Reversible hydrogen spillover at the atomic interface for efficient alkaline hydrogen evolution†

Tingting Chao,‡ab Wenbo Xie,‡cd Yanmin Hu,‡ab Ge Yu,‡ Tonghui Zhao,‡ Cai Chen,‡ Zedong Zhang,‡ Xu Hong,‡ Huile Jin,‡ Dingsheng Wang,‡ Wei Chen,‡ Xinhua Li,‡* P. Hu‡cd and Yadong Li‡e

Ruthenium-based electrocatalysts exhibit promising potential as alternatives to platinum for catalyzing the hydrogen evolution reaction (HER) in alkaline media. However, the hydrogen binding ability and sluggish water dissociation kinetics of Ru catalysts require further optimization. Herein, we report a novel dual-site synergistic catalyst, Ru1–Mo2C, that simultaneously achieved high activity and stability for the HER via a reversible hydrogen spillover mode. The electronic metal–support interaction significantly modulated the charge redistribution of Ru1–Mo2C, resulting in an optimized d-band center and binding strength of H*. Density functional theory calculations revealed that water dissociation proceeded on Mo2C, and the generated hydrogen atoms were subsequently transferred to adjacent Ru single atom sites for H2 formation and release, enabling the reaction to adopt a reversible hydrogen spillover mechanism. As a consequence, Ru1–Mo2C exhibited an excellent HER performance with an ultralow overpotential of 10.8 mV at 10 mA cm−2 and mass activity of 8.67 A mgPJM−1 (f100 mV), which is 16.7 times greater than that of commercial Pt/C catalysts. Alkaline exchange membrane water electrolysis with Ru1–Mo2C as a cathodic catalyst achieved 1.0 A cm−2 at 1.83 V and remained stable at 500 mA cm−2 for over 200 hours.

Broader context
Water electrolysis for hydrogen production is environmentally friendly, and alkaline conditions are cost-effective for large-scale applications. However, the alkaline hydrogen evolution reaction (HER) is less efficient than the acidic HER due to an extra step for water dissociation. To remedy this, we created a Ru1–Mo2C catalyst with single atomic Ru sites on defect-rich Mo2C nanosheets. Through experiments and theory, we found that the unique structure of Ru1–Mo2C adjusted electron distributions, aiding H* activation and H2 release. The Mo and Ru sites on Ru1–Mo2C promoted water dissociation and H* adsorption, respectively, driving the HER through a reversible hydrogen spillover mechanism. Ru1–Mo2C showed remarkable performance with a low overpotential (10.8 mV at 10 mA cm−2) and high mass activity (8.67 A mgcat−1 at 100 mV), surpassing Pt/C catalysts. This work deepens our comprehension of catalytic mechanisms in the alkaline HER and provides valuable guidance for designing more effective catalysts.

Hydrogen production via water electrolysis is an effective and environmentally friendly pathway for generating high-purity hydrogen gas.1–3 Compared to acidic water electrolysis, there is greater cost-effectiveness and stability when the hydrogen evolution reaction (HER) is performed in alkaline media, especially at high current densities, which offers great potential for large-scale applications.4–6 Nevertheless, the alkaline HER is two orders of magnitude inferior than that in acid media due to the additional Volmer step (H2O + e− ↔ HOH + H+) required for water dissociation.7,8 Consequently, the development of efficient catalysts for the alkaline HER to enhance its reaction kinetics is of paramount importance.

Because ruthenium (Ru)-based catalysts exhibit hydrogen adsorption free energy that is similar to that of Pt, they have been extensively explored in recent years to determine their suitability in performing alkaline water electrolysis.9–13 However, because of the low storage and high cost of precious metals, there have been severe constraints on their widespread application. Single-atom catalysts (SACs) have shown great advantages in reducing the amount of metal usage and achieving the maximum utilization of precious metals.14–17 Although several studies have demonstrated
that Ru single-atom catalysts display remarkable efficiency in acidic HER reactions, their performance in alkaline HER is subpar.\textsuperscript{18–20}

Experimental and theoretical analyses by Cho et al. have revealed that the limited capacity of Ru SACs for water dissociation ultimately restricts the overall reaction kinetics, despite their suitable binding energy for hydrogen (H\textsuperscript{*}).\textsuperscript{21} Furthermore, Ru single atoms exhibit strong adsorption to the OH produced in the Volmer step, which can lead to catalyst surface poisoning and decreases the HER reaction rate.\textsuperscript{22–24} Therefore, identifying a suitable support with robust water dissociation ability to immobilize single Ru atoms is crucial for enhancing the HER catalytic activity.

As is well known, support materials play a pivotal role in stabilizing SACs and optimizing their electronic structure through strong metal–support interaction.\textsuperscript{25–29} However, SACs based on conventional supports such as metallic oxide, sulfide, or phosphide are far from satisfactory due to their lack of electric conductivity and stability in the alkaline HER.\textsuperscript{30,31} Studies have shown that transition metal carbides from groups 4–6 exhibit excellent chemical and thermal stability, superior corrosion resistance, and high conductivity.\textsuperscript{32–34} Moreover, the low electronegativity of carbon may be beneficial for optimizing the electronic structure and enhancing the HER activity of Ru single-atom catalysts, unlike strongly electronegative atoms such as O/N/P/S that can deplete the d electrons involved in the reaction kinetics.\textsuperscript{35,36}

Specifically, metal carbide supports can promote atomic dispersion of the supported metal through strong electronic interactions, triggering orbital hybridization and charge polarization at the interface to regulate catalytic activity.\textsuperscript{37–39} More importantly, it has been reported that carbides exhibit commendable water-splitting activity,\textsuperscript{40–42} which can improve the Volmer step reaction rate, and subsequently generate additional surface H\textsuperscript{*}. When combined with the excellent H\textsuperscript{*}-binding energy of Ru SACs, this will further promote the overall efficiency of the HER. Despite numerous advantages, there have been few studies that have focused on the fine-tuning of the interfacial interaction between carbides and single-atom Ru for the HER and their synergistic mechanisms.

Herein, we report the construction of single atomic Ru sites on Mo\textsubscript{2}C nanosheet arrays (NSAs) with abundant defects (Ru\textsubscript{1–}Mo\textsubscript{2}C), with the goal of designing excellent catalysts for the alkaline HER and studying their synergistic catalysis mechanism. Experimental analysis combined with density functional theory (DFT) calculations revealed that the charge redistribution induced by the introduction of single Ru atoms in Ru\textsubscript{1–}Mo\textsubscript{2}C optimized the d band center away from the Fermi level, which facilitated H\textsuperscript{*} activation and the subsequent H\textsubscript{2} desorption. Additionally, the Mo active sites and Ru single atoms on Ru\textsubscript{1–}Mo\textsubscript{2}C exhibited favorable adsorption affinities for H\textsubscript{2}O and H\textsuperscript{*}, respectively, synergistically facilitating water dissociation and hydrogen recombination for the HER through a reversible hydrogen spillover mechanism.

Consequently, the Ru\textsubscript{1–}Mo\textsubscript{2}C manifested an ultralow overpotential of 10.8 mV at 10 mA cm\textsuperscript{2} and mass activity of 8.67 A mg\textsubscript{Ru} cm\textsuperscript{−1} @100 mV), which is 16.7-fold larger than that of commercial Pt/C catalysts. An alkaline exchange membrane water electrolysis (AEMWE) device with a Ru\textsubscript{1–}Mo\textsubscript{2}C cathodic catalyst reached 1.0 A cm\textsuperscript{2} at a low voltage of 1.83 V and survived after 200 h of operation at 500 mA cm\textsuperscript{−2}.

Ru SAC-covered Mo\textsubscript{2}C nanosheets (Ru\textsubscript{1–}Mo\textsubscript{2}C NSs) were synthesized by a wet-impregnation method, as depicted in Fig. 1a. First, a mixture of ammonium molybdate tetrahydrate and ethylenediamine was reacted at 150 °C for 12 h under suitable pH values adjusted using acetic acid. The above precursor was calcinated at 450 °C for 2 h under a 5% H\textsubscript{2}/N\textsubscript{2} atmosphere to acquire Mo\textsubscript{2}C NSs. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images in Fig. S1 (ESI†) show that Mo\textsubscript{2}C synthesized at a rather low temperature possessed the morphology of curled nanosheets with abundant vacancies and defects in the surface, which can provide sufficient attachment sites for single atoms (Fig. S2, ESI†).\textsuperscript{43,44} Then, the as-prepared Mo\textsubscript{2}C NSs were impregnated with a solution including RuCl\textsubscript{3}·xH\textsubscript{2}O at a concentration of 1.6 mM at room temperature for 24 h. Finally, the adsorbed Ru species were reduced at 300 °C for 2 h under a 5% H\textsubscript{2}/N\textsubscript{2} atmosphere to obtain Ru\textsubscript{1–}Mo\textsubscript{2}C NSs.

The SEM image in Fig. 1b indicates that the curled nanosheet structure was maintained for the Ru\textsubscript{1–}Mo\textsubscript{2}C NSs, which are difficult to stack together and conducive to structural stability. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images in Fig. 1c and Fig. S3 (ESI†) further visualize the nanosheet structure with numerous pores and holes in the surface of the Ru\textsubscript{1–}Mo\textsubscript{2}C NSs, which can ensure its high surface area. Moreover, no obvious nanoparticles appeared after the deposition of Ru, excluding the formation of Ru particles. Scanning transmission electron microscopy energy-dispersive X-ray spectroscopy (STEM-EDS) elemental mapping in Fig. 1d demonstrated that the nanosheet was mainly composed of Mo and C elements, as well as a small amount of Ru (Fig. S4, ESI†). The amount of Ru in the Ru\textsubscript{1–}Mo\textsubscript{2}C NSs was 0.41 wt%, which was identified by the inductively coupled plasma and atomic emission spectrum (ICP-AES) results. The lattice spacings in Fig. 1e were 0.206 nm, and were ascribed to the (200) crystal facets of Mo\textsubscript{2}C. The magnified HAADF-STEM image in Fig. 1f shows discrete light dots encircled in red, which indicate Ru atoms that exist as single atom sites. The line intensity profile taken along the yellow dashed rectangle and the corresponding surface intensity profile also demonstrate that the Ru atoms were atomically dispersed on the Mo\textsubscript{2}C surface with a dramatically enhanced brightness contrast (Fig. 1g).

The crystal structures of Mo\textsubscript{2}C and Ru\textsubscript{1–}Mo\textsubscript{2}C were investigated by the X-ray diffraction (XRD) technique. In Fig. S5 (ESI†), the characteristic diffraction peaks at 37.47°, 43.66°, and 63.44° are indexed to the (111), (200), and (220) crystal planes of PDF#15-0457, respectively. For the Ru\textsubscript{1–}Mo\textsubscript{2}C sample, no peak ascribed to metal Ru particles was observed, indicating the single-atom nature of Ru\textsubscript{1}. The surface chemical composition and valence state of Ru\textsubscript{1–}Mo\textsubscript{2}C were assessed by X-ray photoelectron spectroscopy (XPS) measurements (Fig. S6, ESI†). As compared to pure Mo\textsubscript{2}C, the peaks corresponding to Ru species were detected in the Ru\textsubscript{1–}Mo\textsubscript{2}C sample (Fig. 2a). In the Ru 3p XPS spectra, there were two peaks of 3p\textsubscript{3/2} and 3p\textsubscript{1/2} in Ru\textsubscript{1–}Mo\textsubscript{2}C at approximately...
461.92 eV and 484.1 eV, respectively, which were much lower than those of RuO₂ (464.12 and 486.33 eV). This revealed the valence state of Ru₁ in the Ru₁–Mo₂C range between Ru(0) and Ru(IV). 45,46 Fig. 2b exhibits the Mo 3d XPS spectra of Mo₂C and Ru₁–Mo₂C. The binding energies for Mo₂C can be deconvoluted into six peaks, attributed to Mo²⁺ (228.91 and 232.06 eV), Mo⁴⁺ (230.01 and 233.15 eV), and Mo⁶⁺ (232.08 and 235.26 eV) species. The Mo⁶⁺ and Mo⁴⁺ species are commonly observed in two-dimensional Mo-based materials mainly because of the O, OH, or H terminations on the Mo₂C surface.47,48 The slight negative shift of the Mo 3d peaks for Ru₁–Mo₂C in comparison to Mo₂C imply a charge transfer between Mo₂C and Ru.

The electronic structural change in Ru₁–Mo₂C and Mo₂C can be further verified by the X-ray absorption near-edge structure (XANES). As shown in Fig. 2c, the Mo K-edge XANES spectra demonstrate that the absorption edge of Ru₁–Mo₂C is located between that of Mo foil and MoO₃, signifying that the oxidation state of Mo species is between 0 and +6. Furthermore, the XANES of the Mo K-edge of Ru₁–Mo₂C shows a negative shift compared to that of Mo₂C, suggesting a decrease in the Mo oxidation state after introducing Ru, which was consistent with the XPS results. The white line intensity of Ru₁–Mo₂C was lower than that of Mo₂C, yet higher than that of Mo foil, indicating the presence of unsaturated Mo coordination species.

The Fourier transform (FT) Mo K-edge extended X-ray absorption fine structure (EXAFS) of Ru₁–Mo₂C exhibited a major peak located at approximately 1.42 Å that was ascribed...
to the Mo–C coordination in the first shell, which is lower than that of Mo2C (approximately 1.53 Å) and revealed the Mo–C compression in Ru1–Mo2C (Fig. 2d). The second shell of Ru1–Mo2C was located at approximately 2.69 Å, which was attributed to the Mo–M (M = Mo, Ru) scattering paths. Furthermore, wavelet transform (WT) of the Mo K-edge EXAFS oscillations of samples was performed, which offers high-resolution capabilities in K and R spaces (Fig. 2e). From the WT contour plots of Ru1–Mo2C, the maximum intensity values at 5.5 and 7.0 Å/C0 corresponded to the Mo–C and Mo–M (where M = Mo, Ru) contributions, respectively.

The electrochemical HER performance of Ru1–Mo2C NSs was evaluated in N2-saturated 1.0 M KOH electrolyte with a typical three-electrode system. For comparison, samples of Mo2C NSs, NF, Ru/NF, commercial Pt/C and Ru/C were tested under the same conditions. The HER polarization curves in Fig. 3a reveal the strongest electrocatalytic activity of Ru1–Mo2C NSs, with the synergistic effects of isolated Ru atoms and Mo2C substrate. As displayed in Fig. S7a (ESI†), the required overpotentials at the current density of 10 mA cm−2 (η10) and 100 mA cm−2 (η100) for the Ru1–Mo2C NSs are 10.8 mV and 56.8 mV, respectively. The overpotentials are much lower than those of the contrasting samples: Mo2C NSs (η10 = 68.6 mV, η100 = 170.7 mV), NF (η10 = 159.7 mV, η100 = 304.2 mV), Ru/NF (η10 = 33.4 mV, η100 = 115.3 mV), commercial Pt/C (η10 = 29.9 mV, η100 = 175.5 mV), and Ru/C (η10 = 34.9 mV, η100 = 245.5 mV). The deposition of a trace amount of Ru realizes the goal of lower overpotential to attain a greater current density. Moreover, Fig. 3b indicates that the Tafel slope of the Ru1–Mo2C NSs is 38.5 mV dec−1, which is less than those of Mo2C NSs (87.7 mV dec−1), NF (136.5 mV dec−1), Ru/NF (55.4 mV dec−1), commercial Pt/C (41.0 mV dec−1), and Ru/C (75.5 mV dec−1). The lower Tafel slope suggests faster kinetics on Ru1–Mo2C NSs, which is believed to follow the Volmer–Heyrovsky mechanism.

The electrochemical impedance spectroscopy (EIS) in Fig. S7b (ESI†) indicates that the Ru1–Mo2C NSs possess a smaller charge transfer resistance (Rct) of 1.03 Ω as compared to those of other samples, which further demonstrates a more rapid HER kinetic process for the Ru1–Mo2C NSs. Impressively, the Ru1–Mo2C NS catalysts exhibited a remarkably high mass activity compared with previously reported HER electrocatalysts (Fig. 3c and Table S1, ESI†), indicating a high utilization of noble metals. The electrochemical double-layer capacitance (Cdl), which is generally considered to be proportional to the electrochemical surface area (ECSA), was investigated and is presented in Fig. 3d and Fig. S8 (ESI†). The value of Cdl for the Ru1–Mo2C NSs was 31.8 mF cm−2, which is much higher than those of Mo2C NSs (3.49 mF cm−2) and Ru/NF (11.0 mF cm−2). Thus, there is exposure of a greater number of catalytic active sites on the surface of the Ru1–Mo2C NSs, which is closely correlated with its excellent activity. Exchange current density (j0) is an important parameter that indicates the electron transfer rate between the electrode and catalyst surface, and can be obtained by extrapolating the Tafel plots. As shown in Fig. S9 (ESI†), the exchange current density

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Fig. 2 Structural characterization. XPS spectra of (a) Ru 3p and (b) Mo 3d for different catalysts. (c) XANES spectra and (d) the FT-EXAFS spectra for Mo k-edge. (e) Wavelet transforms for the k3-weighted Mo k-edge EXAFS signals of Mo foil, Mo2C, Ru1–Mo2C, and MoO3.
of the Ru$_1$–Mo$_2$C NSs is 4.04 mA cm$^{-2}$, which is 2.78-fold and 2.22-fold higher than those of Mo$_2$C NSs (1.45 mA cm$^{-2}$) and Ru/NF (1.82 mA cm$^{-2}$), respectively.

According to the estimated number of active sites, the turnover frequency (TOF) values of various catalysts were calculated to assess their intrinsic HER performance (Fig. 3e). As shown in Fig. 3f and Fig. S10 (ESI†), the Ru$_1$–Mo$_2$C NSs exhibited an ultrahigh TOF value of 3.16 H$_2$ s$^{-1}$ and mass activity of 8.67 A mg PGM$^{-1}$ under an overpotential of 100 mV, which are much higher values than those of commercial Pt/C (0.46 H$_2$ s$^{-1}$, 0.52 A mg$_{Pd}$ m$^{-2}$), Ru/NF (0.88 H$_2$ s$^{-1}$, 1.82 A mg$_{Ru}$ m$^{-2}$), and Ru/C (0.17 H$_2$ s$^{-1}$, 0.36 A mg$_{Ru}$ m$^{-2}$). To the best of our knowledge, Ru$_1$–Mo$_2$C NSs exhibit an extremely low overpotential with low Ru loading that is superior to state-of-the-art noble metal-based electrocatalysts (Fig. 1g and Table S2, ESI†).

Electrocatalytic durability represents another important criterion that can be used to determine the practical application potential of a catalyst. A continuous cycling test was conducted at a potential range from 0.05 V to 0.2 V to evaluate the stability of the Ru$_1$–Mo$_2$C NSs. As displayed in Fig. 3h, the HER activity of the Ru$_1$–Mo$_2$C NSs showed negligible attenuation after 10 000 continuous cycles, and probably resulted from the strong anchoring ability of the Mo$_2$C substrate. In contrast, Ru/NF and commercial Pt/C exhibited a marked decrease in activity after 10 000 cycles (Fig. S11, ESI†). In addition, long-term chronoamperometry at the potential of $-56.8$ mV was performed to further monitor the stability of the Ru$_1$–Mo$_2$C NSs. The inset in Fig. 3h indicates that the current density of Ru$_1$–Mo$_2$C NSs was well maintained even after 140 h, which demonstrated its superior stability during the HER catalytic process.
process. The above results reveal that the rapid charge transfer capability, fully exposed electrocatalytically active sites, and strong metal–support electronic interaction endow the Ru1–Mo2C NS catalyst with superior HER activity and stability.

To further confirm the exceptional activity and durability for the HER, the Ru1–Mo2C catalyst was integrated into a membrane electrode assembly (MEA) and evaluated under practical water electrolysis working conditions. As shown in Fig. 4a, an alkaline exchange membrane water electrolysis (AEMWE) device was constructed with Ru1–Mo2C as the cathodic catalyst and NiFe layered double hydroxide (LDH) on Ni foam as the anode. Fig. 4b illustrates the current–voltage curves for Ru1–Mo2C and a commercial Pt/C-based MEA at 65 °C. Impressively, the Ru1–Mo2C-based electrolyser achieved industrial-level current densities of 1.0 and 2.0 A cm⁻² at low cell voltages of 1.83 and 2.03 V, respectively, which were much lower than that of commercial Pt/C (2.03 V@1.0 A cm⁻² and 2.42 V@2.0 A cm⁻²).

The Ru1–Mo2C-based MEA achieved a current density of 1.0 A cm⁻² at a cell voltage that is comparable to that of a recently reported Pt-based MEA (Table S3, ESI†), despite approximately 1 order of magnitude lower platinum-group metal (PGM) loading (approximately 13 μgRu cm⁻²). Considering the ultralow PGM loading of the Ru1–Mo2C, the mass activity of Ru1–Mo2C reached 21.1, 68.3, and 138.5 A mg⁻¹ at working potentials of 1.6, 1.8, and 2.0 V, respectively, which was approximately 28 times larger than that of commercial Pt/C (Fig. 4c) and demonstrated a significant improvement in the mass activity for Ru1–Mo2C as compared to commercial Pt/C. Moreover, remarkable stability was exhibited for AEMWE with Ru1–Mo2C as the cathode, and it maintained a consistent voltage of approximately 1.70 V with no significant increase over 200 hours of continuous operation at an industrial current density of 500 mA cm⁻² (Fig. 4d). Hence, it can be inferred that Ru1–Mo2C holds promising potential for application in an AEMWE device.

As for the HER under alkaline conditions, the electrocatalysis primarily relies on the dissociation of water molecules to provide hydrogen atoms. Therefore, it is crucial for catalysts to possess a robust ability to adsorb water molecules to facilitate the water-dissociation process. Potential-dependent in situ Raman measurements were carried out in 1 M KOH to assess the H₂O adsorption capacity of the catalysts. The operando Raman spectra of Ru1–Mo2C and Ru/NF were conducted over a potential range from +0.3 to −0.2 V (vs. RHE), covering the transition from non-faradaic to the HER region (Fig. S12, ESI†). The signal at 1630 cm⁻¹ was attributed to the H–O–H bending mode of the interfacial water.¹³,⁴⁹ The adsorption of H₂O on Ru1–Mo2C exhibited a clear trend of increasing intensity as the potential decreased from +0.30 to 0.00 V vs. RHE (Fig. S12a, ESI†). However, Ru/NF displayed a notably weak adsorption intensity (Fig. S12b, ESI†). The enhanced water adsorption capability of Ru1–Mo2C was thought to expedite the Volmer
step, thereby supplying an ample quantity of hydrogen atoms for the subsequent reaction stage. The decrease in the $H_2O$ adsorption intensity on $Ru_1-Mo_2C$ and Ru/NF in the HER region from 0.00 V to $-0.20$ V vs. RHE was attributed to the process of water dissociation.

To obtain a more in-depth molecular-level understanding of the HER process on Ru$_1$-Mo$_2$C, DFT calculations were carried out to further confirm the active sites and reaction mechanisms. The experimental results above show that Ru atoms were dispersed on the surface, forming a Ru$_1$-Mo$_2$C SAC, and they

![Theoretical calculations](image-url)
played a dominant role in achieving superior HER performance compared to Ru and Mo2C. Herein, we investigated the reaction pathways of HER on the Ru1–Mo2C(200) surface, as well as on the Mo2C(200) and Ru(0001) surfaces for comparison.

There are three key steps in the proposed HER reaction mechanism: H2O adsorption, H2O* dissociation, and the formation of H2. A theoretical model with a Ru atom embedded into Mo2C(200) by replacing a Mo atom was adopted in this work, shown in Fig. S13 (ESI†), and the complete HER reaction on Ru1–Mo2C(200) is depicted in Fig. 5a. For the water adsorption step, the calculated binding energies of H2O on Mo2C, Ru1–Mo2C, and Ru(0001) are −0.63, −0.71, and −0.47 eV, respectively. The water dissociation was calculated because the HER efficiency relies on water dissociation to provide ample hydrogen atoms. The identified key intermediates and transition states for the water dissociation steps on Ru(0001), Mo2C, and Ru1–Mo2C are shown in Fig. 5a, Fig. S14–S19 and Table S4 (ESI†).

As shown in Fig. 5b, the activation energy barrier for water dissociation is quite high (0.86 eV) on the Ru(0001) surface, implying that it is kinetically unfavorable for water molecules to dissociate under normal conditions. This can be attributed to the weaker interaction between H2O and the Ru(0001) surface, and therefore, it is challenging for water molecules to dissociate. In contrast, the energy barriers for breaking the O-H bond on Mo2C and Ru1–Mo2C are 0.42 and 0.33 eV, respectively, indicating that the dissociation is relatively easy and both surfaces are active for water activation, leaving an OH* and a H* on the surface. Because H2O preferred to adsorb on the Mo site of Ru1–Mo2C, hydrogen atoms can be easily extracted from water with the assistance of surface Mo.

The ability to produce H2 was also evaluated (Fig. 5d and Fig. S20–S22, ESI†) because it is another key factor for HER activity. The produced OH* from water dissociation is subsequently dissolved back into the solution, freeing the site for another H2O to adsorb. The H* on the surface and the H* from the newly adsorbed H2O* then combine, leading to the desorption of an H2 molecule. It was calculated that the free energy barrier of this step is 0.57 eV on Mo2C and 0.42 eV on Ru1–Mo2C. The higher energy barrier on Mo2C indicates that the reaction step is hindered, which can be rationalized by the strong adsorption of H* on the Mo2C surface with a value of −0.94 eV. As shown in Fig. 5d, the free energy change in this step is −0.77 eV, representing a highly exothermic dissociation process.

This suggests that the formed H2* strongly interacts with the surface and is less likely to desorb. Unlike the reaction on Mo2C, ΔGΔH on Ru(0001) is −0.53 eV, which indicates a more active H* on the surface. Therefore, the presence of the Ru atom in the catalyst structure enhances hydrogen production by providing proton acceptors for the activation of the dissociated H*. This point can also be further confirmed by the well-established d-band center theory.56,51 The projected density of states (PDOS) analysis (Fig. 5c) shows that the ed (−1.55 eV) on Ru1–Mo2C is much farther away from the Fermi level than that (−1.15 eV) on Mo2C, which results in a much weaker binding strength on Ru1–Mo2C. The adsorption energy of H* was consequently decreased to −0.69 eV when binding to the Ru atom embodied in the Ru1–Mo2C. This created a feasible and less exothermic pathway (−0.29 eV), which indicates a weaker bonding of H2 and is beneficial because it allows for a more efficient release of H2. Hence, the well-designed Ru1–Mo2C SAC structure not only inherits and enhances the water dissociation ability of Mo2C, but it also boosts the hydrogen production by the presence of the incorporated Ru atom, thus effectively creating dual active sites and enabling the reaction to adopt a hydrogen spillover mechanism. This overcomes the limitations of pure Mo2C, leading to a significant improvement in HER performance, as experimentally observed.

In summary, we report the construction of single-atom Ru sites on Mo2C nanosheets with abundant defects, exhibiting excellent alkaline HER performance. Specifically, Ru1–Mo2C demonstrated a remarkably low overpotential of 10.8 mV at 10 mA cm−2 and a mass activity of 8.67 A mg PGM−1 (@100 mV), which is 16.7 times higher than that of commercial Pt/C catalysts. As evidenced by experimental analysis and DFT calculations, we attribute the superior activity of the catalyst to the optimized H* binding strength and synergistic effect of the isolated Ru site and Mo2C.

In brief, the charge redistribution caused by the electron transfer from Ru single atoms to Mo atomic sites optimizes the center of the d-band away from the Fermi level, facilitating H* activation and subsequent H2 desorption. Moreover, the Mo sites and Ru single-atom sites on Ru1–Mo2C displayed favorable adsorption affinities for water and H* species, respectively. The complementary adsorption behavior synergistically facilitated water dissociation and hydrogen recombination, promoting the HER through a reversible hydrogen spillover mechanism. These findings enhance our understanding of alkaline HER catalytic mechanisms and offer valuable insights for the development of efficient catalysts.

Author contributions
T. C., W. C., X. L., and Y. L. conceived the idea and co-wrote the paper. T. C., Y. H., and T. Z. carried out the sample synthesis and HER measurements. G. Y., X. H., H. J., and D. W. contributed to the sample characterization. Z. Z. and C. C. assisted with the XAFS measurements and discussion. W. X. and P. H. performed the DFT calculations. All authors contributed to the overall scientific interpretation and edited the manuscript.

Conflicts of interest
There are no conflicts to declare.

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