Ru Single Atoms and Sulfur Anions Dual-Doped NiFe Layered Double Hydroxides for High-Current-Density Alkaline Oxygen Evolution Reaction

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New anodic electrocatalysts with high performance and cost-effectiveness at large current densities help advance the emerging anion exchange membrane water electrolyzer (AEMWE) technology. To this end, a ruthenium (Ru) single atoms and sulfur (S) anions dual-doped NiFe layered double hydroxides (Ru-S-NiFe LDH) catalyst is reported with remarkably low alkaline oxygen evolution reaction (OER) overpotentials, high mass activities and prolonged stabilities at high current densities. Inspiringly, the AEMWE performance on Ru-S-NiFe LDH is also superior to the NiFe LDH. In-depth mechanism investigations reveal that Ru single atoms not only act as the highly active sites, but also facilitate the conductivity of NiFe LDH. Meanwhile, S anions accelerate the electrochemical reconstruction of NiFe LDH to OER-active NiFeOOH and alleviate the over-oxidation issue on Ru active sites. Benefiting from these, Ru-S-NiFe LDH shows significantly enhanced OER activity and stability. Theoretical calculations further validate the decreased OER free energy difference brought about by the Ru single atoms and S anions dual-doping. This study offers a proof-of-concept that the noble metal single atoms and anions dual-doping is a feasible strategy to construct the promising 3d transition metal-based electrocatalysts toward the practical alkaline water electrolyzer.

1. Introduction

In response to the global call for environmental protection and conservation of non-renewable resources, it is imperative to discover clean and renewable energy resources to replace fossil fuels. Future energy sources are expected to be led by hydrogen (H₂) due to its high energy density, non-carbon emission, and renewability.^[1] With the aim of implementing clean generation of H₂, tremendous efforts are devoted to water electrolysis. The anodic oxygen evolution reaction (OER) and cathodic hydrogen evolution reaction (HER) are the two processes involved in electrochemical water splitting, in which the anode side involves a complicated four-electron transfer process and slow reaction kinetics, limiting the efficiency of H₂ production.^[2–6] Seeking an efficient electrocatalyst is extremely crucial for decreasing the

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OER energy barrier and promoting the overall water electrolysis performance.

At present, the benchmark OER catalysts are focused on the noble iridium (Ir) and ruthenium (Ru) oxides, however, high cost, scarcity, and limited catalytic performance have severely restricted their large-scale commercial applications.^[7] In view of the cheap cost and plentiful reserves, 3d transition metal-based electrocatalysts including oxides and hydroxides have attracted more attentions.^[8–10] Among which, the layered double hydroxides (LDH) with intercalated ions stand out as one of the most promising alternatives for alkaline OER owing to the advantages of lamellar structure and tunable composition. Nevertheless, the LDH usually suffers from poor electrochemical conductivity, poor long-term stability as well its intrinsically low OER activity cannot satisfy the requirement for industrial water electrolyzer in a large degree.^[11-15] To solve these issues, one feasible approach is to incorporate the foreign 4d/5d noble metal single atoms into the 3d transition metal-based LDH carrier to induce a strong orbital hybridization, which is in favor of speeding up the rate of charge transfer rate and supplementing more active sites to improve the OER performances.^[16,17] Notably, the amount of noble metals required for the single-atom strategy is extremely low, thus the additional cost of catalyst preparation is almost negligible.^[18–21] However, although the OER activity on 3dtransition metal-based LDHs can be effectively enhanced via the 4d/5d noble metal single atoms doping, their stability is hardly satisfactory. Typically, these reported noble metal single atoms doped LDHs can only operate stably for less than 50 h, which is mainly caused by the leaching issue on active sites. On the other hand, the doping of anions including sulfur (S), nitrogen (N), and phosphorus (P) is proved to be an available strategy for enhancing the stability of materials via redistributing the charges with coordinated metal sites.^[22-25] In addition, these doped anions also play important roles in facilitating the electrochemically reconstruction of 3*d* transition metal-based LDHs, whereas the activity enhancement is limited due to the intrinsic property of LDHs.^[26-28] Motivated by above findings, the dual-doping of noble metal single atoms and anions into 3d transition metalbased LDH may simultaneously take the catalytic advantages of both, realizing the further boosted OER performance. Since the active and economic NiFe LDH has been proved to be the most ideal OER catalyst among all bimetallic LDH materials composed of 3*d* transition metals. Ru is one of cheapest noble metals and S has the most similar ionic radius and physiochemical properties as O among all anions, simultaneously doping the Ru single atoms and S anions into NiFe LDH may fully stimulate the catalytic potential, resulting in a promising candidate with low cost and high performance for alkaline OER.^[29,30] However, this novel catalyst has rarely been reported due to the complicated preparation process of co-doping and the high susceptibility of forming metal sulfide nanoparticles. Moreover, the introduction of multiple dopants into the basic catalysts poses a greater challenge in accurately distinguishing the real active sites and disclosing the mechanism, which usually requires the assistance of cuttingedge techniques, especially the operando characterization techniques under operation conditions. Furthermore, most recently discovered OER catalysts were only evaluated in the half-cell system, where the oxidative voltage and corrosive electrolyte are milder than those in the industry-oriented anion membrane water electrolyzer (AEMWE). Consequently, anodic catalysts including NiFe LDH and commercial RuO₂ will suffer the severe electrochemical performance degradations in the practical AEMWE. Therefore, the urgent status for advancing the development of alkaline water electrolysis technology is to explore the anodic catalysts with improved activity and prolonged stability at the large current densities.^[31]

In this regard, we successfully develop a one-pot approach to synthesize the NiFe LDH with Ru single atoms and S anions dualdoping (Ru-S-NiFe LDH) via the facile hydrothermal reaction. As expected, at the high current densities of 100 and 250 mA cm⁻², the fabricated Ru-S-NiFe LDH delivers overpotentials of 279 and 321 mV, respectively, outperforming the NiFe LDH and the commercial RuO₂. Additionally, the mass activity of Ru-S-NiFe LDH is 382 times as high as RuO₂, indicating its superior economic efficiency. Significantly, the long-term durability at the large current densities can be extended to more than 100 h without obvious activity loss after simultaneously incorporating the Ru single atoms and S anions into NiFe LDH. Notably, Ru-S-NiFe LDH only delivers a AEMWE potential of 1.92 V to achieve 1.0 A cm⁻², superior to NiFe LDH. Moreover, Ru-S-NiFe LDH also retains an excellent AEMWE stability for 80 h at 1.0 A cm⁻². Advanced characterizations validate that Ru single atoms and Ni atoms are the true active sites that directly participate in OER charge transfer process. In-depth mechanism investigations also indicate that the doped Ru single atoms can also speed up the conductivity of NiFe LDH, while the doped S anions are responsible for accelerating the electrochemical reconstruction of NiFe LDH to OER- active NiFeOOH and alleviating the Ru over-oxidation issue, collectively boosting the activity and stability of Ru-S-NiFe LDH. Density function theory (DFT) calculations further validate the decreased OER free energy difference caused by Ru single atoms and S anions co-doping. This research offers a feasible guideline for designing the promising electrocatalysts with high costeffectiveness, activity, and stability through concurrently doping the noble metal single atoms and anions into the 3*d* transition metal-based support.

2. Results and Discussion

2.1. Structural Characterizations of Ru-S-NiFe LDH

Typically, the Ru-S-NiFe LDH was synthesized by homogeneously mixing the metal precursors (RuCl₃, NiCl₂.6H₂O, and $FeCl_3.6H_2O$ with thiourea and Na_2CO_3 in water, followed by an aging process via the hydrothermal reaction (see Methods for details). As depicted in Figures 1a and S1a,b (Supporting Information), transmission electron microscopy (TEM) indicates that Ru-S-NiFe LDH features a flat-spread nanosheet with a diameter close to 100 nm. Atomic force microscopy (AFM) was subsequently adopted and revealed that the thickness of Ru-S-NiFe LDH is \approx 2.5 nm; such an ultrathin morphology and large aspect ratio is commonly beneficial for maximizing the surface active sites and increasing the reaction area (Figure 1b).^[32,33] The detailed microstructure of the Ru-S-NiFe LDH was further characterized through the high-resolution TEM (HR-TEM), where a lattice spacing is determined to be 2.4 Å, which can be ascribed to the (015) facet of LDH. Meanwhile, the selected area electron diffraction (SAED) image indicates several diffraction points that





Figure 1. a) TEM, b) AFM, c) HR-TEM images and corresponding SAED (inset) of Ru-S-NiFe LDH. d) Experimental XRD patterns and corresponding fitting patterns on Ru-S-NiFe LDH and NiFe LDH. e) Raman spectra of Ru-S-NiFe LDH and NiFe LDH. f) AC HAADF-STEM image of Ru-S-NiFe LDH, with the Ru single atoms marked with circles. g) The enlarged areas in (f) and corresponding atomic intensity profiles along the dashed lines. h) Corresponding elemental mappings of Ru-S-NiFe LDH.

are clearly identified as the (015) and (110) facets (Figure 1c; Figure S1c, Supporting Information). Subsequently, the inductively coupled plasma-optical emission spectrometry (ICP-OES) and the scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) jointly confirm that the atomic and mass ratios of Ru in Ru-S-NiFe LDH are determined to be 0.53 at% and 1.9 wt.% (Figure S1d and Table S1, Supporting Information).

To make a direct comparison, the NiFe LDH, S-doped NiFe LDH (S-NiFe LDH) and Ru-doped NiFe LDH (Ru-NiFe LDH) were prepared and their corresponding ultrathin nanosheet morphologies and precise elemental compositions were also confirmed in Figures S2–S4 (Supporting Information). The XRD pat-

terns in Figure S5 (Supporting Information) suggest these four samples have the identical structural phases, on which no explicit peaks assigned to Ru or S can be found, indicating that no Ru or metal sulfide nanoparticles are generated. Specifically, the primary diffraction peaks located at $\approx 11.5^{\circ}$, 23.2°, 33.6°, 34.5°, 39.0°, 60.1°, and 60.6° are well ascribed to the (003), (006), (101), (012), (015), (110), and (113) facets of standard Ni₃Fe LDH (JCPDS No.40-0215). Furthermore, fitting operations were conducted on these XRD patterns: the detailed lattice parameters are a = 12.112 Å, b = 6.313 Å, c = 23.220 Å and V = 1537.6 Å³ for NiFe LDH, as compared to a = 12.116 Å, b = 6.317 Å, c = 23.227 Å and V = 1539.5 Å³ for Ru-S-NiFe LDH (Figure 1d). The

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enlarged lattice parameters of the later is attributed to the introduction of Ru and S atoms with bigger radii into the NiFe LDH (Tables S2 and S3, Supporting Information).^[19] In addition, all samples exhibit the similar Raman spectra, in which the Raman peak at 1057 cm⁻¹ proves the inserted anion in the interlayer is the CO₃^{2–}, which is consistent with the synthesis procedure (Figure S6, Supporting Information).^[34] The $a_{1,g}$ (532 cm⁻¹), e_{g} (457 cm⁻¹) and e_g (300 cm⁻¹) Raman peaks on NiFe LDH are ascribed to the Ni^{II}-O vibration, Ni^{II}-OH vibration, and Ni^{II}O-H vibration, respectively. Meanwhile, Ru-S-NiFe LDH also presents the similar a_{1g} and e_g Raman peaks as the NiFe LDH, indicating the dual-doping of Ru single atoms and S anions has negligible influence on the layered hydroxide structure. Notably, compared with the NiFe LDH, Ru-S-NiFe LDH displays decreased peak intensities, broaden peak widths, and slightly redshifted peak positions on these a_{1g} and e_g Raman peaks, which are mainly attributed to the partial variation of the coordination environment, local lattice distortion and decreased crystal symmetry of NiFe LDH caused by foreign atoms doping effect. This phenomenon also indicates the successful incorporation of Ru single atoms and S anions (Figure 1e).[35,36]

Furthermore, for the aim of distinguishing the states of doped Ru species, the aberration-corrected high-angle annular dark field-scanning TEM (AC HAADF-STEM) with atomic resolution was used to characterize the Ru-S-NiFe LDH. Because of the larger *Z*-contrast of Ru atom than Ni or Fe atom, the bright spots with isolated dispersions can be clearly observed on the crystal support, demonstrating that the doped Ru species primarily exist as single atoms (Figure 1f). Moreover, two different crystal regions are selected in Figure 1f, and corresponding atomic intensity profiles along line 1 and line 2 were plotted in Figure 1g, from which the distinct peaks with higher intensities are attributed to Ru, further confirming the isolated states of Ru atoms.^[37,38] On the other hand, the elemental mappings in Figure 1h indicate that Ru, Ni, Fe, O, and S atoms are homogeneously dispersed over the whole Ru-S-NiFe LDH nanosheet.

2.2. Electronic and Atomic Structure Analysis of Ru-S-NiFe LDH

Subsequently, the X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure (EXAFS) were adopted to investigate the electronic properties and local atomic arrangement structures of Ru-S-NiFe LDH. As revealed in Figure 2a, the normalized Ru K-edge absorption energy edge position of Ru-S-NiFe LDH is located between the Ru foil and RuO₂, implying the valence state of Ru species is between 0 and +4 in Ru-S-NiFe LDH.^[39] After carefully establishing the liner relationship between the positions of the absorption energy edge and the oxidation states of the standard references, it is calculated that the Ru valence state in Ru-S-NiFe LDH and Ru-NiFe LDH are +1.98 and +3.58, respectively. The lower valence state of the former is due to that S atom has a smaller electronegativity and will attract less electron density from surrounding metal atoms than O atom (Figure S7, Supporting Information).^[40] In addition, Ru K-edge EXAFS results reveal that Ru-S-NiFe LDH only shows a main peak at ≈ 1.67 Å, the lack of a discernible Ru-Ru peak (2.43) Å) and Ru-O-Ru peak (3.18 Å) confirms the existence of singleatom Ru species rather than Ru or RuO₂ nanoparticles in the

Ru-S-NiFe LDH, which is identical to the previous AC HAADF-STEM characterization results. Interestingly, it can also be found that the radial distance of the main peak in Ru-S-NiFe LDH is a little bit longer than the Ru-O bond (1.48 Å) in RuO₂, suggesting that the coordination atoms of the isolated Ru atoms may simultaneously include O and S atoms (Figure 2b).^[41,42] Therefore, a fitting operation that based on the EXASF data was carried out on Ru-S-NiFe LDH (Figures S8 and S9 and Table S4, Supporting Information). As depicted in Figure 2c, it is calculated that the first shell coordination consists of Ru-O and Ru-S scatterings, forming a full coordination environment of the isolated Ru atoms. Furthermore, above findings are also determined by the wavelet transform (WT)-EXAFS in Figure 2d. Ru-S-NiFe LDH exhibits a maximized center at k = 5.44 Å⁻¹, which is clearly different from the Ru-O scattering in RuO₂ ($k = 5.06 \text{ Å}^{-1}$) and Ru-Ru scattering in Ru foil ($k = 9.41 \text{ Å}^{-1}$), further proving the participation of coordinated O and S atoms as well as the absence of agglomerated Ru.^[43] Additionally, the L_{2.3} edge soft X-ray absorption spectroscopy (sXAS) of 3d transition metal is extremely sensitive to its chemical state. Figure 2e demonstrates Ni L2.3 edge sXAS spectrum of Ru-S-NiFe LDH with NiO as the reference, their identical energy positions and spectra profiles can determine that Ni presents the oxidation state of +2 in Ru-S-NiFe LDH. Similarly, its Ni K-edge XANES spectrum also exhibits the same absorption energy edge position as the NiO, further validating the Ni chemical state is +2 (Figure 2f). As shown in Figure 2g, the Ni K-edge EXAFS spectrum of Ru-S-NiFe LDH reveals two coordination peaks. To deeply reveal the coordination environment of Ni atoms, the fitting operation was performed (Figure S10a and Table S5, Supporting Information). Detailed parameters indicate that the first coordination peak is ascribed to Ni-O bond. According to the SEM-EDS result that the atomic ratio of O: S is 72: 1.8, the absence of Ni-S bond is mainly attributed to low doping amount of S anions. In addition, the second coordination peak in the Ni K-edge EXAFS of Ru-S-NiFe LDH shows a larger radial distance than the Ni-O-Ni bond in NiO, confirming the coordination atoms in its second shell are not only Ni atoms. Further combining with the fitting result, it is confirmed that the second coordination peak is mainly ascribed to the Ni-O-M bond (M = Ni/Fe/Ru), indicating the interaction between Ni and surrounding metal atoms via the O bridge in Ru-S-NiFe LDH. Meanwhile, both Fe $L_{2,3}$ edge sXAS and Fe K-edge XANES spectra of Ru-S-NiFe LDH show the same profile and absorption energy edge position as the Fe₂O₃ reference, indicating that the Fe valence state in Ru-S-NiFe LDH is +3 (Figure 2h,i). Similarly, Ru-S-NiFe LDH also presents the Fe-O bond and Fe-O-M bond (M = Ni/Fe/Ru) in the Fe K-edge EXAFS spectrum (Figure 2); Figure S10b, Supporting Information).^[44–47]

Moreover, X-ray photoelectron spectroscopy (XPS) was employed to probe the surface electronic structures of these samples. As demonstrated in Figure S11a (Supporting Information), the survey XPS spectra clearly display the appearance of Ru 3*p* signals in both Ru-NiFe LDH and Ru-S-NiFe LDH, suggesting the successful incorporation of Ru atoms. In addition, the S 2*p* XPS spectra of S-NiFe LDH and Ru-S-NiFe LDH can be deconvoluted as the S-O peak and S-Metal peak, respectively. The existence of the bond between S anions and metal validates that the S anions are successfully doped in S-NiFe LDH and Ru-S-NiFe LDH RU-S-NiFe L





Figure 2. a) The normalized Ru *K*-edge XANES spectra of Ru-S-NiFe LDH, Ru foil, RuO₂, and Sr₂GdRuO₆. b) Ru *K*-edge EXAFS spectra of Ru-S-NiFe LDH, Ru foil and RuO₂. c) Ru *K*-edge EXAFS fitting spectrum and simulated atomic model of Ru-S-NiFe LDH. d) Corresponding wavelet-transformed k^2 -weighted EXAFS spectra of Ru-S-NiFe LDH, RuO₂ and Ru foil. e) Ni $L_{2,3}$ sXAS spectra of Ru-S-NiFe LDH and NiO. Ni *K*-edge f) XANES and g) EXAFS spectra of Ru-S-NiFe LDH, Ni foil, and NiO, and the EXAFS fitting spectrum of Ru-S-NiFe LDH. h) Fe $L_{2,3}$ sXAS spectra of Ru-S-NiFe LDH, Ni foil, and NiO, and the EXAFS fitting spectrum of Ru-S-NiFe LDH. h) Fe $L_{2,3}$ sXAS spectra of Ru-S-NiFe LDH, and Fe₂O₃. Fe *K*-edge i) XANES and j) EXAFS spectra of Ru-S-NiFe LDH, Fe foil, and Fe₂O₃, and the EXAFS fitting spectrum of Ru-S-NiFe LDH.

Supporting Information).^[48] Also, there is a negative shift of the Ru 3*p* XPS binding energy of Ru-S-NiFe LDH compared with the Ru-NiFe LDH, which coincides with the Ru *K*-edge XANES result that Ru-S-NiFe LDH has a lower Ru valence state than that of Ru-NiFe LDH (Figure S11c, Supporting Information). As revealed in Figure S11d, e (Supporting Information), all samples exhibit similar Fe and Ni chemical states on the surface due to their identical Fe 2*p* and Ni 2*p* binding energy positions, while the few oxidized species such as Ni³⁺ may be due to exposure in air.^[49] Furthermore, Figure S11f (Supporting Information) displays the O 1*s* spectra, where the prominent peak at 530.9 eV corresponds to OH⁻ in these samples, in accord with their characteristics as layered hydroxides.^[50]

2.3. Electrocatalytic Performances of Ru-S-NiFe LDH

After characterizing the detailed structure of Ru-S-NiFe LDH, its electrochemical performances toward OER were conducted in the laboratory via a three-electrode system. We also tested the OER catalytic performances of NiFe LDH, S-NiFe LDH, Ru-NiFe, LDH, and RuO₂ in 1 \bowtie KOH electrolyte for comparisons.

Corresponding TEM images of the selected commercial RuO₂ are shown in Figure S12 (Supporting Information). All detected potentials were calibrated to the reversible hydrogen electrode (RHE).^[21] As expected, the polarization curve (LSV) with a 95% iR compensation of Ru-S-NiFe LDH was extended to a large current density of more than 300 mA cm⁻², which is clearly superior to other curves, indicating that Ru-S-NiFe LDH is the most active OER catalyst among those samples (Figure 3a). Tafel slope measurements were further conducted in Figure 3b, Ru-S-NiFe LDH has the smallest value of 81.65 mV dec⁻¹ among all studied samples, on account of the incorporation of Ru single atoms and S anions contributes the accelerated reaction kinetics and the enhanced OER activity.^[51] To be specific, Ru-S-NiFe LDH only delivers a much smaller overpotential of 279 mV to reach the current density of 100 mA cm⁻², the overall activity tendency is Ru-S-NiFe LDH>Ru-NiFe LDH>S-NiFe LDH>NiFe LDH>RuO₂. It is worth noting that the activity gap between Ru-S-NiFe LDH and other samples is further enlarged when the current density achieves 250 mA cm⁻². As revealed in Figure 3c, corresponding OER overpotentials for Ru-S-NiFe LDH, Ru-NiFe LDH, S-NiFe LDH, NiFe LDH, and RuO₂ at 250 mA cm⁻² are 321, 345, 428, 466, and 523 mV, respectively. A synopsis of alkaline OER overpotentials

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Figure 3. a) Polarization curves and b) corresponding Tafel slopes of Ru-S-NiFe LDH, Ru-NiFe LDH, S-NiFe LDH, NiFe LDH, and commercial RuO_2 . c) Overpotentials of the studied catalysts at the current densities of 100 and 250 mA cm⁻². d) Mass activities and TOF values of Ru-S-NiFe LDH and RuO_2 at 1.55 V. e) Comparisons of OER performances between Ru-S-NiFe LDH and RuO_2 . f) Chronopotentiometric measurements of Ru-S-NiFe LDH, NiFe LDH and RuO_2 at the current densities of 100 and 250 mA cm⁻². g) The AEMWE polarization curves of Ru-S-NiFe LDH // commercial Pt/C and NiFe LDH // commercial Pt/C at the current densities of 100 and 250 mA cm⁻². g) The AEMWE stability of Ru-S-NiFe LDH // commercial Pt/C at the current density of 1.0 A cm⁻². Note: error bars represent the standard deviation of three independent measurements.

and Tafel slopes on reported 3d transition metal-based electrocatalysts is listed in Figure S13 and Table S6 (Supporting Information), in which Ru-S-NiFe LDH exhibits the obvious superiority. In addition, the double-layer capacitance (C_{dl}) approach was used to calculate the electrochemical surface area (ECSA), while the C_{dl} can be determined through performing cyclic voltammetry (CV) under various scanning rates (Figure S14, Supporting Information). Figure S15 (Supporting Information) discloses that the highest C_{dl} of Ru-S-NiFe LDH leads to the largest ECSA values (1.55 cm²) and the most active sites. As a result, when normalized the OER current density to the ECSA value, Ru-S-NiFe LDH possesses the highest specific activity (161.3 mA cm⁻²) than other samples, indicating its highest intrinsic activity.^[19] To preclude the effect of morphology on evaluating activity, the BET areas and corresponding specific activities were investigated. It can be observed that the specific activity normalized to the BET area of Ru-S-NiFe LDH also outperforms those of other catalysts

(Figure S16, Supporting Information). Moreover, the preparation cost is an essential factor that influences the availability of an electrocatalyst for practical applications. Given that Ru is a noble metal, it is indispensable to normalize the OER current density to the Ru usage in Ru-S-NiFe LDH to evaluate the economic efficiency. As a result, the mass activity at 1.55 V (vs RHE) of Ru-S-NiFe LDH is 52.63 A mg $^{-1}$ _{Ru}, reaching 382 times as high as the RuO_2 (0.14 A mg⁻¹_{Ru}) (Figure 3d). Surprisingly, given that Ru is the only active sites in Ru-S-NiFe LDH, the calculated turnover frequency (TOF) of Ru-S-NiFe LDH (13.78 s⁻¹) also reaches 383 folds greater than that of the commercial RuO_2 (0.036 s⁻¹). In addition, the TOF value on Ru-S-NiFe LDH is also calculated based on the assumption that both Ru and Ni are active sites. As shown in Figure S17a (Supporting Information), the TOF value is determined to be 0.41 s⁻¹, which is still superior to commercial RuO₂. The TOF values with respect to ECSA normalized polarization information are also calculated on Ru-S-NiFe LDH. The



result indicates that the ECSA-normalized TOF values are 8.89 and 0.26 s⁻¹ based on assuming that Ru as well as both Ru and Ni are active sites, respectively (Figure S17b, Supporting Information). Together, these results indicate that although the noble metal Ru is adopted for optimizing the OER performance, the employment of the single-atom strategy ensures the high atomic utilization of Ru, large activity enhancement, and low preparation cost of Ru-S-NiFe LDH (Figure 3e). Additionally, electrochemical impedance spectroscopy (EIS) in Figure S18 (Supporting Information) shows that Ru-S-NiFe LDH has the smallest semicircle radius, implying its fastest charge transfer rate. Then, the fitting operation was performed on these EIS plots through simulating the equivalent circuit. As a result, the specific charge transfer resistances (R_{ct}) on Ru-S-NiFe LDH, Ru-NiFe LDH, S-NiFe LDH, NiFe LDH, and RuO₂ are determined to be 1.19, 1.35, 2.78, 2.86, and 7.27 Ω , respectively (Table S7, Supporting Information). Particularly, it is noteworthy that Ru-S-NiFe LDH and Ru-NiFe LDH, as well as S-NiFe LDH and NiFe LDH show the similar R_{ct} values, suggesting the doped S anions cannot accelerate the conductivity. However, after the incorporation of Ru, Ru-S-NiFe LDH exhibits an obviously decreased R_{ct} compared with S-NiFe LDH, and Ru-NiFe LDH also shows lower R_{ct} than that of NiFe LDH. This is a clear evidence that the doped Ru single atoms play essential roles on enhancing the conductivity of NiFe LDH and speeding up the OER kinetics.^[52] In addition, Faradaic efficiency (FE) is also a critical indicative performance factor, thus we employed the dual-electrode voltammetry (DECV) method to confirm the OER FE on Ru-S-NiFe LDH. As shown in Figure S19 (Supporting Information), almost no ring current is found when the disk current is 0. However, after employing 200 µA on the disk to generate O_2 , an observable current derived from O_2 reduction is detected from the ring of the rotating ring-disk electrode (RRDE). Since the collection coefficient of RRDE is confirmed to be 0.37, the average OER FE on Ru-S-NiFe LDH is calculated to be 97.8%. Actually, such a high FE value indicates that the current on Ru-S-NiFe LDH originates exclusively from OER.^[53]

Besides the enhanced activity, another critical parameter for assessing one alkaline OER electrocatalyst is the long-term stability. Therefore, taking the 1 м KOH as the electrolyte, the chronopotentiometry (CP) tests were initially carried out on Ru-S-NiFe LDH, Ru-NiFe LDH, S-NiFe LDH, NiFe LDH, and RuO₂ at the constant current density of 100 mA cm⁻². Consequently, Ru-S-NiFe LDH presents a highly desirable durability for more than 100 h with negligible activity degradation. In sharp contrast, the Ru-NiFe LDH, S-NiFe LDH, NiFe LDH, and RuO_2 can only endure for almost 74, 51, 41, and 12 h, respectively (Figure 3f; Figure S20, Supporting Information). In order to evaluate the electrochemical corrosion problems on these catalysts, the dissolved metal ion concentrations after CP experiments were examined by ICP-OES. As revealed in Figure S21 (Supporting Information), the reason that results in the deactivation of RuO₂ is the severe Ru ion leaching phenomenon during the OER process, whereas only slight Ru ion dissolution occurs on Ru-S-NiFe LDH. In addition, owing to the doped Ru single atoms and S anions, both Ni and Fe ion dissolutions are also alleviated, leading to the improved stability of Ru-S-NiFe LDH. The structures of Ru-S-NiFe LDH after the stability test at 100 mA cm⁻² were characterized and demonstrated in Figure S22 (Supporting Information). Corresponding LDH characteristic diffraction peaks of (003), (006), (012), and

(110) facets are well-remained on the XRD pattern. However, Ru 3p, S 2p, Ni 2p, and Fe 2p XPS spectra all exhibit an obvious tendency toward the higher binding energy, which is a signal that the Ru, S, Ni, and Fe elements are oxidized after the long-time catalysis.^[54] The post-stability microscopic characterizations on Ru-S-NiFe LDH indicate that its ultrathin 2D structure and detailed crystal structure are well preserved. In addition, elemental mappings indicate that Ru, Ni, Fe, S, and O elements are still uniformly distributed on the Ru-S-NiFe LDH after the stability test. Encouraged by the prolonged stability of Ru-S-NiFe LDH at 100 mA cm⁻², a higher current density of 250 mA cm⁻² was employed on the Ru-S-NiFe LDH to create a harsher environment and monitor the stability. Strikingly, only slight decay is found on Ru-S-NiFe LDH after a long-term durability test of 100 h, whereas the commercial RuO₂, NiFe LDH, S-NiFe LDH, and Ru-NiFe LDH show sharp activity degradations after stably operating for only 4, 29, 32, and 59 h, respectively (Figure 3f; Figure S20b, Supporting Information). In addition, even at such a large current density, Ru, Ni, and Fe ion leaching problems on Ru-S-NiFe LDH are far less serious than those in NiFe LDH and RuO₂ (Figure S21, Supporting Information). Therefore, these electrochemical test results demonstrate that the Ru-S-NiFe LDH possesses the merits of high cost-effectiveness and performance as compared with the conventional NiFe LDH and RuO₂, endowing it a bright potential as an anodic candidate in the industrial water electrolyzer.

Encouraged by the obviously enhanced alkaline OER performance, we further carried out the AEMWE testing by assembling the cathodic Ru-S-NiFe LDH with the anodic commercial Pt/C to demonstrate the practical feasibility of Ru-S-NiFe LDH in industrial water splitting. Meanwhile, the NiFe LDH and commercial Pt/C system was also tested to make a direct comparison. As revealed in Figure 3g, Ru-S-NiFe LDH exhibits a higher AEMWE activity than the benchmark NiFe LDH. Specifically, Ru-S-NiFe LDH needs 1.92 and 2.00 V to achieve the high current densities of 1.0 and 1.5 A cm⁻², whereas NiFe LDH delivers the cell potentials of 2.05 and 2.18 V, respectively (without iR correction) (Figure S23, Supporting Information). In addition, the AEMWE stability of Ru-S-NiFe LDH was also carried out at 1.0 A cm⁻². Commonly, due to the inherent physicochemical properties, it is difficult for conventional 3d transition metal-based LDH catalysts to maintain stability for more than 50 h at current densities exceeding 1 A cm⁻² (Table S8, Supporting Information). However, through the dual-doping modification of Ru single atoms and S anions, Ru-S-NiFe LDH can achieve a high stability over 80 h at such a high current density (Figure 3h). Overall, the improved AEMWE activity and prolonged AEMWE stability emphasize the significance of Ru single atoms and S anions dual-doping, which attest that Ru-S-NiFe LDH is a prospective anodic replacement of the noble metal oxides for the practical water electrolysis device.

2.4. Mechanistic Insights into Alkaline OER

Considering the significantly enhanced performance on the elaborately fabricated Ru-S-NiFe LDH, a deep investigation of the activated mechanism toward the alkaline OER is meaningful and instructive. As mentioned before, XAS is the most powerful tool to determine the detailed structure. Herein, the advanced *operando* ADVANCED SCIENCE NEWS ______



Figure 4. The *operando* XANES spectra at the a) Ru K-edge, b) Ni K-edge, and c) Fe K-edge of the Ru-S-NiFe LDH at the states of Pristine, OCP, the applied OER voltages of 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, and 2.0 V, and Off. The *operando* EXAFS spectra at the d) Ru K-edge, e) Ni K-edge, and f) Fe K-edge of the Ru-S-NiFe LDH at the states of Pristine, OCP, and the applied OER voltages of 1.3, 1.4, 1.5, 1.6, 1.7, and 1.8 V. g) The calculated formation energies for dehydrogenations of NiFe LDH and S-NiFe LDH to NiFeOOH and S-NiFeOOH. h) The free energy diagrams of Ru-S-NiFeOOH, NiFeOOH, and RuO₂ toward the alkaline OER.

XAS technology is applied to directly monitor the dynamic evolutions of chemical states and atomic structures on Ru-S-NiFe LDH with the continuously applied potentials (Figure S24, Supporting Information). It can be observed in Figure 4a that the Ru *K*-edge absorption energy edge exhibits a positive shift when the deployed OER potential was increased from the open circuit potential (OCP) to 2.0 V (vs RHE), which is a clear signal that the Ru species in Ru-S-NiFe LDH are oxidized to higher valence states, suggesting that the isolated Ru species serve as the real active catalytic sites for OER.[55-57] Interestingly, it can be observed that the rise of Ru valence state shows an overall tendency to be faster and then slower, and has almost no change after 1.8 V (vs RHE). After establishing the standard curves in Figure S25 (Supporting Information), the Ru valence state at 2.0 V (vs RHE) is determined to be +3.73. It is recognized that the unsatisfied durability of Ru-based electrocatalysts during OER is mainly attributed to

the over-oxidation of Ru active sites. Specifically, the high OER potentials will oxidize the Ru active sites and increase their valence states to more than +4, during this process the high-valence Ru sites will be soluble and more easily to leach from the catalyst, leading to the poor stability.^[28,31] However, even under the high applied oxidation voltage of 2.0 V (vs RHE), the Ru valence state on Ru-S-NiFe LDH is still lower than +4, which validly prevents the dissolution of Ru single atoms. Moreover, the ion leaching experiment determined by ICP-OES also confirms the suppressed Ru leaching phenomenon on Ru-S-NiFe LDH, corroborating the operando Ru K-edge XANES characterization result. The alleviated Ru over-oxidation issue on Ru-S-NiFe LDH is primarily due to the surrounding coordinated S anions, which can lower the valence states of Ru single atoms via donating the electrons during OER, and significantly promoting the stability.^[58-60] In addition, as indicated in Figure 4b, Ni in Ru-S-NiFe LDH also plays

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a critical role in activating the alkaline OER owing to its continuously incremental valence states with the positively applied voltages, which is revealed by the operando Ni K-edge XANES. Actually, many related papers have concluded that the Ni species with high valence states in the (oxy)hydroxide that generated through the electrochemical activation and surface reconstruction of NiFe LDH are the active phases toward OER.^[61] This is in accordance with the operando Ni K-edge XANES result and is further experimentally verified by the operando Fe K-edge XANES. As disclosed in Figure 4c, almost no significant shift with the imposed voltages can be distinguished on the Fe K-edge absorption energy edge, confirming that Fe species in Ru-S-NiFe LDH do not directly take part in the OER charge transfer process, whose primary functions may be stabilizing the layered structure via balancing the electronic neutralization, enhancing the conductivity and promoting the formation of Ni with high valence state via acting as the Lewis acid.^[62-65] Moreover, it is recognized that the absorption edges of Ru K-edge, Ni K-edge, and Fe K-edge XANES spectra still maintain at the high energy positions after ceasing the applied OER potentials (Off), which indicates that the oxidized states of Ru, Ni and Fe elements on Ru-S-NiFe LDH are irreversible. Furthermore, the real-time changes on the atomic coordination microenvironments of Ru-S-NiFe LDH were explored by the operando EXAFS. Only one prime peak that can be ascribed to the Ru-O/S bond appears and no visible peak related to Ru-Ru bond can be observed in the operando Ru K-edge EX-AFS, which confirms that Ru atoms remain the isolated dispersion and no Ru aggregation occurs in the OER process. Moreover, with the oxidized potential is gradually increased from the OCP to 1.8 V (vs RHE), the bond length and the coordination number of Ru-O/S bond present the downward and shrinkage tendency, suggesting the local atomic arrangement of Ru single atoms is slightly changed and Ru valence state continues to increase in Ru-S-NiFe LDH (Figure 4d).^[45] Meanwhile, the operando Ni Kedge EXAFS of Ru-S-NiFe LDH in Figure 4e reveals that the intensity of the main Ni-O bond decreases and the corresponding bond length contracts as the applied OER potential rises to 1.8 V (vs RHE). This maybe indicate the electrochemical surface reconstruction of LDH to (oxy)hydroxide, in agreement with the finding of operando Ni K-edge XANES.^[61] Interestingly, similar to the operando Fe K-edge XANES result, changes are barely detectable on the Ru-S-NiFe LDH in the operando Fe K-edge EXAFS in the reaction process, further evidencing that Fe species are not reaction sites for the alkaline OER (Figure 4f).

While the dynamic evolutions of valence state and atomic structure have been resolved, the catalytic mechanism of the doped S anions is still unclear. Hence, CV tests were first performed between 1.15 and 1.65 V (vs RHE). As depicted in Figure S26 (Supporting Information), all samples possess an optimization progress during the 100 cycles of CV, in accordance with the well-known reconstruction phenomenon. Notably, after the incorporation of S atoms, the current densities on S-NiFe LDH and Ru-S-NiFe LDH are greater than those on NiFe LDH and Ru-NiFe LDH, respectively, demonstrating that the doped S anions can accelerate the electrochemical activation of LDH to the OER-active phase of (oxy)hydroxide.^[66] In addition, the advanced *operando* Raman techniques were further employed to intuitively monitor the surface reconstruction with the OER potential range of 0.376–0.776 V (vs Hg/HgO) (Figure S27, Supporting Infor-

mation). As observed in Figure S28 (Supporting Information), the phase transformation can be divided into two stages on Ru-S-NiFe LDH during OER. In stage I, the Ru-S-NiFe LDH displays the same characteristic peaks belongs to Ni^{II}-OH and Ni^{II}-O from 0.376 to 0.576 V (vs Hg/HgO) as the pristine state, indicating that almost no structural change takes place in this potential region. However, at 0.626 V (vs Hg/HgO) (stage II), an apparent blue Raman shift appears and the peak intensity begins to decrease. The newly emerged Raman peaks at 0.676 V (vs Hg/HgO) are indexed to the a_{1g} stretching vibration and e_{g} bending of Ni^{III}-O in NiOOH, evidencing the complete surface reconstruction from LDH to active (oxy)hydroxide at this stage. Nevertheless, similar Ni^{III}-O Raman peaks appear on NiFe LDH until the applied OER potential reaches 0.776 V (vs Hg/HgO). Accordingly, the facile generation of the electrochemically activated (oxy)hydroxide phase on Ru-S-NiFe LDH compared to NiFe LDH further demonstrates that the doped S anions can facilitate the activation and electrochemical reconstruction on the electrocatalyst surface, contributing to the promoted electrochemical activity.[27,40,66,67]

Furthermore, for the aim of elucidating the OER activation mechanism, we adopted the density functional theory (DFT) calculations to provide the theoretical evidences. The atomic models for all LDH samples and corresponding electrochemically reconstructed (oxy)hydroxide including NiFeOOH, S-NiFeOOH and Ru-S-NiFeOOH were optimized, in which the contents of doped Ru and S atoms were set to be consistent with the physical characterization results (Figures S29-S31, Supporting Information). As revealed in Figure 4g, the energy barriers of reconstructed (oxy)hydroxides derived from the NiFe LDH and S-NiFe LDH were calculated. Consequently, a high value of 0.659 eV per atom is required to activate the NiFe LDH to NiFeOOH, on the contrary, the formation energy of S-NiFeOOH drops to 0.180 eV per atom on S-NiFe LDH. The remarkably decreased formation energy offers the theoretic evidence that the incorporated S anions can facilitate the surface reconstruction rate of NiFe LDH. This result is well consistent with the previous electrochemical and operando Raman results.^[54,66] Since it has been shown that the converted (oxy)hydroxide is the true active phase toward OER, free energy profiles of Ru-S-NiFeOOH, NiFeOOH, and RuO₂ were calculated through the four-step elemental reaction process.^[52,68,69] The free energy diagram in Figure 4h indicates that the rate determining step (RDS) for both NiFeOOH and RuO₂ are the conversion of *OOH from *O with OER free energy differences of 0.88 and 1.00 eV, respectively. However, the RDS is changed as the step of transforming *OH to *O on Ru-S-NiFeOOH with a significantly decreased OER free energy difference value of 0.56 eV. The calculated energy difference values highly correlate the experimental activity results that Ru-S-NiFe LDH possess the highest activity among all calculated electrocatalysts, which also suggests that the co-doped Ru single atoms and S anions can effectively optimize the intermediate adsorption in the alkaline OER process and thus enhance the catalytic performance.^[70]

3. Conclusion

In conclusion, the Ru single atoms and S anions dual-doped NiFe LDH was fabricated through a facile hydrothermal reaction.

Advanced operando XAS technique reveals that both Ru and Ni species in Ru-S-NiFe LDH are active sites that directly participate in the OER charge transfer process. Detailed mechanism investigations further disclose that the doped Ru single atoms can promote the poor conductivity of NiFe LDH, as well the main functions of S anions are accelerating the electrochemical reconstruction of NiFe LDH to OER-active NiFeOOH and alleviating the over-oxidation issue of Ru active sites, collectively contributing to the significantly improved activity and stability of Ru-S-NiFe LDH. DFT calculations further confirm the decreased energy difference caused by the Ru single atoms and S anions dual-doping. Consequently, as a promising alkaline OER electrocatalyst, Ru-S-NiFe LDH delivers remarkably decreased overpotentials, improved mass activities and prolonged stabilities compared with the benchmark NiFe LDH at the high current densities of 100 and 250 mA cm⁻². Furthermore, the AEMWE that employs Ru-S-NiFe LDH in the anode only delivers cell potentials of 1.92 and 2.0 V to reach 1.0 and 1.5 A $\rm cm^{-2},$ respectively, outperforming the NiFe LDH. Moreover, Ru-S-NiFe LDH also displays a robust stability for lasting more than 80 h at 1.0 A cm⁻². This research highlights the feasibility of designing the 3d transition metalbased electrocatalysts with reduced cost and enhanced performance through the dual-doping strategy, which possesses a broad prospect in practical applications.

4. Experimental Section

Materials: Ruthenium trichloride (RuCl₃, solid, 99.5%), ruthenium oxide (RuO₂, solid, 99%), potassium hydroxide (KOH, solid, \geq 98%), ethanol (C₂H₆O, liquid, \geq 99.7%), thiourea (CH₄N₂S, solid, \geq 99.0%) and sodium carbonate anhydrous (Na₂CO₃, solid, 99.8%) were purchased from Innochem. Iron trichloride hexahydrant (FeCl₃.6H₂O, solid, \geq 99%) and nickel chloride hexahydrant (NiCl₂.6H₂O, solid, \geq 98%) were purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China).

Catalyst preparation: In a typical synthesis, the metal precursors including 1188 mg NiCl₂.6H₂O, 450 mg FeCl₃.6H₂O, and 40 mg RuCl₃ as well as 33.8 mg thiourea were completely dissolved in 16.66 mL DI water under continuously stirring for 30 min at first. Meanwhile, 1413 mg Na₂CO₃ was added in another beaker containing 13.33 mL DI water to form a homogeneous solution, followed with quickly pouring it into the former metal precursor solution. After stirring the mixed solution for 30 min, the mixture was added into the autoclave and aged in the oven at 100 °C for 20 h. Finally, the brown precipitate was washed by water for five times and collected by centrifugation, and then dried in the vacuum oven at 80 °C for 12 h to obtain the Ru-S-NiFe LDH. The Ru-NiFe LDH, S-NiFe LDH, except that the corresponding RuCl₃ or thiourea precursor was not added in the above synthesis process.

Characterization: The TEM and HR-TEM images were determined by a JEOL 2100 F instrument at a working voltage of 200 kV. AC HAADF-STEM images and corresponding elemental mappings were collected on a Thermo Scientific Themis Z microscope operated at 200 kV. SEM-EDS spectra were collected on a Zeiss Supra 55 at an acceleration voltage of 5 kV. The mass fraction and the dissolved ion concentration in the electrolyte after stability test were determined by ICP-OES on an Agilent ICP-OES 730. The XRD data was collected on a Bruker D8 Advance powder diffractometer (operating at 40 kV, 40 mA) equipped with a Cu-K α source ($\lambda 1 = 1.5405$ Å, $\lambda 2 = 1.5443$ Å) and fitted with a beryllium window at room temperature. The lattice parameters of XRD patterns were fitted by the TOtal Pattern Analysis solutions (TOPAS) software of Bruker.

The XPS was carried out on a Thermo Scientific Escalab 250Xi with an Al- $K\alpha$ source. The XANES and EXAFS data of Ru *K*-edge, Ni *K*-edge, and Fe *K*-edge were conducted at the 44A beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The sXAS of Ni $L_{2.3}$ -edge

and Fe $L_{2,3}$ -edge were collected at the TLS 20A1 beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The *operando* XAS experiments were conducted at the 44A beamline of the NSRRC using a Si (111) quick-scanning monochromator. Chronoamperometry was performed on the catalyst in a custom-built electrochemical reaction cell, during which the *operando* XAS average signal at each potential was collected. All XAS data were collected under the room temperature and analyzed by using the standard program Demeter.

The operando Raman spectra were collected on a LabRAM HR Evolution Raman spectrometer equipped with a 532 nm laser, catalyst inks were directly dropped on the carbon paper (1 cm^2) as the working electrode, Hg/HgO electrode and carbon rod were used as the reference electrode and counter electrode, respectively. The catalysts were activated at each potential in 1 m KOH solution for 5 min and then characterized by the Raman technique. The Raman spectra were collected after three sweeps of 10 s from 200 to 1200 cm⁻¹ to evaluate the electrochemical surface reconstruction in the OER process. These spectra were collected at the room temperature and ambient pressure.

Electrochemical Measurement: The OER performance evaluation was conducted on the CHI 760E electrochemical workstation with a typical three-electrode system. The working, reference and counter electrodes were the carbon paper with an area of 1 cm², calomel electrode, and graphite rod, respectively. Before testing, the working electrode was washing three times by DI water and dried. Then, 5 mg prepared sample (Ru-S-NiFe LDH, Ru-NiFe LDH, S-NiFe LDH, NiFe LDH) or commercial RuO2 was added in 1 mL ethanol, 0.9 mL water and 0.1 mL Nafion solution (5 wt.%, Aldrich), followed with sonication for 6 h to obtain a uniform catalyst ink. Afterward, 100 µL of the catalyst ink was carefully dropped on the prepared carbon paper (1 cm²) and dried under infrared light. The total catalyst loadings for all samples were controlled at 0.25 mg cm⁻². All potentials in this study were calibrated with respect to RHE scale. The OER activity was evaluated by iR-corrected LSV method under the room temperature with a scanning rate of 5 mV s⁻¹. The iR compensation for all polarization curves was auto-achieved by the electrochemical stations and the value was maintained as 95%. Tafel slopes were determined by plotting the overpotential versus the logarithm of current density (log |j|). Stability tests were evaluated by conducting the chronopotentiometry on Ru-S-NiFe LDH, Ru-NiFe LDH, S-NiFe LDH, NiFe LDH and RuO2 at the constant OER current densities of 100 and 250 mA cm⁻², respectively. EIS for all samples was determined at 1.5 V versus RHE in the frequency range between 0.01 and 100 kHz. The fitting operations of EIS were performed on the ZView2 Software via simulating the equivalent circuit.

Calculation of the Electrochemically Surface Area: ECSAs were determined by evaluating the electrochemical double-layer capacitance (C_{dl}) on catalytic surface of studied catalysts according to Equation (1):

$$ECSA = R_f S = \frac{C_{dl}}{C_s} S$$
(1)

where C_{dl} was measured from the scan-rate-dependent CVs in the non-Faradaic region from 1.1 to 1.2 V versus RHE with scanning rates of 20, 40, 60, 80, and 100 mV s^{-1} in 1 $\,$ M KOH solution. S represents the real surface area of the smooth metal electrode, which generally equals to the geometric area of working electrode (S = 1 cm²). The specific capacitance (C_s) for a flat surface was generally adopted as 20–60 μ F cm⁻². In this work, a C_s value of 60 μ F cm⁻² was used for determine the ECSA.^[71,72]

Calculation of the Turnover Frequency: The turnover frequency (TOF) values of studied catalysts are determined based on the Equation (2):

$$TOF = \frac{\#number of toal oxygen turnover/cm_{geo}^{2}}{\#number of active sites/cm_{geo}^{2}}$$
(2)

the oxygen turnover can be calculated according to Equation (3):

O₂ turnover per grometric area

$$= j_{geo} \times \frac{1 \text{ Cs}^{-1}}{1000 \text{ mA}} \times \frac{1 \text{ mol}}{96485.3 \text{ C}} \times \frac{1}{4} \times \frac{6.02 \times 10^{23}}{1 \text{ mol } o_2}$$
(3)

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The number of the active sites per geometric area was determined by ICP-OES result. For example, assuming that all Ru sites are accessible for OER, the upper limit of Ru site density in Ru-S-NiFe LDH is:

$$0.25 \text{ mg} \times 1.9\% \times \frac{1 \text{ mmol}}{101.07 \text{ mg}} \times \frac{6.02 \times 10^{20} \text{ site}}{1 \text{ mmol}} \times \frac{1}{1 \text{ cm}^2} = 2.83 \times 10^{16} \frac{\text{sites}}{\text{ cm}^2} \quad (4)$$

At the potential of 1.55 V (vs RHE), the OER current density for Ru-S-NiFe LDH was 250 mA cm⁻². And the corresponding TOF value normalized to geometric area was calculated to be:

$$\mathsf{TOF}_{\mathsf{geo}} = \frac{1.56 \times 10^{15} \frac{O_2}{\mathrm{cm}^2} \, \mathrm{s}^{-1} \mathsf{per} \frac{\mathrm{mA}}{\mathrm{cm}^2} \times 250 \frac{\mathrm{mA}}{\mathrm{cm}^2}}{2.83 \times 10^{16} \frac{\mathrm{ster}}{\mathrm{cm}^2}} = 13.78 \, \mathrm{s}^{-1} \tag{5}$$

The TOF value that normalized to Ru and Ni sites is based on assuming that all Ru and Ni sites were accessible for OER.

Computational Details: The first-principles calculations were performed based on density functional theory. The structure relaxations and electronic properties were carried out using the projector-augmented wave method,^[73] implemented in the ab initio simulation package (VASP) code along with the generalized gradient approximation and the Perdew, Burke, and Ernzerhof functional.^[74,75] The electron wave functions were expanded using a plane-wave cut-off of 520 eV. To prevent periodic interactions, vacuum layers of 20 Å were introduced. The Monkhorst Pack & point scheme was employed to sample the reciprocal space using a $3 \times 3 \times 1$ mesh grid. The structures were subjected to relaxation until the total energy variation was less than 10^{-5} eV, and the forces on each atom were below 0.05 eV Å. The overall OER in alkaline media can be written:

$$4OH^- - 4e^- \rightarrow O_2 + 2H_2O \tag{6}$$

In the model, the OER is processed via four electrons:

$$OH^- + * \to OH^* + e^- \tag{7}$$

$$OH^* + OH^- \to O^* + e^- + H_2O(I)$$
 (8)

$$OH^- + O^* \to OOH^* + e^- \tag{9}$$

$$OOH^* + OH^- \rightarrow O_2(g) + e^- + H_2O(l)$$
 (10)

where the * represents an active site on the surface of catalyst. (I) and (g) were used to denote the liquid and gas phases, respectively. The reaction free energy of ΔG for each step is defined by the following equation:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S + \Delta G_{pH} + \Delta G_{U}$$
(11)

 ΔE and ΔZPE denote the different energy change and zero-point energy change of the reaction, respectively. T ΔS is the entropy contribution to the reaction at T = 298.15 K. The ΔE is calculated by DFT, while the ΔZPE , and ΔS are obtained from the values of Table I in ref. [76]

MEA Preparation for AEMWE Single Cell Measurements: The full cell measurements were conducted using a commercial 5 cm² electrolysis cell (Carbon and FuelCell) equipped with parallel flow fields made out of TiO₂ (anode) and carbon (cathode). The electrodes were in two-electrode mode directly connected with the potentiostat (Gamry Reference 3000 and 30 K Booster), anode was set as working electrode the cathode was set as counter and reference electrode. As anode, blank Nickel Felt (NF) was used as porous transport layer (PTL), the anode catalysts were spraycoated on the membrane (IONOMR, 75 µm AF3-HWK9-75 reinforced) to prepare a catalyst coated membrane (CCM). 50 mg of the respective anode catalyst were sonified in 50 μL Mili-Q, 2 mL i-PrOH, and the necessary amount of 5 wt.% AP binder solution to provide a I/C of 0.3. An overall anode catalyst loading of 1 mg cm⁻² was adjusted by spray coating the prepared catalyst ink manually on the membrane. The membrane was fixed on a commercial heating vacuum plate equipped with temperature control (Carbon and Fuel Cell) and a dry vacuum pump/compressor

(Welch, WOB-L 2511). The table temperature was set to 55 °C. Furthermore, a mask (5 cm²) was used. Spraying and drying of the membrane followed by weighting was conducted alternatingly until the desired loading was achieved.

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For the preparation of the cathode spray-coting technique was applied, aiming at a loading of 0.1 mg_{Pt} cm⁻² (Umicore, 48.46 wt.% Pt at carbon). For the preparation of the catalyst ink 100 μ L Mili-Q and 10.28 g i-PrOH were added to 120 mg Pt-C (Umicore, 48.46 wt.% at carbon) and sonified subsequently, ionomer solution (5 wt.% AP3; IONOMR) were added during the sonification, resulting in a 1 wt.% dispersion of the catalytic active material. To guarantee the targeted loading, a commercial automated spray system (ExactaCoat, Sonotek Corp.) was used. The measurements were conducted in 0.1 m KOH with an electrolyte flow of 100 mL min⁻¹ at 60 °C, the electrochemical protocol is listed in detail in Table S9 (Supporting Information). The electrochemical impedance spectra were recorded at 1.63 V (Cell Voltage) while the applied frequency was varied from 500 kHz to 1 Hz for each sample. For the investigation of the AE-MEW stability, a current hold at 5 A (1 A cm⁻²) was added after the last PEIS.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords

alkaline oxygen evolution reaction, anion exchange membrane water electrolyzer, layered double hydroxides, Ru single atoms, sulfur anions

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- H.-F. Wang, L. Chen, H. Pang, S. Kaskel, Q. Xu, Chem. Soc. Rev. 2020, 49, 1414.
- P. Huang, N. Meng, G. Zhou, P. Wang, W. Wei, H. Li, R. Huang, F. Liu,
 L. Liu, *Proc. Natl. Acad. Sci. USA* **2023**, *120*, 2219661120.
- [3] J. Kang, X. Qiu, Q. Hu, J. Zhong, X. Gao, R. Huang, C. Wan, L.-M. Liu, X. Duan, L. Guo, *Nat. Catal.* **2021**, *4*, 1050.
- [4] J. Kibsgaard, I. Chorkendorff, Nat. Energy 2019, 4, 430.
- [5] H. Zhang, T. Yang, H. Zhou, Y. Wang, X. Yang, W. Liang, D. Wu, P. Yuan, T. Yu, M. He, W. Wei, *Appl. Catal. B Environ.* **2024**, *342*, 123391.
- [6] J. Xu, L. Yu, B. Dong, F. Yang, L. Feng, J. Colloid Interf. Sci. 2024, 654, 1080.
- [7] M.-Y. Ding, W.-J. Jiang, T.-Q. Yu, X.-Y. Zhuo, X.-J. Qin, S.-B. Yin, J. Electrochem. 2023, 29, 2208121.
- [8] S. Sha, R. Ge, J. M. Cairney, R. Zheng, S. Li, B. Liu, J. Zhang, W. Li, Front. Energy 2024, 18, 265.
- [9] I. Roger, M. A. Shipman, M. D. Symes, Nat. Rev. Chem. 2017, 1, 0003.
- [10] Z. Xiao, Y.-C. Huang, C.-L. Dong, C. Xie, Z. Liu, D. S. Du, W. Chen, D. Yan, L. Tao, Z. Shu, G. Zhang, H. Duan, Y. Wang, Y. Zou, R. Chen, S. Wang, J. Am. Chem. Soc. 2020, 142, 12087.
- [11] G. Fan, F. Li, D. G. Evans, X. Duan, Chem. Soc. Rev. 2014, 43, 7040.
- [12] M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, J. Am. Chem. Soc. 2013, 135, 8452.
- [13] C. Li, M. Wei, D. G. Evans, X. Duan, Small 2014, 10, 4469.
- [14] J. Feng, Y. He, Y. Liu, Y. Du, D. Li, Chem. Soc. Rev. 2015, 44, 5291.
- [15] G. Chen, T. Wang, J. Zhang, P. Liu, H. Sun, X. Zhuang, M. Chen, X. Feng, Adv. Mater. 2018, 30, 1706279.
- [16] P. Li, X. Duan, Y. Kuang, Y. Li, G. Zhang, W. Liu, X. Sun, Adv. Energy Mater. 2018, 8, 1703341.
- [17] P. Li, M. Wang, X. Duan, L. Zheng, X. Cheng, Y. Zhang, Y. Kuang, Y. Li, Q. Ma, Z. Feng, W. Liu, X. Sun, *Nat. Commun.* **2019**, *10*, 1711.
- [18] J. Wei, H. Tang, L. Sheng, R. Wang, M. Fan, J. Wan, Y. Wu, Z. Zhang, S. Zhou, J. Zeng, *Nat. Commun.* **2024**, *15*, 559.
- [19] Y. Zhu, J. Wang, T. Koketsu, M. Kroschel, J.-M. Chen, S.-Y. Hsu, G. Henkelman, Z. Hu, P. Strasser, J. Ma, *Nat. Commun.* **2022**, *13*, 7754.
- [20] S. J. Park, T. H. Nguyen, D. T. Tran, V. A. Dinh, J. H. Lee, N. H. Kim, *Energy Environ. Sci.* **2023**, *16*, 4093.
- [21] Y. Zhu, M. Klingenhof, C. Gao, T. Koketsu, G. Weiser, Y. Pi, S. Liu, L. Sui, J. Hou, J. Li, H. Jiang, L. Xu, W.-H. Huang, Z.-W. Pao, M. Yang, Z. Hu, P. Strasser, J. Ma, *Nat. Commun.* **2024**, *15*, 1447.
- [22] S. Li, L. Wang, H. Su, A. N. Hong, Y. Wang, H. Yang, L. Ge, W. Song, J. Liu, T. Ma, X. Bu, P. Feng, *Adv. Funct. Mater.* **2022**, *32*, 2200733.
- [23] H. Hu, H.-C. He, R.-K. Xie, C. Cheng, T. Yan, C. Chen, D. Sun, T.-S. Chan, J. Wu, L. Zhang, *Nano Energy* **2022**, *99*, 107390.
- [24] J. Wang, S.-J. Kim, J. Liu, S. Choi, J. Han, H. Shin, S. Jo, J. Kim, F. Ciucci, H. Kim, Q. Li, W. Yang, X. Long, S. Yang, S.-P. Cho, K. H. Chae, M. G. Kim, H. Kim, J. Lim, *Nat. Catal.* **2021**, *4*, 212.
- [25] J. Zhang, Z. Zhao, Z. Xia, L. Dai, Nat. Nanotechnol. 2015, 10, 444.
- [26] J. Kim, J. Park, J. Lee, W.-G. Lim, C. Jo, J. Lee, Adv. Funct. Mater. 2021, 31, 2010882.
- [27] Z. Wan, Z. Ma, H. Yuan, K. Liu, X. Wang, ACS Appl. Energy Mater. 2022, 5, 4603.
- [28] Q. Wen, K. Yang, D. Huang, G. Cheng, X. Ai, Y. Liu, J. Fang, H. Li, L. Yu, T. Zhai, Adv. Energy Mater. 2021, 11, 2102353.
- [29] F. Dionigi, Z. Zeng, I. Sinev, T. Merzdorf, S. Deshpande, M. B. Lopez, S. Kunze, I. Zegkinoglou, H. Sarodnik, D. Fan, A. Bergmann, J. Drnec, J. F. D. Araujo, M. Gliech, D. Teschner, J. Zhu, W.-X. Li, J. Greeley, B. R. Cuenya, P. Strasser, *Nat. Commun.* 2020, *11*, 2522.
- [30] M. Klingenhof, H. Trzesniowski, S. Koch, J. Zhu, Z. Zeng, L. Metzler, A. Klinger, M. Elshamy, F. Lehmann, P. W. Buchheister, A. Weisser, G. Schmid, S. Vierrath, F. Dionigi, P. Strasser, *Nat. Catal.* **2024**, *7*, 1213.
- [31] H. Liu, Z. Zhang, J. Fang, M. Li, M. G. Sendeku, X. Wang, H. Wu, Y. Li, J. Ge, Z. Zhuang, D. Zhou, Y. Kuang, X. Sun, *Joule* **2023**, *7*, 558.

- [32] L. Zu, X. Qian, S. Zhao, Q. Liang, Y. E. Chen, M. Liu, B.-J. Su, K.-H. Wu, L. Qu, L. Duan, H. Zhan, J.-Y. Zhang, C. Li, J. Y. Juang, J. Zhu, D. Li, A. Yu, D. Zhao, J. Am. Chem. Soc. 2022, 144, 2208.
- [33] J. Yan, L. Kong, Y. Ji, J. White, Y. Li, J. Zhang, P. An, S. Liu, S.-T. Lee, T. Ma, Nat. Commun. 2019, 10, 2149.
- [34] W. Jiang, A. Y. Faid, B. F. Gomes, I. Galkina, L. Xia, C. M. S. Lobo, M. Desmau, P. Borowski, H. Hartmann, A. Maljusch, A. Besmehn, C. Roth, S. Sunde, W. Lehnert, M. Shviro Ma, *Adv. Funct. Mater.* **2022**, *32*, 2203520.
- [35] H. Liao, G. Ni, P. Tan, Y. Liu, Y. Chen, G. Wang, M. Liu, J. Pan, Appl. Catal. B Environ. 2022, 317, 121713.
- [36] D. Wang, Q. Li, C. Han, Q. Lu, Z. Xing, X. Yang, Nat. Commun. 2019, 10, 3899.
- [37] H. Yang, F. Li, S. Zhan, Y. Liu, W. Li, Q. Meng, A. Kravchenko, T. Liu, Y. Yang, L. Wang, J. Guan, I. Furo, M. S. G. Ahlquist, L. Sun, *Nat. Catal.* **2022**, *5*, 414.
- [38] Y. Ren, Y. Tang, L. Zhang, X. Niu, X. Liu, L. Li, S. Miao, D. S. Su, A. Wang, J. Li, T. Zhang, *Nat. Commun.* **2019**, *10*, 4500.
- [39] X. Zheng, J. Yang, Z. Xu, Q. Wang, J. Wu, E. Zhang, S. Dou, W. Sun, D. Wang, Y. Li, Angew. Chem. 2022, 134, 202205946.
- [40] Y. Fang, C. Dai, X. Liu, Y. Wang, C. Ju, S. He, R. Shi, Y. Liu, J. Zhang, Y. Zhu, J. Wang, *Nano Energy* **2024**, 127, 109754.
- [41] L. Liu, Y. Ji, W. You, S. Liu, Q. Shao, Q. Kong, Z. Hu, H. Tao, L. Bu, X. Huang, Small 2023, 19, 2208202.
- [42] H. Shang, X. Zhou, J. Dong, A. Li, X. Zhao, Q. Liu, Y. Lin, J. Pei, Z. Li, Z. Jiang, D. Zhou, L. Zheng, Y. Wang, J. Zhou, Z. Yang, R. Cao, R. Sarangi, T. Sun, X. Yang, X. Zheng, W. Yan, Z. Zhuang, J. Li, W. Chen, D. Wang, J. Zhang, Y. Li, *Nat. Commun.* **2020**, *11*, 3049.
- [43] L. He, M. Li, L. Qiu, S. Geng, Y. Liu, F. Tian, M. Luo, H. Liu, Y. Yu, W. Yang, S. Guo, *Nat. Commun.* **2024**, *15*, 2290.
- [44] F. Wang, R. Zhang, Y. Zhang, Y. Li, J. Zhang, W. Yuan, H. Liu, F. Wang, H. L. Xin, Adv. Funct. Mater. 2023, 33, 2213863.
- [45] L. Zeng, Y. Chen, M. Sun, Q. Huang, K. Sun, J. Ma, J. Li, H. Tan, M. Li, Y. Pan, Y. Liu, M. Luo, B. Huang, S. Guo, *J. Am. Chem. Soc.* 2023, 145, 17577.
- [46] S. Lee, L. Bai, X. Hu, Angew. Chem., Int. Ed. 2020, 59, 8072.
- [47] J. Kang, X. Qiu, Q. Hu, J. Zhong, X. Gao, R. Huang, C. Wan, L.-M. Liu, X. Duan, L. Guo, *Nat. Catal.* **2021**, *4*, 1050.
- [48] X. Han, N. Li, J. S. Baik, P. Xiong, Y. Kang, Q. Dou, Q. Liu, J. Y. Lee, C. S. Kim, H. S. Park, *Adv. Funct. Mater.* **2023**, *33*, 2212233.
- [49] H. You, D. Wu, D. Si, M. Cao, F. Sun, H. Zhang, H. Wang, T.-F. Liu, R. Cao, J. Am. Chem. Soc. 2022, 144, 9254.
- [50] H. S. Chavan, C. H. Lee, A. I. Inamdar, J. Han, S. Park, S. Cho, N. K. Shreshta, S. U. Lee, B. Hou, H. Im, H. Kim, ACS Catal. 2022, 12, 3821.
- [51] C. Lin, J.-L. Li, X. Li, S. Yang, W. Luo, Y. Zhang, S.-H. Kim, D.-H. Kim, S. S. Shinde, Y.-F. Li, Z.-P. Liu, Z. Jiang, J.-H. Lee, *Nat. Catal.* **2021**, *4*, 1012.
- [52] F. Wang, P. Zou, Y. Zhang, W. Pan, Y. Li, L. Liang, C. Chen, H. Liu, S. Zheng, *Nat. Commun.* 2023, 14, 6019.
- [53] S. Zhao, Y. Wang, J. Dong, C.-T. He, H. Yin, P. An, K. Zhao, X. Zhang, C. Gao, L. Zhang, J. Lv, J. Wang, J. Zhang, A. M. Khattak, N. A. Khan, Z. Wei, J. Zhang, S. Liu, H. Zhao, Z. Tang, *Nat. Energy* **2016**, *1*, 16184.
- [54] H. Guo, L. Zhang, D. Ou, Q. Liu, Z. Wu, W. Yang, Z. Fang, Q. Shi, Small 2024, 20, 2307069.
- [55] X. Zhong, L. Sui, M. Yang, T. Koketsu, M. Klingenhof, S. Selve, K. G. Reeves, C. Ge, L. Zhuang, W. H. Kan, M. Avdeev, M. Shu, N. Alonso-Vante, J.-M. Chen, S.-C. Haw, C.-W. Pao, Y.-C. Chang, Y. Huang, Z. Hu, P. Strasser, J. Ma, *Nat. Catal.* **2024**, *7*, 546.
- [56] J. Timoshenko, B. R. Cuenya, *Chem. Rev.* **2021**, *121*, 882.
- [57] S. Song, J. Zhou, X. Su, Y. Wang, J. Li, L. Zhang, G. Xiao, C. Guan, R. Liu, S. Chen, H.-J. Lin, S. Zhang, W.-Q. Wang, *Energy Environ. Sci.* 2018, 11, 2945.

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- [58] M. Yang, X. Guan, Z. Shi, H. Wu, Y. Cheng, Z. Wang, W. Liu, F. Xiao, M. Shao, M. Xiao, C. Liu, W. Xing, *Small* **2025**, https://doi.org/10.1002/ smll.202411117.
- [59] S. Hao, M. Liu, J. Pan, X. Liu, X. Tan, N. Xu, Y. He, L. Lei, X. Zhang, *Nat. Commun.* 2020, 11, 5368.
- [60] Z. Shi, J. Li, Y. Wang, S. Liu, J. Zhu, J. Yang, X. Wang, J. Ni, Z. Jiang, L. Zhang, Y. Wang, C. Liu, W. Xing, J. Ge, Nat. Commun. 2023, 14, 843.
- [61] S. Zuo, Z.-P. Wu, G. Zhang, C. Chen, Y. Ren, Q. Liu, L. Zheng, J. Zhang, Y. Han, H. Zhang, Angew. Chem., Int. Ed. 2024, 63, 202316762.
- [62] D. Friebel, M. W. Louie, M. Bajdich, K. E. Sanwald, Y. Cai, A. M. Wise, M.-J. Cheng, D. Sokaras, T.-C. Weng, R. Alonso-Mori, R. C. Davis, J. R. Bargar, J. K. Nørskov, A. Nilsson, A. T. Bell, *J. Am. Chem. Soc.* 2015, 137, 1305.
- [63] N. Li, D. K. Bediako, R. G. Hadt, D. Hayes, T. J. Kempa, F. V. Cube, D. C. Bell, L. X. Chen, D. G. Nocera, *Proc. Natl. Acad. Sci* **2017**, *114*, 1486.
- [64] N. Zhang, X. Feng, D. Rao, X. Deng, L. Cai, B. Qiu, R. Long, Y. Xiong, Y. Lu, Y. Chai, Nat. Commun. 2020, 11, 4066.
- [65] D. Wu, L. Hu, X. Liu, T. Liu, X. Zhu, Q. Luo, H. Zhang, L. Cao, J. Yang, Z. Jiang, T. Yao, *Nat. Commun.* **2025**, *16*, 726.

- [66] H. Lei, L. Ma, Q. Wan, S. Tan, B. Yang, Z. Wang, W. Mai, H. J. Fan, Adv. Energy Mater. 2022, 12, 2202522.
- [67] X. He, X. Han, X. Zhou, J. Chen, J. Wang, Y. Chen, L. Yu, N. Zhang, J. Li, S. Wang, H. Jin, *Appl. Catal. B Environ.* **2023**, *331*, 122683.
- [68] W. He, R. Zhang, H. Liu, Q. Hao, Y. Li, X. Zheng, C. Liu, J. Zhang, H. L. Xin, Small 2023, 19, 2301610.
- [69] M. H. Wang, Z. X. Lou, X. Wu, Y. Liu, J. Y. Zhao, K. Z. Sun, W. X. Li, J. Chen, H. Y. Yuan, M. Zhu, S. Dai, P. F. Liu, H. G. Yang, *Small* **2022**, *18*, 2200303.
- [70] V. Jose, V.-H. Do, P. Prabhu, C.-K. Peng, S.-Y. Chen, Y. Zhou, Y.-G. Lin, J.-M. Lee, *Adv. Energy Mater.* **2023**, *13*, 2301119.
- [71] C. Feng, Z. Zhang, D. Wang, Y. Kong, J. Wei, R. Wang, P. Ma, H. Li, Z. Geng, M. Zuo, J. Bao, S. Zhou, J. Zeng, J. Am. Chem. Soc. 2022, 144, 9271.
- [72] J. Jiang, F. Sun, S. Zhou, W. Hu, H. Zhang, J. Dong, Z. Jiang, J. Zhao, J. Li, W. Yan, M. Wang, *Nat. Commun.* **2018**, *9*, 2885.
- [73] P. E. Blöchl, Phys. Rev. B. 1994, 50, 17953.
- [74] G. Kresse, J. Furthmüller, Comput. Mater. Sci. 1996, 6, 15.
- [75] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.
- [76] J. K. Nørskov, J. Rossmeisi, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard, H. Jonsson, J. Phys. Chem. B 2004, 108, 17886.