The synergistic effect of Hf-O-Ru bonds and oxygen vacancies in Ru/HfO₂ for enhanced hydrogen evolution

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Ru nanoparticles have been demonstrated to be highly active electrocatalysts for the hydrogen evolution reaction (HER). At present, most of Ru nanoparticles-based HER electrocatalysts with high activity are supported by heteroatom-doped carbon substrates. Few metal oxides with large band gap (more than 5 eV) as the substrates of Ru nanoparticles are employed for the HER. By using large band gap metal oxides substrates, we can distinguish the contribution of Ru nanoparticles from the substrates. Here, a highly efficient Ru/HfO₂ composite is developed by tuning numbers of Ru-O-Hf bonds and oxygen vacancies, resulting in a 20-fold enhancement in mass activity over commercial Pt/C in an alkaline medium. Density functional theory (DFT) calculations reveal that strong metal-support interaction via Ru-O-Hf bonds and the oxygen vacancies in the supported Ru samples synergistically lower the energy barrier for water dissociation to improve catalytic activities.
Hydrogen produced from water splitting powered by various renewable energy sources is regarded as a sustainable and clean energy alternative to non-renewable, reserveless, and environmentally unfriendly fossil fuels\textsuperscript{1-3}. The alkaline-water electrolysis technology has been commercialized, in which Ni or Fe mesh is generally used as the electrocatalyst. The current density and energy efficiency of this technology are \(-0.25\) A/cm\(^2\) and 60\%, respectively\textsuperscript{4}, which can be further improved by developing more highly active electrocatalysts. Among the known electrocatalysts, platinum group metals and alloys show excellent activities for the hydrogen evolution reaction (HER), for example, Pt/C is the benchmark electrocatalyst for HER, and its analogs Ru/C also exhibits a large room for improvement in activity because of its similar bond strength with hydrogen as Pt\textsuperscript{4-13}. Recently, our group explored the dominant role of atomic- and Ru nanoparticles as for the HER\textsuperscript{11}, in which atomic-Ru plays a dominant role for the HER in acid electrolyte because of its appropriate H\(^+\) adsorption strength, and meanwhile Ru NPs facilitate the dissociation of H\(_2\)O in alkaline electrolyte. Other groups also reported a few highly efficient Ru/C HER catalysts, such as Ru nanoparticles anchored on N-doped carbon, graphene nanoplatelet, and carbon quantum dot\textsuperscript{7,10,13}. Among the above electrocatalysts, heteroatom-doped carbon-based substrates not only had excellent electrocatalyst activity but also showed some activities for the HER. However, the Ru nanoparticles often fall off from the carbon substrates and thus cause catalyst failure. To enhance the stability of Ru nanoparticles, transition metal oxides often were chosen as the substrates, such as TiO\(_2\), CeO\(_2\) and ZrO\(_2\), the strong interaction between Ru nanoparticles and metal oxides can suppress detachment of catalysts from the substrates. Importantly, the interaction can tune surface electronic structure and energy level of Ru nanoparticles by the formation of Ru-O-M (M = Ti, Ce, Zr) bonds in Ru/MO\(_2\) nanocomposites that were used for various thermal-catalysis reactions, such as carbon oxide methanation\textsuperscript{14}, dry reforming of methane\textsuperscript{15} and hydrogenation of levulinic acid\textsuperscript{16}. Huang et al. reported a Ru-doped TiO\(_2\) HER electrocatalyst in an alkaline solution, in which the Ru\(^{3+}\) and Ti\(^{3+}\) synergistically enhanced the activity with appropriate hydrogen-adsorption Gibbs free energies\textsuperscript{17}. In addition, the crystalline, morphology, and electronic structure of metal oxides themselves also have a profound effect on the electrocatalytic performance of Ru/MO\(_2\) nanocomposites, for example, the enriched surface defects of CeO\(_2\) are favorable for the formation of Ru-O-Ce bonds by Ru ions diffusing into CeO\(_2\) surface lattice\textsuperscript{18}. So far, the H\(_2\)O is seldom used as the substrate or active component in electrocatalysis because of its large bandgap. However, it had been applied in thermal catalysis. As a Lewis acid site, isolated Hf facilitates acetone conversion to isobutene\textsuperscript{19}. Pd/H\(_2\)O\(_2\) has been reported to be highly active for methane combustion\textsuperscript{20}. By constructing a composite of Ru nanoparticles supported by H\(_2\)O\(_2\) substrate with oxygen defect, can the surface electronic structure of Ru nanoparticles be well optimized as highly efficient HER electrocatalyst?

In this work, we demonstrate that Ru nanoparticles supported by oxygen vacancies-riched H\(_2\)O\(_2\) (V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP, V\(_O\), O, and P refer to oxygen vacancies, oleylamine, and polyvinyl pyrrolidone, respectively) exhibit excellent HER activity and stability in alkaline electrolytes. The Ru content is only 0.9 wt%, which greatly decreases the price of the catalyst compared with that of commercial Ru/C and Pt/C. The interaction between Ru nanoparticles and H\(_2\)O\(_2\) by Ru-O-Hf bonds as well as V\(_O\) in the substrate synergistically promote the water dissociation. DFT calculations reveal that the d-band center of Ru could be tuned closer to the Fermi level owing to the synergistic effects of the Ru-O-Hf bonds and V\(_O\), which is beneficial for the adsorption of water, as it lowers the energy barrier for water dissociation.

### Results and discussion

#### Phase and structural characterizations

Preparation of V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP was conducted in two continuous steps. First, a modified polyol process with oleylamine and polyvinyl pyrrolidone as structure-directing agents was employed to prepare pristine Ru/Ru/H\(_2\)O\(_2\)-OP. Second, V\(_O\) was introduced by annealing under a H\(_2\)/Ar atmosphere. The primary crystalline phase in V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP was identified as monoclinic H\(_2\)O\(_2\) with the lattice parameters of \(a = 0.512\) nm, \(b = 0.517\) nm, and \(c = 0.530\) nm (PDF No. 97-005-7385) by X-ray diffraction (XRD) patterns (Fig. 1a). No diffraction peaks of Ru can be detected because of the ultralow content of Ru in the composite, which is only 0.9 wt%, as determined by inductively coupled plasma atomic emission spectrometry. Field-emission scanning electron microscopy (FESEM) shows that the V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP nanoparticles are uniformly dispersed (Fig. 1b). Figure 1c and Supplementary Fig. 1 show the typical TEM images of V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP, which demonstrate that the nanoparticles have a porous structure and a diameter of 60–80 nm. The high-resolution TEM (HRTEM) image shown in Fig. 1c corresponds to the region depicted in Fig. 1d, marked with a brown rectangle. The measured lattice spacing of 0.261 nm was attributed to the (002) plane of monoclinic H\(_2\)O\(_2\). The hexagonal close-packed (hcp) lattice with a lattice spacing of 0.234 nm is assigned to Ru nanoparticles\textsuperscript{21}. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image shown in Fig. 1f further demonstrates the porous structure of the V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP catalyst. The corresponding elemental mappings (Fig. 1g–i) show that Hf, O, and Ru are uniformly distributed in the nanoparticles. V\(_{O}\)-Ru/H\(_2\)O\(_2\)-P, V\(_{O}\)-Ru/H\(_2\)O\(_2\)-O, and pristine H\(_2\)O\(_2\) were also prepared following a similar synthetic procedure to that for V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP, except for the addition of oleylamine, PVP, or RuCl\(_3\)-xH\(_2\)O. The basic physical characterizations of V\(_{O}\)-Ru/H\(_2\)O\(_2\)-P, V\(_{O}\)-Ru/H\(_2\)O\(_2\)-O, and pristine H\(_2\)O\(_2\) are shown in Supplementary Figs. 2–6. The XRD pattern of V\(_{O}\)-Ru/H\(_2\)O\(_2\)-P shows clear diffraction peaks corresponding to the hexagonal crystal structure of Ru (PDF No. 99-000-3234) (Supplementary Fig. 3a). The average diameter of the Ru nanoparticles in V\(_{O}\)-Ru/H\(_2\)O\(_2\)-P is 7 nm, calculated according to the Debye–Scherrer equation\textsuperscript{22}, which is comparable to the EDS elemental linear scanning result (Supplementary Fig. 5b). The larger size of Ru nanoparticles in V\(_{O}\)-Ru/H\(_2\)O\(_2\)-P indicates the key role of oleylamine in tuning the size of the Ru nanoparticles. The addition of PVP as a stabilizer effectively prevented the aggregation of H\(_2\)O\(_2\) nanoparticles.

Advanced characterization techniques, including X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) measurements, were employed to gain insights into the valence state and elemental composition of the prepared catalysts. The XPS survey spectrum further reveals that Hf, O, and Ru are dominant in V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP (Supplementary Fig. 7). The XPS of V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP depicts a Ru 3d\(_{5/2}\) peak, which shows a significant shift to a higher binding energy relative to that of bulk Ru (Fig. 2a). These positive core level shifts involved in the smaller metal clusters supported on less conductive substrates can be interpreted by final state effects\textsuperscript{23,24}. As the final state of the photoemission process, the positive hole can be less efficiently screened, leading to a positive core level shift with decreasing particle size\textsuperscript{25}. Thus, the size of the Ru cluster in the V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP is much smaller than that of the bulk Ru. In contrast, V\(_{O}\)-Ru/H\(_2\)O\(_2\)-P shows a negative shift of 0.4 eV compared to that of V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP, owing to the larger Ru cluster size of V\(_{O}\)-Ru/H\(_2\)O\(_2\)-P. The binding energy for Ru 3d\(_{5/2}\) of V\(_{O}\)-Ru/H\(_2\)O\(_2\)-O is located in the middle of V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP and V\(_{O}\)-Ru/H\(_2\)O\(_2\)-P, demonstrating that the Ru cluster size in V\(_{O}\)-Ru/H\(_2\)O\(_2\)-O is between those of V\(_{O}\)-Ru/H\(_2\)O\(_2\)-OP and V\(_{O}\)-Ru/H\(_2\)O\(_2\)-P. The smaller size of the Ru...
cluster signifies more Ru-O-Hf bonds. Besides, the three peaks around at 284.6, 286.2, and 288.8 eV in spectra of C 1\text{s} and Ru 3\text{d} of Ru, V\text{O}-Ru/HfO\text{2}-O, and V\text{O}-Ru/HfO\text{2}-OP belong to C=C, C-O, and O-C=O, respectively, derived from the carbon contamination on the catalysts surface\textsuperscript{26}. Meanwhile, the three peaks centered at 279.7, 280.7, and 282.4 eV in the spectra of C 1\text{s} and Ru 3\text{d} of VO-Ru/HfO\text{2}-P are attributed to Ru 3\text{d}_{5/2} of Ru\textsuperscript{0}, Ru\textsuperscript{4+}, and Ru\textsuperscript{5+} \textsuperscript{17,27}, respectively, indicating the possible oxidation of catalyst sample when exposed in the air. While the remaining three peaks at 284.2, 286.0, and 288.3 eV in C 1\text{s} and Ru 3\text{d} XPS spectra of VO-Ru/HfO\text{2}-P are assigned to C 1\text{s} originated from adsorbed carbon species\textsuperscript{17}. As corroborated by Fig. 2b, the high-resolution O 1\text{s} of the as-synthesized VO-Ru/HfO\text{2}-OP catalyst presents three peaks at \sim530.1, 531.3, and 532.2 eV, corresponding to lattice oxygen, oxygen vacancies, and adsorbed water molecules, respectively, demonstrating the presence of VO\textsuperscript{28,29}. A signal at g = 2.001 resulting from the unpaired electrons trapped by VO is detected through electron paramagnetic resonance (EPR) (Supplementary Fig. 8), which further confirms the presence of VO. The binding energies of Hf 4f\textsubscript{5/2} and Hf 4f\textsubscript{7/2} core levels for VO-Ru/HfO\text{2}-OP are 18.4 and 16.7 eV (Supplementary Fig. 9a), respectively, which are in good agreement with the values of Hf 4f\textsubscript{5/2} and Hf 4f\textsubscript{7/2} doublet peaks for HfO\textsubscript{2}\textsuperscript{30}. No obvious shift in the O 1\text{s} and Hf 4f peaks of VO-Ru/HfO\text{2}-OP relative to that of pristine HfO\text{2} that could be attributed to the ultralow Ru loading on the HfO\text{2} support was observed.

The Ru K-edge XANES spectra of VO-Ru/HfO\text{2}-OP, V\text{O}-Ru/HfO\text{2}-O, and V\text{O}-Ru/HfO\text{2}-P are shown in Fig. 2c. The energy absorption threshold value of VO-Ru/HfO\text{2}-OP is between that of Ru foil and commercial RuO\textsubscript{2}, indicating that the Ru nanoparticles loaded on HfO\text{2}-OP are positively charged. The pre-edge adsorption of the Ru K-edge for V\text{O}-Ru/HfO\text{2}-P negatively shifted and becomes closer to that of the Ru foil, demonstrating the relatively low oxidation state of Ru in V\text{O}-Ru/HfO\text{2}-P than that in V\text{O}-Ru/HfO\text{2}-OP. The Ru in V\text{O}-Ru/HfO\text{2}-O exhibits a slightly higher valence state than that in V\text{O}-Ru/HfO\text{2}-OP and is closer to that of RuO\textsubscript{2}. The Fourier transform (FT) of the EXAFS spectra of the synthesized catalysts and references are shown in Fig. 2d. For VO-Ru/HfO\text{2}-OP, two scattering peaks originating from Ru-O-Hf coordination at \sim1.62 Å and Ru-Ru coordination at \sim2.36 Å were detected. The spectrum of VO-Ru/HfO\text{2}-P shows a higher intensity peak at 2.49 Å ascribed to Ru-Ru interaction and a relatively low-intensity Ru-O-Hf peak at 1.85 Å. Both peaks shifted to a higher distance compared to those of V\text{O}-Ru/HfO\text{2}-OP. The qualitative evaluation of the spectra implies that the intensity of the Ru-O-Hf bond in V\text{O}-Ru/HfO\text{2}-OP is higher than that in V\text{O}-Ru/HfO\text{2}-OP. In contrast, the intensity of the Ru-Ru bond in the catalyst is lower than that of V\text{O}-Ru/HfO\text{2}-OP. In other words, the number of Ru-O-Hf bonds in V\text{O}-Ru/HfO\text{2}-OP is greater than that in V\text{O}-Ru/HfO\text{2}-OP. The XANES spectra for the Hf L\text{3}-edge of pristine HfO\text{2}, V\text{O}-Ru/HfO\text{2}-OP, V\text{O}-Ru/HfO\text{2}-O, and V\text{O}-Ru/HfO\text{2}-P are shown in Supplementary Fig. 9b. The white line peak position of Hf L\text{3}-edge XANES for V\text{O}-Ru/HfO\text{2}-OP is located at the same position as that of pristine HfO\text{2}. Moreover, the higher white line suggests that Hf in the V\text{O}-Ru/HfO\text{2}-OP composite possesses more empty d-orbital states and thus less electron
The corresponding FT curves of the above four catalysts are shown in Supplementary Fig. 9c.

To further explore changes in the electronic structure and valence state, wavelet transform (WT) with high resolution in both k and R space analyses were carried out. Figure 2e shows the WT EXAFS contour plots of VO-Ru/HfO2-OP, VO-Ru/HfO2-O, and VO-Ru/HfO2-P. The WT EXAFS contour plots of commercial Ru and RuO2 are shown in Supplementary Fig. 10. The maximum-intensity value at $k \approx 6.5 \text{ Å}^{-1}$ ascribed to Ru-O-Hf backscattering contributions is clearly detected for VO-Ru/HfO2-OP and VO-Ru/HfO2-O. In contrast, the Ru-Ru WT signal of VO-Ru/HfO2-OP and VO-Ru/HfO2-O is very weak, which further reveals the increase in Ru-O-Hf bonds and decrease in Ru-Ru bonds tuned by oleylamine surfactants. In contrast, no obvious WT signal could be detected for Ru-O-Hf bonds of VO-Ru/HfO2-P in the lower coordination shell; however, a strong WT signal near 9.6 Å$^{-1}$ corresponding to Ru-Ru contribution was observed. Qualitative EXAFS curve fitting for both R and k space was carried out to determine the structural parameters, as shown in Supplementary Table 1; the corresponding fitting results are shown in Fig. 2f, g and Supplementary Fig. 11. The local structural parameters further demonstrate the stronger Ru-O-Hf bonds and weaker Ru-Ru bonds of VO-Ru/HfO2-OP compared to those in VO-Ru/HfO2-P, which might favor a superior HER catalytic activity.

Activity and stability evaluation. The catalytic properties of the as-synthesized VO-Ru/HfO2 series were investigated in a typical three-electrode setup using 1.0 M KOH solution as the electrolyte. Commercial Pt/C and Ru/C were used as the references. The typical polarization curves of HfO2, VO-Ru/HfO2-OP, VO-Ru/HfO2-O, and VO-Ru/HfO2-P, commercial Ru/C (Ru: 5 wt%), and Pt/C (Pt: 20 wt%) at a scan rate of 5 mV s$^{-1}$ are presented in Fig. 3a. Impressively, VO-Ru/HfO2-OP demonstrated substantially better catalytic activity than Ru/C, VO-Ru/HfO2-O, and VO-Ru/HfO2-P, indicating that a higher number of Ru-O-Hf bonds is critical to increase the HER catalytic performance. Nevertheless, pristine HfO2 is HER-inert with a negligible current, even at a high applied potential. The measured overpotential corresponding to 10 mA cm$^{-2}$ is 39, 79, 90, and 145 mV for VO-Ru/HfO2-OP, Ru/C, VO-Ru/HfO2-O, and VO-Ru/HfO2-P (Supplementary Fig. 12), respectively. As a result, VO-Ru/HfO2-OP exhibited the best catalytic activity among the investigated samples and was even close to that of state-of-the-art Pt/C. Figure 3b illustrates the Tafel slopes based on the corresponding LSV curves shown in Fig. 3a. The values are 22, 29, 44, 66, and 133 mV dec$^{-1}$ for Pt/C, VO-Ru/HfO2-OP, Ru/C, VO-Ru/HfO2-O, and VO-Ru/HfO2-P, respectively. The lower Tafel slope of VO-Ru/HfO2-OP with a higher number of Ru-O-Hf bonds highlights the effective facilitation of the hydrogen evolution kinetics. The VO-Ru/HfO2-OP also showed ultra-high mass activity (A$_{\text{noble metal}}^{-1}$ normalized by
the mass of noble metal), which is ~20 times and 17 times higher than those of commercial Pt/C and Ru/C, respectively, at an overpotential of 0.1 V (Fig. 3c). A series of CVs were employed to study the effect of electrochemically active surface areas on the intrinsic activities of the Ru/HfO2 series (Supplementary Fig. 13). As illustrated in Fig. 3d, the electrochemical double-layer capacitance (Cdl) of VO-Ru/HfO2-OP increased to 2.8 times higher than that of VO-Ru/HfO2-O, VO-Ru/HfO2-P, although it is still smaller than that of VO-Ru/HfO2-O. Next, the electrochemical Impedance spectroscopy (EIS) curves systematically studied. Evidently, the VO-Ru/HfO2-OP catalyst dosage, and the ratio of O (oleylamine) to P (PVP), were optimized to achieve the higher number of active sites as well as improved intrinsic catalytic activity, synergistically resulting in enhanced HER performance.

The electrochemical impedance spectroscopy (EIS) curves shown in Fig. 3e display a smaller charge transfer resistance (Rct) of VO-Ru/HfO2-OP (49.1 ohm) than that of Ru/C (116.5 ohm), VO-Ru/HfO2-O (200.1 ohm), VO-Ru/HfO2-P (301.7 ohm) (Supplementary Fig. 15 and Supplementary Table 2), and pristine HfO2 (4276.0 ohm), suggesting the facilitated electron transfer and thus faster electrocatalytic kinetics for HER. The increased over-potential value is merely 5 mV at a current density of 10 mA cm−2 for VO-Ru/HfO2-OP after continuous 5000 CV cycles, which is superior to that of Pt/C (7 mV) (Fig. 3f).

The chronoamperometry (CA) test results further confirmed the better long-term durability of VO-Ru/HfO2-OP than that of Pt/C. No obvious current attenuation can be observed for VO-Ru/HfO2-OP after continuous testing at a benchmark of 10 mA cm−2 for 28 h (Fig. 3g). The Fig. 3h and i show the operando Ru K-edge XANES spectra and corresponding Fourier-transformed (FT) magnitudes in operando Ru K-edge EXAFS spectra of VO-Ru/HfO2-OP before and after CA testing at −0.039 V (vs. RHE) for 12 h. Evidently, both the XANES and EXAFS are similar to the initial open-circuit voltage (OCV) ones when the applied potential returned to OCV after long-term CA testing, indicating the high stability. The optimal synthetic conditions, including the optimal molar ratio of the raw material of Ru to Hf, the optimal calcination temperature, the PVP dosage, and the ratio of O (oleylamine) to P (PVP), were systematically studied. Evidently, the VO-Ru/HfO2-OP catalyst prepared with a molar ratio of Ru to Hf of 1:1, an annealing temperature of 750 °C, the 50 mg PVP, and the ratio of O to P of 4:5 showed the best electrocatalytic activity for HER (Supplementary Figs. 16–19).

In situ and operando XAS analysis of VO-Ru/HfO2-OP. In order to monitor the electronic state of the Ru active sites during the HER, potential-dependent Ru K-edge XAS measurements were performed using a home-made operando three-electrode cell
system. Figure 4a, b and Supplementary Fig. 20 present the operando Ru K-edge XANES spectra recorded at different potential from open-circuit condition to −0.6 V (vs. RHE). Three important peaks labeled as pre-edge peak (1s → 4d transition), white line peak (1s → 5p transition), and maximum peak (1s → 5p transition multiple scattering), are obviously changed along with the applied potentials. The variation can be more clearly discerned from the differentiated Ru K-edge XANES intensity (1Ith − 1Ist) in operando Ru K-edge XANES spectra. (c) Three-dimensional plot of operando Ru K-edge XANES spectra recorded at different potential from OCV to −0.6 V (vs. RHE). The reversible change of Ru valence state during the electrocatalytic HER process: 1 refers to electrode − OCV: oxidation; 2 refers to OCV − 0 V: reduction; 3 refers to 0 V − −0.1 V − −0.25 V: oxidation; 4 refers to −0.25 V − −0.4 V − −0.5 V: reduction; 5 refers to −0.5 V − −0.6 V: oxidation; 6 refers to −0.6 V − OCV back: reduction. (d) Three-dimensional plot of operando Ru K-edge FT-EXAFS spectra of V6O-Ru/HfO2-OP. Changes in the distances and intensities of Ru-Ru and Ru-O-Hf in the operando Ru K-edge FT-EXAFS spectrum of V6O-Ru/HfO2-OP.

Density functional theory calculations. Spin-polarized DFT calculations implemented in the Vienna ab initio simulation package (VASP) were performed to gain a better understanding of the enhanced performance of V6O-Ru/HfO2-OP for HER in alkaline electrolytes. The experimental results showed that the
HER performance can be improved by increasing the number of Ru-O-Hf bonds in the Ru/HfO$_2$ series. The size of the Ru nanoparticles is inversely proportional to the number of Ru-O-Hf bonds; thus, the model system for the active sites could use Ru nanoparticles with different sizes. Consequently, correlative theoretical models including Ru (001), HfO$_2$ (001), Ru$_3$, Ru$_8$, Ru$_{10}$, and Ru$_{13}$ clusters, and supported Ru clusters denoted as Ru$_x$/HfO$_2$, V$_O$-Ru$_x$/HfO$_2$, Ru$_x$/HfO$_2$, Ru$_{10}$/HfO$_2$, and Ru$_{13}$/HfO$_2$ were constructed, as shown in Supplementary Figs. 22, 23. Previous ab initio thermodynamic phase diagrams show that the (001) face is indeed a thermodynamically stable face of HfO$_2$.

The O-terminated (001) surface is the most stable surface for HfO$_2$, as revealed by total energy-based DFT calculations (Supplementary Fig. 24). Thus, the O-terminated (001) plane of HfO$_2$ was selected as the substrate for loading Ru clusters with different numbers of Ru-O-Hf bonds. In addition, to better understand the effect of oxygen vacancies, HfO$_2$ without and with O defects, the position of V$_O$ localizing, as well as V$_O$ concentration were also taken into account. As revealed by total energy-based DFT calculation, the oxygen vacancy localized on the surface of HfO$_2$ is the most stable (Supplementary Fig. 25). The calculated most stable adsorption structures of Ru$_3$ on HfO$_2$ and V$_O$-HfO$_2$ (HfO$_2$ with one O defect and the V$_O$ concentration is 1.56%) are shown in Fig. 5a, b and Supplementary Fig. 26a, respectively. The adsorption energy of Ru$_3$ on V$_O$-HfO$_2$ (−7.20 eV) is higher than that on HfO$_2$ (−5.63 eV), and hence, the Ru clusters supported on oxygen-deficient HfO$_2$ is more stable. To further increase V$_O$ concentration, a model of HfO$_2$ with double O defect (V$_2$O$_2$/HfO$_2$), and the concentration of V$_O$ is 3.12% were constructed (Supplementary Fig. 27). The larger adsorption energy of Ru$_3$ on V$_2$O$_2$/HfO$_2$ (−8.60 eV) than that on V$_O$-HfO$_2$ (−7.20 eV), demonstrating that the Ru clusters supported on V$_2$O$_2$/HfO$_2$ is more stable. The interaction between the metal and the support plays a very important role in controlling the catalysis of supported metal catalysts.

A net stronger electron transfer of 0.28 e from the Ru$_3$ cluster to defective HfO$_2$ was revealed by charge density difference analysis, which is an effective method for visualizing the charge transfer between different components as well as the bonding structures of a catalyst (Fig. 5c). Moreover, the projected density of states calculation indicates a strong orbital overlap between Ru 4$d$, Hf 5$d$, and O 2$p$ orbitals for V$_O$-Ru$_x$/HfO$_2$-OP (Fig. 5d), effectively demonstrating the strong interaction between Ru and the V$_O$-HfO$_2$ substrate.

In alkaline media, the overall HER reaction pathways include the dissociation of H$_2$O and the formation of adsorbed hydrogen intermediates (H$_2$O + e$^-$ + * → H$^+$ + OH$^-$), as well as the final hydrogen generation (H$^+$ + e$^-$→ 1/2H$_2$)\textsuperscript{40-42}. Therefore, superior alkaline HER electrocatalysts should simultaneously possess moderate H binding energy and a relatively low H$_2$O dissociation barrier. Figure 5e and Supplementary Fig. 28 show the calculated adsorbed free energy (Δ$G_{\text{H diffusion}}$) of the hydrogen intermediate on the active sites of Ru (001) (−0.32 eV), Ru$_3$/HfO$_2$-OP (−0.37 eV), V$_O$-Ru$_x$/HfO$_2$-OP (−0.34 eV), V$_2$O$_2$-Ru$_x$/HfO$_2$-OP (−0.31 eV), Ru$_x$/HfO$_2$ (−0.31 eV), Ru$_{10}$/HfO$_2$ (−0.29 eV), and Ru$_{13}$/HfO$_2$ (−0.35 eV), which varied from −0.37 to −0.29 eV, indicating favorable energetics for hydrogen adsorption and desorption to form H$_2$ from all Ru-based catalysts. However, the Δ$G_{\text{H diffusion}}$ value was 1.12 eV for HfO$_2$(001) (Supplementary Fig. 29a). Such high free energy for hydrogen adsorption hinders the formation of the H intermediate\textsuperscript{11,44}, resulting in HER-inert pristine HfO$_2$. Except for Δ$G_{\text{H diffusion}}$, the faster kinetics of water dissociation is a prerequisite for hydrogen evolution in alkaline electrolytes, which directly determines the HER activity\textsuperscript{45}. The computed adsorption energy of H$_2$O for Ru(001), Ru$_3$/HfO$_2$, Ru$_8$/HfO$_2$, Ru$_{10}$/HfO$_2$, and Ru$_{13}$/HfO$_2$ were −0.48, −0.78, −0.71, −0.68, and −0.69 eV, respectively (Fig. 5f and Supplementary Fig. 30), demonstrating the substantially stronger binding of water molecules to Ru/HfO$_2$ catalysts than those of Ru(001), and unsupported Ru clusters. Moreover, the calculated adsorption energy of H$_2$O is −0.21 eV for HfO$_2$(001) and −0.25 eV for V$_O$-HfO$_2$ (Supplementary Fig. 31), indicating the ignorable effect of V$_O$ on the adsorption of water. However, it is worth noting that the water adsorption energy of V$_O$-Ru$_3$/HfO$_2$ was −0.89 eV, it was even lower to −1.16 eV for V$_2$O$_2$-Ru$_3$/HfO$_2$ (Supplementary Fig. 27c); in fact, it is the lowest among all the Ru/HfO$_2$ series. These results suggest that the V$_O$ do not directly participate in the adsorption of water but play a primary role in perturbing the electron distribution of the Ru cluster. As reported in a previous study\textsuperscript{46}, the adsorption energy and dissociative kinetic barrier of H$_2$O have a linear Bronsted–Evans–Polanyi (BEP) relationship. Thus, the adsorption energy of H$_2$O can be used as an activity descriptor for the kinetic barrier of water dissociation. As shown in Supplementary Fig. 32, the energy barrier of water dissociation for Ru (001) is 0.77 eV, which is higher than that of HfO$_2$-supported Ru$_x$ (x = 3, 6, 10, 13) (Fig. 5g and Supplementary Figs. 33–36). In Ru$_x$/HfO$_2$, the energy barrier for water dissociation is 0.65 eV; hence, the Ru site in Ru/HfO$_2$ is more effective in cleaving HO-H bonds than that in Ru (001). Notably, the energy barrier is even reduced to 0.62 eV for V$_O$-Ru$_3$/HfO$_2$-OP (Supplementary Fig. 37), and 0.54 eV for V$_2$O$_2$-Ru$_3$/HfO$_2$-OP (Supplementary Fig. 38), suggesting that the HER activity of Ru/HfO$_2$ can be enhanced by introducing V$_O$ and the V$_O$ concentration also significantly influences the HER activity (Supplementary Table 3). By considering all steps of H$_2$ evolution under alkaline conditions, we can conclude that Ru/HfO$_2$-OP with O defect has the optimized energies for the dissociation of water and adsorption of hydrogen, as well as for the desorption of hydrogen to form H$_2$.

The differential charge density analysis shown in Fig. 5h shows that more charge transfer occurs from the Ru sites of V$_O$-Ru$_x$/HfO$_2$ (0.23 | e | ) to the O atom of adsorbed H$_2$O than that of Ru (001) (0.15 | e | ). Such charge transfers elongate the H-O bond of V$_O$-Ru$_x$/HfO$_2$ (1.50 | e | ) to the O atom of adsorbed H$_2$O than that of Ru (001) (1.12 | e | ), resulting in an increased adsorption energy of H$_2$O. The integrated-crystal orbital Hamilton population (ICOHP) value of Ru and adsorbed O atom in H$_2$O is −0.98 Å in free H$_2$O to 0.98 Å in adsorbed H$_2$O, making the H$_2$O molecule activated and easier to split. Figure 5i shows the PDOS of adsorbed H$_2$O and the 4$d$ orbital of the Ru atom with the corresponding 4$d$-band center. Evidently, the 4$d$-band center of V$_O$-Ru$_x$/HfO$_2$ is at −0.98 eV, which is closer to the Fermi level compared to those of Ru$_3$/HfO$_2$ (−1.04 eV) and Ru (001) (−1.50 eV). The upward shift of the Ru 4$d$-band center of V$_O$-Ru$_x$/HfO$_2$ can decrease the occupation of antibonding states and lead to strong binding to H$_2$O\textsuperscript{47}, resulting in an increased adsorption energy of H$_2$O. The integrated-crystal orbital Hamilton population (ICOHP) value of Ru and adsorbed O atom in H$_2$O is −1.90 eV for V$_O$-Ru$_3$/HfO$_2$ (Fig. 5j), which is lower than that of Ru$_3$/HfO$_2$ (−1.86 eV) and Ru (001) (−1.46 eV), further demonstrating the stronger binding between the active-surface Ru and adsorbed H$_2$O in V$_O$-Ru$_3$/HfO$_2$. These results indicate that water can be captured at a faster rate to facilitate the Volmer reaction on the V$_O$-Ru$_3$/HfO$_2$ surfaces.

Overall, the Ru supported on the HfO$_2$ catalyst with more Ru-O-Hf bonds and V$_O$ could significantly reduce the energy barrier for breaking the H-OH bond to accelerate water dissociation. In addition, strong metal–support interactions result in optimized energy for hydrogen adsorption and desorption. These phenomena synergistically rationalized the enhanced activity and favorable kinetics of V$_O$-Ru/HfO$_2$-OP for catalytic hydrogen evolution in alkaline electrolytes.

In summary, we developed a highly efficient electrocatalyst composed of Ru nanoparticles with V$_O$-HfO$_2$ for the HER in an alkaline electrolyte. The interaction between Ru nanoparticles and HfO$_2$ is a key factor in determining the HER activity. A series of Ru/HfO$_2$ catalysts were purposely prepared by choosing different surfactants to tune the number of Ru-O-Hf bonds. DFT calculations and experimental results demonstrate that the HER activity of
Fig. 5 DFT calculations. The most stable structure and adsorption energy of the Ru3 cluster adsorbed on a HfO2-OP and b VO-Ru/HfO2-OP. c The differential charge density distributions between Ru3 clusters and VO-HfO2 with the isovalue of 0.001 e Å⁻³. Yellow represents positive charges and olive represents negative charges. d The Projected density of states (PDOS) of Ru, Hf, and O atoms at V2-Ru/HfO2-OP. e The Gibbs free energy diagrams for hydrogen evolution reaction (HER) relative to standard hydrogen electrode, f water adsorption energy and g kinetic barrier of water dissociation on the active sites of different catalysts. IS, TS, and FS represent initial, transition state, and final state, respectively. h Differential charge density distributions between adsorbed H2O and catalysts for Ru (001) (up) and V2-Ru/HfO2-OP (down) with the isovalue of 0.002 e Å⁻³. Yellow represents positive charges and olive represents negative charges. i The PDOS of adsorbed H2O and the 4d orbital of Ru atom that directly involved in HER for Ru (001), Ru/HfO2-OP, and V2-Ru/HfO2-OP, with corresponding Ru 4d-band center denoted by dash lines. j Crystal Orbital Hamilton population (COHP) of active Ru atom and adsorbed O atom for Ru (001), Ru/HfO2-OP, and V2-Ru/HfO2-OP.

Vo-Ru/HfO2-OP can be enhanced by controlling the number of Ru-O-Hf bonds. At the same time, VO also plays a key role in promoting HER activity. The strong metal–support interactions via Ru-O-Hf bonds and introduced VO could significantly reduce the energy barrier for breaking the H-OH bond to accelerate water dissociation. The study results can be used to improve the design and fabrication of high-performance catalysts for application in various renewable energy-conversion devices.

Methods
**Synthesis of Vo-Ru/HfO2-OP catalysts.** About 0.25 mmol of RuCl₃·xH₂O, 0.25 mmol of HCl, and 60 mL of ethylene glycol under vigorous stirring. Then, 4 mL of oleylamine and 50 mg of PVP were added to the above solution. After stirring for 1 h, the reactor was flushed by Ar gas for 30 min to absolutely exhaust the air. Afterward, the solution was heated rapidly to 200 °C and maintained for 3 h under Ar flowing. When the reaction was completed, the resultant products were collected and fully washed two times with ethanol and two times with cyclohexane. Thereafter, the products were vacuum dried at 60 °C for 4 h and then, annealed at 750 °C for 2 h under H2/Ar (H2: 5%) atmosphere with a heating rate of 5 °C min⁻¹. The prepared catalyst was labeled as V2-Ru/HfO2-OP and directly used for electrochemical measurements.

**Synthesis of Vo-Ru/HfO2-O and Vo-Ru/HfO2-P catalysts.** The catalysts of Vo-Ru/HfO2-O and Vo-Ru/HfO2-P were prepared using a similar procedure with that of V2-Ru/HfO2-OP, but without adding PVP or oleylamine, respectively.

**Synthesis of HfO2 catalyst.** The catalyst of HfO2 was prepared using a similar procedure with that of VO-Ru/HfO2-OP, but without adding the RuCl₃·xH₂O.

Data availability
The data that support the findings of this study are available from https://figshare.com/s/2023b44b6c31c2ecab6. Source data are provided with this paper.

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