

HER performance in an industrial relevant reactor

To evaluate the applicability of Cl-Pt/LDH as a cathodic catalyst under practical relevant operating conditions, we constructed an anion exchange membrane-based membrane electrode assemblies (MEA) electrolyser by using the pristine NiFe-LDH as the anode. MEA electrolyzers based on commercial Pt/C and Ir/C were built and tested for comparison. The current-voltage profiles were obtained under $60$ °C (Fig. 5a). Without further optimizations (reactor design, membrane choice and operating conditions, etc.), the electrolyser based on Cl-Pt/
LDH / NiFe-LDH exhibits a much lower cell voltage (1.87 V) than those of the Cl-Pt/LDH / Ir/C (1.99 V) and the Pt/C / Ir/C (2.66 V) based electrolyser at current density of 1.0 A cm\(^{-2}\). Under this condition, their corresponding energy conversion efficiencies are 80%, 75% and 56%, respectively (Fig. 5b). The electrolyser were also subjected to water electrolysis for a 20 h-long stability tests at 1.0 A cm\(^{-2}\). As shown in Fig. 5c, the Cl-Pt/LDH / Ir/C electrolyser exhibits good stability with negligible overpotential loss (Supplementary Fig. 43), demonstrating promising potentials for future implementation for green hydrogen production. As shown in Fig. 5d–f, it is obvious that the activation overpotentials of Cl-Pt/LDH / NiFe-LDH or Cl-Pt/LDH / Ir/C are much lower that of Pt/C / Ir/C, leading to the enhanced energy efficiency originated from the superior HER activity of Cl-Pt/LDH.

In summary, we present Pt-SACs anchored on NiFe-LDH nanoarrays with different axial ligands (−F, −Cl, −Br, −I, and −OH) as highly active alkaline HER electrocatalysts prepared by a facile irradiation-impregnation procedure. Cl-Pt/LDH exhibits the highest HER activity among the Pt-SACs as well as the commercial Pt/C. The enhanced intrinsic activity of Cl-Pt/LDH towards alkaline HER is attributed to the largest first electron affinity of the axial ligand which poses strong electronic effect on the Pt-single-sites. DFT calculations suggest that the introduction of axial ligand on Pt-single-sites can tune the average energy levels of the isolated electrons occupied Pt-d-orbitals, and further the H* and *OH adsorption free energies. Finally, Cl-Pt/LDH was also evaluated in a MEA-based alkaline water electrolyser at industrially relevant reaction rates, energy efficiency as high as 80% was obtained, demonstrating its promising application for hydrogen production. Overall, our work highlights the benefits of tailoring the chemical environments around the catalytic center, both the synthetic strategy and the constructive axial-ligand effect reported here can guide future SACs design with improved performance for large-scale green hydrogen production.

**Methods**

**Chemicals and materials**

Nickel (II) nitrate hexahydrate (Ni(NO\(_3\))\(_2\)-6H\(_2\)O), iron (III) nitrate nonahydrate (Fe(NO\(_3\))\(_3\)-9H\(_2\)O), Hexadecyltrimethylammonium bromide (CTAB), chloroplatinic acid hydrate (H\(_2\)PtCl\(_6\)-xH\(_2\)O), potassium thiocyanate (KSCN), sodium fluoride (NaF), sodium chloride (NaCl), sodium bromide (NaBr), sodium iodide (NaI), hydrochloric acid (HCl), 5,5-Dimethyl-1-pyrroline N-oxide (DMPO), Nafion 117 containing solution (5% in a mixture of lower aliphatic alcohols and water) were
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Fig. 5 | Alkaline HER in the MEA electrolyser. a LSV curves of the MEA reactors using Cl-Pt/LDH / NiFe-LDH, Cl-Pt/LDH / Ir/C, and commercial Pt/C / Ir/C as the cathodic and anodic electrodes, respectively. b Cell voltage at current density of 1 A cm$^{-2}$ in Fig. 5a, and the corresponding energy efficiency. c Stability tests of the MEA water electrolyser at the current density of 1 A cm$^{-2}$ at 60 °C. Breakout of the ohmic overpotential and activation overpotential for (d) Cl-Pt/LDH / NiFe-LDH, (e) Cl-Pt/LDH / Ir/C and (f) commercial Pt/C / Ir/C. The Pt loading of Cl-Pt/LDH, and Pt/C is 1.01 × 10$^{-2}$ and 0.8 mgPt cm$^{-2}$, respectively.

The nickel-iron layered double hydroxide (LDH) nanosheet arrays in-situ growing on nickel foam were synthesized through a facile one-pot solvothermal method. Typically, 0.9 mmol Ni(NO$_3$)$_2$·6H$_2$O and 0.6 mmol Fe(NO$_3$)$_3$·9H$_2$O and 1.4 mmol CTAB were dissolved in a mixture of 36 mL MeOH and 6 mL water and stirred to form a clear solution. Nickel foam (about 4 × 3 cm) was carefully cleaned with the concentrated HCl solution (37 wt.%) in an ultrasound bath for 5 min to remove the surface NiO layer, and then water and MeOH were used for 5 min to ensure the surface of Ni foam was cleaned. Both the Ni foam and the solution were transferred to a 50 mL Teflon-lined stainless-steel autoclave. The as-prepared Ni foam was vertically immersed into the solution. The in-situ growth was carried out in an oven for 24 h at 180 °C. After the naturally cooling to the room temperature, a thin brown film on the Ni foam was formed, donated as NiFe-LDH. Subsequently, the NiFe-LDH was rinsed with water and MeOH for 3 min with the assistance of ultrasonication, and then dried at 80 °C overnight. The average loading amount of LDH on Ni foam is 1.4 mg cm$^{-2}$. Besides, the powder-based catalysts were also collected by scraping the deposited materials on Ni foam, donated as NiFe-LDHp.

**Synthesis of Cl-Pt/LDH**

The Cl-Pt/LDH was synthesized through electrochemical deposition in a three-electrode system, in which NiFe-LDH was used as the working electrode, graphite rod acted as the counter electrode, and the mercury/mercury oxide (Hg/HgO) electrode was employed as the reference electrode. The NiFe-LDH on Ni foam was cut into small size to afford the geometric area of the working electrode to be 1 cm$^2$. The NiFe-LDH was firstly activated by cyclic voltammetry (CV) with a scan rate of 10 mV s$^{-1}$ between 0.05 and −0.50 V versus reversible hydrogen electrode (RHE) for 30 cycles in 1 M KOH. Subsequently, the system was transferred into 1 M KOH solution containing 0.15 mmol L$^{-1}$ H$_2$PtCl$_6$ for further electrodeposition of Pt single atoms. The Cl-Pt/LDH was fabricated by CV with a scan rate of 5 mV s$^{-1}$ between 0.05 and −0.50 V versus RHE for 40 cycles. The Pt/C on Ni foam was fabricated by drop casting with a loading of 2 mg cm$^{-2}$. The powder-based Cl-Pt/LDH$_p$ was fabricated based on NiFe-LDH$_p$ by CV with a scan rate of 50 mV s$^{-1}$ between 0.05 and −0.70 V versus RHE for 20 cycles, this adjustment was made due to the different electrode surface area. When testing powder-based NiFe-LDH$_{H_p}$ and corresponding X-Pt/LDH$_{P_h}$, glassy carbon electrode with geometric area of 0.196 cm$^2$; and different catalyst loading (0.1 mg cm$^{-2}$ or 0.004 mg cm$^{-2}$) was used. All electrochemical curves were IR-corrected according to the equation: $E_{\text{corr}} = E - I \times R_s$.

**Synthesis of HO-Pt/LDH**

The Cl ligand can be removed and replaced by the hydroxide group under the irradiation of visible light in water. PLS-SXE300 from Beijing perfectlight with a spectral region from 320 nm to 780 nm was used as the light source with an output power density of 3.75 mW cm$^{-2}$. After 30 min irradiation, the HO-Pt/LDH was fabricated after the washing and drying process. The HO-Pt/LDH$_{P_h}$ was synthesized via a similar procedure using Cl-Pt/LDH$_{P_h}$.

**Synthesis of R-X-Pt/LDH (X = F, Cl, Br, or I)**

The axial-ligand on Pt-single-atom can be easily reversed from hydroxide group to halogen by simple impregnation strategy. In a typical process, the R-F-Pt/LDH was fabricated by immersed HO-Pt/LDH in 2 M NaF solution at 40 °C for 4 h under magnetic stirring. Similarly, R-Cl-Pt/
LDH, R-Br-Pt/LDH and R-I-Pt/LDH can be synthesized by changing the solution into NaCl, NaBr, and NaI, respectively. All the reversed catalysts were activated by two CV cycles at HER region in 1 M KOH in absence of light irradiation before elemental mapping and XPS measurements to remove the influence of possible anion intercalation in LDH supports. The R-X-Pt/LDH was synthesized via the same procedure using HO-Pt/LDHp.

Synthesis of Pt\textsubscript{np}/LDH
The fabrication process of Pt\textsubscript{np}/LDH however with increased CV cycles (100 cycles).

Characterizations
Field-emission scanning electron microscopy (FESEM) images were taken on a Zeiss SUPRA 55. The transmission electron microscopy (TEM) images were carried out by a Hitachi HT7700 transmission electron microscopy. The crystal structures of the samples were examined by X-ray diffraction (XRD, Bruker D8) with Cu Kα radiation (λ = 0.154178 nm). High-resolution TEM (HR-TEM) and the corresponding energy-dispersive X-ray (EDX) mapping were taken on a JEOL JEM-2100F microscope. Aberration-corrected high-angle annular dark field scanning transmission electron microscopy (AC-HAADF-STEM) was performed on a JEM-ARM 200 F TEM/STEM with a spherical aberration corrector. All samples for TEM measurements were prepared by ultrasonic dispersion in ethanol and were drop-casting onto copper grids covered with a carbon film. Raman spectra were recorded on a Lab Ram ARAMIS Raman spectrometer (HORIBA) at an excitation wavelength of 633 nm. UV-vis absorption spectra were collected on a Shimadzu 2600 UV-visible spectrophotometer. Detailed chemical compositions were analyzed by X-ray photoelectron spectroscopy (XPS) on an ESCALAB 250Xi photoelectron spectrometer using monochromate Al Kα 150 W X-ray beam (1486.6 eV). All binding energies were referenced to the C 1 s peak (284.8 eV). The concentration of Pt was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) from iCAP6300. The concentration of Cl was titrated by the ZDCL-2 chloride ion titrator (INESA). The electron paramagnetic resonance (EPR) spectra were collected on an Elexys 580 spectrometer (ν = 9.86 GHz) with a center field at 3320 G and a sweep width of 140 G at room temperature. The X-ray absorption spectra (XAS) at the Pt L\textsubscript{3}-edge of the samples were recorded at room temperature in transmission mode using ion chambers (referenced samples) and fluorescence excitation mode using a Lytle detector (controlled samples) at beamline (BL) 14W1 of Shanghai Synchrotron Radiation Facility (SSRF).

EXAFS Measurement
The X-ray absorption spectra (XAS) at the Pt L\textsubscript{3}-edge of the samples were recorded at room temperature in transmission mode using ion chambers (referenced samples) and fluorescence excitation mode using Lytle detector and Solid-State-Detector (controlled samples) at beamline (BL) 14W1 of Shanghai Synchrotron Radiation Facility (SSRF). The station was operated with a Si (111) double crystal monochromator. During the measurement, the synchrotron was operated at 3.5 GeV and the current was between 150–210 mA. The data for each sample were calibrated with standard Pt metal foil. The XAS raw data were background subtracted, normalized, and Fourier transformed by standard procedures within the ATHENA program (version 0.9.26)\textsuperscript{2}. The oxidation states and formal d-band hole counts of the samples were recorded at room temperature in transmission mode using ion chambers and the total path length R\textsubscript{c} of the photoelectron. The dependence of the EXAFS oscillatory structure on path length and energy is reflected by the sin(2kR\textsubscript{c}+ϕ\textsubscript{c}) term, where ϕ\textsubscript{c} is the effective scattering phase shift for path c. F\textsubscript{c}(k, R\textsubscript{c}) denotes the effective scattering amplitude for path c. The amplitude decay due to inelastic scattering is captured by the exponential term exp(−2R\textsubscript{c}/λ(k)), where λ(k) is the photoelectron mean free path. The additional broadening effect due to thermal and structural disorder in the absorber-scatterer(s) path lengths is accounted for by the Debye-Waller term exp(−2σ\textsubscript{D}Ω). S\textsubscript{0} is a many-body amplitude-reduction factor due to excitation in response to the creation of the core hole. In this work, although the scattering amplitudes and phase shifts for all paths, as well as the photoelectron mean free path, were theoretically calculated by ab-initio code FEFF8.0,\textsuperscript{2} the variable parameters that are determined by using the EXAFS equation to fit the experimental data are N\textsubscript{c}, R\textsubscript{c}, and σ\textsubscript{D}. S\textsubscript{0} parameter was determined in the fit of Pt foil standards and used as fixed value in the rest of the EXAFS models. All fits were performed in the A space with k-weight of 2. The EXAFS R-factor (R\textsubscript{F}), which measures the percentage misfit of the theory to the data, was used to evaluate the goodness of the fit.\textsuperscript{15} The k\textsuperscript{2} weighting, k-range of 3-12.5 Å\textsuperscript{-1} and R range of 1-3 Å were used for the fitting. The model of bulk Pt, K\textsubscript{2}PtCl\textsubscript{4}, PtO\textsubscript{2} and DFT optimized structures were used to calculate the simulated scattering paths. For Wavelet Transform (WT) analysis, the χ(k) exported from Athena was imported into the Hama Fortran code.\textsuperscript{27} The parameters were listed as follow: R range, 1-4 Å, k range, 0-12 Å\textsuperscript{-1}; k weight, 2; and Morlet function with k = 10, σ = 1 was used as the mother wavelet to provide the overall distribution.\textsuperscript{28} Additional EXAFS simulations based on the best-fitted models were performed with FEFF8.0, and the thermal disorder was considered by using the correlated Debye model with Debye temperature of 475 K. CO chemisorption measurement via Fourier-transformed infrared (FT-IR) spectroscopy
The FT-IR spectra of CO chemisorption measurements were performed on the Nicolet 380 model (Thermo Electron Corporation) equipped with an MCT-A detector cooled by liquid nitrogen. The sample was first pre-reduced in the cell under 10% H\textsubscript{2}/Ar flow (20 mL min\textsuperscript{-1}) at 100 °C for 1 h to remove any contaminant. After cooling the sample to room temperature under Ar flow (20 mL min\textsuperscript{-1}), a background spectrum was collected. Then the sample was exposed to 10% CO/Ar (20 mL min\textsuperscript{-1}) for 1 h until saturation. Subsequently, pure Ar (99.999%) was introduced at a flow rate of 20 mL min\textsuperscript{-1} for another 1 h to remove the gas-phase CO and then the FT-IR was collected with 64 scans at a resolution of 2 cm\textsuperscript{-1}.

In-situ Raman measurement
A Lab Ram ARAMIS Raman spectrometer (HORIBA) with a 633 nm stream-line laser excitation and the Cell with a quartz window (Shanghai chuxi industrial Co., LTD) were used for the in-situ Raman
measurements. The obtained catalyst, Ag/AgCl and Pt wire were employed as the working, reference, and counter electrode, respectively. The laser beams were focused on the sample through the quartz window to collect Raman spectrum. The chronoamperometry method was employed to applied different voltages to the electrode with 25 mV intervals in the range of 0 to −0.1 V vs. RHE.

Surface characterizations to gas bubbles
The gas-bubble contact angle with the volume of ~0.5 μL was measured by the captive-bubble method and recorded using a microscope (SZX16, Olympus) mounted on a high-speed CCD camera (i-SPEED 3, AOS Technologies). The illumination was achieved by a fiber-optic illuminator system (CEL-TCX 250).

CO stripping measurement
The CO stripping measurement was conducted in a three-electrode system in a H-type electrochemical cell. The glassy carbon rod, silver/silver chloride electrode, and the obtained catalyst is used as counter electrode, reference electrode, and working electrode, respectively. Pure CO gas was first adsorbed on the working electrode at a fixed potential of 0.1 V vs. RHE in a CO-saturated 1 M KOH electrolyte for 10 min. All the CV of CO stripping were collected after purging with Ar gas at a scan rate of 20 mV s⁻¹.

Electrochemical Measurement for HER
All the electrochemical measurements were finished by a biologic potentiotstat VMP3 electrochemical workstation with a three-electrode configuration at room temperature, in which the fabricated samples were performed as the working electrode, graphite rod acted as a counter electrode, and the mercury/mercury oxide (Hg/HgO) electrode acted as a reference electrode. For the powder-based samples, the glass carbon electrode coupled with a RDE was carried out as the working electrode with the rotating speed at 1600 rotation per minute (rpm). The electrolyte (1 M KOH solution) was purged with pure H₂ for at least 30 min to obtain the H₂ saturated solution before HER test. All potentials were corrected with IR compensation and then converted to RHE. The CV and linear sweep voltammetry (LSV) were performed at a scan rate of 50 mV s⁻¹ and 10 mV s⁻¹, respectively. For powder-based samples, the catalyst ink was prepared as following: 4 mg catalyst was ultrasonically dispersed in 1000 μL solution containing 480 μL water, 480 μL EtOH and 40 μL NaFion 117 ionomer solution. Electrochemical impedance spectroscopy (EIS) curves were obtained by a frequency range from 100 kHz to 1 Hz under different potential. The electrochemical active surface area (ECSA) was estimated based on ECSA = C_dil / C_r, where C_dil corresponds to the double-layer charging current versus the scan rate and C_r corresponds to a specific capacitance. The capacitance fit (C_dil) for NiFe-LDH, Pt/C, Cl-Pt/LDH and HO-Pt/LDH are 2.94, 5.4L, 9.62 and 6.88 mF cm⁻², respectively. Compared with the specific capacitance (40 μF cm⁻²) of a smooth planar surface LDH with 1.0 cm² surface area, the ECSAs can be estimated as 73.5, 1285, 240.5 and 90.4 mF cm⁻², the ECSA of Pt/SACs supercell with ~100 atoms are a = 12.35 Å, b = 12.72 Å, and c = 21.22 Å (Supplementary Fig. 38), which should be sufficient. Thus, the Brillouin zone integration was performed using 2 × 2 × 1 Monkhorst-Pack k-point sampling for all the Pt-SACs structures.

The mechanism for alkaline hydrogen evolution reaction (HER) follows Volmer-Heyrovsky or Volmer-Tafel pathways (Volmer: H₂O + M + e⁻ → M+H* + OH⁻; Heyrovsky: H₂O + e⁻ → M+H* + OH⁻ + M; Tafel: 2M+H* → H₂ + 2 M). To demonstrate mechanism for HER, we introduced the adsorption energies (E_ads), defined as E_ads = E_surface−adsorbate − E_surface−F_adsorbate, where the E_surface was the energy of different Pt SAC surface, E_adsorbate was the energy of the adsorbate, and the E_surface−F_adsorbate was the total energy of the surface with the adsorbate. According to the finite displacement method, the Gibbs free energy correction is necessary to obtain the accurate value for each system under a certain temperature and pressure by calculating the molecular vibration frequency. Among them, the displacement on each degree of freedom is 2 times, and the convergence accuracy of the electronic step is 10⁻⁶ eV. All vibration frequencies lower than 50 cm⁻¹ were set as 50 cm⁻¹ due to the unreasonable contribution to the entropy from low
The adsorption Gibbs free energy under standard atmospheric pressure ($G_{ads}$) is defined as $G_{ads} = E_{ads} + \Delta G(T)$, where $\Delta G(T)$ was the sum of Gibbs free energies corrections at the temperature of $T$. Hence, we can conclude that $\Delta G(T) = \Delta ZPE + \Delta H(T) - T\Delta S(T)$, where $\Delta ZPE$, $\Delta H(T)$, and $\Delta S(T)$ represented by the zero-vibration energy change, the enthalpy change, and the entropy change before and after the adsorption. All the relevant thermodynamic quantities were calculated by vaspkit based on the above molecular vibration frequencies\textsuperscript{100}. It was worth noticing that the correction for the solid surface was not included in the correction of free energy due to the correction value can be cancel out before and after the adsorption. Besides, for the adsorption of single atom $A$, all energy before adsorption had been replaced by $1/n$ of elemental $A$ energy.

The electronic structures of the catalyst were calculated by the density of state (DOS), where the calculation parameters were same with the geometric optimization mentioned above\textsuperscript{76}. The average energy level $\mu$ for a specific orbital of the catalytic active site can be calculated by following:

$$\mu = \frac{\int \varepsilon N(\varepsilon) d\varepsilon}{\int N(\varepsilon) d\varepsilon}$$

where $\varepsilon$ was the energy level and $N(\varepsilon)$ is the number of orbitals at the energy level $\varepsilon$. The parameter $a$ and $b$ were defined as the top or bottom limitation of the energy level for a certain orbital. The d-band center was identical with $\mu$ when $a$ is $\rightarrow b$ is zero and the orbital was d. Surface valence band photoemission spectra were corrected by subtracting the Shirley background\textsuperscript{102}. The dynamic simulation was carried out to obtain the reaction energy barrier of the key primitive steps. Based on the structural optimization above, the related models were annealed to 298 K by the velocity adjustment method with a step value of 1 fs\textsuperscript{111}. For every 25 steps, there was one heating rate adjustment, and the total adjustment number was 60. The restrictive molecular dynamic simulation was performed by using slow growth adjustment, and the total adjustment number was 60. The restrictive molecular dynamic simulation was performed by using slow growth adjustment. During the water dissociation process on Pt sites, the bond length of the broken O-H bond in H$_2$O was taken as the limited freedom degree model with the increment of 0.0005 Å fs$^{-1}$.

MEA measurement

The MEA setup with geometric area of 1 cm$^2$ was purchased from gaossunion. The cathode and the anode were sandwiched with the bottom limitation of the energy level for a certain orbital. The d-band center was identical with $\mu$ when $a$ is $\rightarrow b$ is zero and the orbital was d. Surface valence band photoemission spectra were corrected by subtracting the Shirley background\textsuperscript{102}. The dynamic simulation was carried out to obtain the reaction energy barrier of the key primitive steps. Based on the structural optimization above, the related models were annealed to 298 K by the velocity adjustment method with a step value of 1 fs\textsuperscript{111}. For every 25 steps, there was one heating rate adjustment, and the total adjustment number was 60. The restrictive molecular dynamic simulation was performed by using slow growth adjustment method with the maintain of the step length\textsuperscript{114}. During the water dissociation process on Pt sites, the bond length of the broken O-H bond in H$_2$O was taken as the limited freedom degree model with the increment of 0.0005 Å fs$^{-1}$.

Data availability

All the data generated or analyzed during this study have been included in the manuscript and Supplementary Information. All the data are also available upon reasonable request from the corresponding authors.
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Author contributions
L.W. conceived the project; L.W. and J.F.L. supervised the project; T.Y.Z. and J.J. designed the experiments, carried out most of the experiments and analyzed the results. Y.P.L. and X.H. performed the theoretical simulation. J.M.C. and J.Y.C. helped the MEA measurements. Y.Y.F. assisted the synthesis and characterization. Y.W. conducted the XAFS measurements. T.Y.Z., J.F.L., and L.W. prepared the manuscript. All the authors discussed the results and assisted during the manuscript preparation.

Competing interests
The authors declare no competing interests.

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