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Modulating electronic structure and hydrogen bond network via asymmetric S–Ru–O interfaces for superior alkaline hydrogen oxidation catalysis

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ABSTRACT

Triggering structural asymmetry can induce charge redistribution and modify electronic structures, which is of great significance for the design of high-performance hydrogen oxidation reaction (HOR) electrocatalysts. Herein, we propose a dual anion-induced strategy to create an innovative RuS₂-RuO₂ heterostructure featuring abundant S–Ru–O interfaces (RuS₂-RuO₂@C). This RuS₂-RuO₂@C demonstrates an impressive mass activity of 2.61 mA μg_{Ru}^{-1} and an exchange current density of 2.96 mA cm⁻², surpassing Pt/C and other comparative samples by over 20 times. Durability assessments confirm the superior stability of RuS₂-RuO₂@C, with only minimal performance loss during operation. Density functional theory (DFT) calculations indicate that the asymmetric S–Ru–O configuration optimizes the interfacial electronic structure and shifts the *d*-band center closer to the Fermi level, effectively reducing the energy barrier of the rate-determining step (RDS) in the alkaline HOR process. Moreover, in situ attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) characteristics disclose the formation of a substantial hydrogen bond network at the S–Ru–O interface, which aids in the desorption of H₂O_{ad} and facilitates the vital Volmer step in the HOR pathway.

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1. Introduction

Hydrogen is lauded as a prospective low-carbon energy carrier due to its high energy density, sustainability, and environmental benignity, offering a feasible resolution to the ongoing energy crisis and ecological degradation [1,2]. Fuel cells constitute an alluring technology for harnessing hydrogen [3]. Among them, anion exchange membrane fuel cells (AEMFC) have garnered substantial interest because their alkaline electrolytes are less corrosive and permit the employment of cost-effective non-precious metal catalysts (M-N-C) as efficacious cathodes [4–6]. As an essential component of AEMFC, the anodic hydrogen oxidation reaction (HOR) rate directly affects the whole performance. Regrettably, the crucial aspect of durability, especially the long-term durability under practical application conditions, has not been fully explored. Additionally, the presence of CO in the hydrogen feedstock also has a significant impact on the performance of the AEMFC [1,7]. Despite using the most active Pt-based catalysts, the anodic HOR kinetics in alkaline conditions is still 2–3 orders of magnitude slower than that in acidic settings, thereby mandating a higher Pt loading to attain comparable performance [8–10]. Therefore, developing low-cost, efficient, and highly stable electrocatalysts for HOR is essential for advancing AEMFCs.

In the alkaline HOR process, it is increasingly recognized that the Volmer step $(H_{ad} + OH^- \rightarrow H_2O + e^- + *)$ is pivotal in determining the reaction rate [11]. Accordingly, the adsorption behavior of hydrogen (H_{ad}) and hydroxyl (OH_{ad}) species is a vital indicator of HOR performance, as their adsorption strengths are closely correlated with the activity of electrocatalysts [12]. Ruthenium (Ru) exhibits a favorable combination of oxygen affinity and hydrogen binding energy (HBE) comparable to platinum (Pt), along with significantly lower costs, positioning it as a viable alternative catalyst

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for alkaline HOR [13–15]. However, single Ru catalysts have their inherent limitations. For example, under alkaline conditions, they have an excessively high hydrogen binding energy and insufficient hydroxyl adsorption energy, resulting in slow HOR kinetics and making it difficult to be put into practical applications [12,16]. To overcome these challenges, researchers explored strategies like alloying, vacancy engineering, surface ratio regulation, heteroatom doping, and support optimization to improve the interaction with H_{ad} and OH_{ad}, accelerating the application process in fuel cells [7,14,17]. Recent studies have shown that metal sulfides (RuS₂, Ru-RuS₂) and oxides (Ru-RuO₂) can display remarkable performance in alkaline HOR [18-20]. For example, Luo et al. created a series of RuS₂ model catalysts to systematically examine the relationship between sulfur vacancies and basic HOR activity [18]. Nevertheless, there is currently a lack of research regarding the modulation of the *d*-band center and hydrogen bonding network by inducing structural asymmetry. In light of this, adjusting the *d*-band center and hydrogen bonding network continuity through constructing asymmetric interfaces holds great promise for creating efficient catalysts for alkaline HOR.

Herein, a heterogeneous catalyst (RuS₂-RuO₂@C) featuring abundant S-Ru-O interfaces was successfully synthesized via a dual anion-induced strategy. The existence of asymmetric S-Ru-O interfaces in RuS₂-RuO₂@C was verified by X-ray photoelectron spectroscopy (XPS) and extended X-ray absorption fine structure (EXAFS) spectroscopy. Density functional theory (DFT) calculations indicated that the synergistic effect between RuS₂ and RuO₂, along with sufficient S-Ru-O interfaces, optimized the electronic structure. Specifically, the *d*-band center was moved closer to the Fermi level, which adjusted the adsorption intensity of intermediates and reduced the reaction energy barrier during alkaline HOR. Attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) characteristics demonstrated that the asymmetric S-Ru-O interface strengthened the connectivity of the hydrogen bonding network, thus accelerating the desorption of H₂O_{ad} and promoting Volmer kinetics. As expected, RuS₂-RuO₂@C displayed superior catalytic performance in alkaline HOR compared to the original RuS2@C, RuO2@C, and Ru-RuO2@C, attaining mass activity and exchange current density values of 2.61 mA μg_{Ru}^{-1} and 2.96 mA cm⁻², respectively. Therefore, it is anticipated that Ru-based catalysts can remarkably improve HOR performance by introducing asymmetric interfaces.

2. Experimental

2.1. Chemicals

All chemicals and reagents were used as bought without any further purification. These chemicals comprised ruthenium trichloride (RuCl₃·xH₂O, Aladdin, ~40 wt% Ru), sublimation sulfur (S, Xilong Science, 99%), oleylamine (OAm, Aladdin Industrial, 80%– 90%), commercial Pt/C (Alfa Aesar, 20 wt%), hexane (Sinopharm Chemical Reagent, ≥97%), absolute ethanol (Sinopharm Chemical Reagent, ≥99.5%), nafion solution (Alfa Aesar, 5 wt%), and carbon black (Vulcan, XC-72R). The deionized water (18.25 M Ω cm⁻¹) from a water purification system (Ulupure) was used throughout the whole experiment.

2.2. Synthesis of RuS₂-RuO₂@C

In order to adjust the *d*-band center with the aid of the asymmetric interface, reduce the adsorption strength of the intermediate products, and enhance the catalytic activity of the HOR, we designed the following experimental scheme. 20 mg RuCl₃·xH₂O, 30 mL ethanol, 15 mg carbon black and 30 mg S were mixed in 5 mL OAm with stirring at 75 °C for 20 min to achieve a uniform

suspension. The mixture was then transferred to a 100 mL Teflon-lined autoclave and heated at 160 °C for 24 h. The sample was harvested by centrifugation, washed several times with ethanol, and dried in vacuum oven overnight. The obtained sample was then annealed at 400 °C for 1 h at a heating rate of 5 °C min⁻¹ in an N₂ atmosphere. After naturally cooling, the obtained sample was denoted as RuS₂-RuO₂@C, with a specific Ru content of 3.59 wt%, which was verified by inductively coupled plasma-mass spectrometry (ICP-MS) measurements. Following the same line of thought, we obtained other catalysts at different temperatures, labelled RuS₂-RuO₂@C-350 °C and RuS₂-RuO₂@C-450 °C, respectively.

 $Ru-RuO_2@C$ and $RuO_2@C$ were synthesized following the same method as $RuS_2-RuO_2@C$. For $Ru-RuO_2@C$, no S source was added. As for $RuO_2@C$, the S source was omitted and the annealing gas was also changed to air.

2.3. Synthesis of RuS₂@C

The synthesis method of $RuS_2@C$ was generally the same as that of $RuS_2-RuO_2@C$. The main differences were as follows: in the solvothermal step, no S source was added. Moreover, during the subsequent treatment of the precursor obtained from solvothermal synthesis, the precursor and 500 mg of sulfur powder were respectively placed in the middle and upper parts of the quartz tube for annealing, rather than following the corresponding operations in the synthesis process of $RuS_2-RuO_2@C$.

2.4. Materials characterization

Powder X-ray diffraction (XRD, Rigaku D/Max 2500 V/PC, Japan, Cu K_{α} radiation over the 2θ range of 10° – 90°) was measured to investigate the crystal structure and phase composition of samples. Scanning electron microscopy (SEM, FEI Quanta 200 FEG) and transmission electron microscopy (TEM, JEM-2100F) were recorded to characterize the morphology and elemental distribution of the catalysts. The Ru L₃-edge X-ray absorption spectra (XAS) were collected at the 1W1B beamline of Shanghai Synchrotron Radiation Facility. The chemical state and electronic structure of the samples were analyzed by X-ray photoelectron spectroscopy (XPS, JPS-9010 Mg K_{α}). Metal contents in the catalysts were examined using inductively coupled plasma-mass spectroscopy (ICP-MS, PerkinElmer corporation, FLexar-NexION300X). The Brunauer-Emmett-Teller (BET) method was used to measure the specific surface area and pore size distribution of the samples. Ultraviolet photoelectron spectroscopy (UPS) was performed on X-ray photoelectron spectroscopy (PHI5000 VersaProbe III).

2.5. Electrochemical test

All the electrocatalytic measurements were performed in a standard three-electrode system by the CHI 760E (Shanghai, China) electrochemical analyzer. In this work, glassy carbon electrode (GCE, diameter: 5 mm, disk area: 0.196 cm²) was chosen as the working electrode; graphite rod and saturated KCl-filled with Ag/ AgCl were served as counter electrode and reference electrode, respectively. Electrochemical impedance spectroscopy (EIS) was measured using a multichannel potentiostat (Biologic VMP3) at the given potential with frequencies ranging from 200 kHz to 10 mHz.

Before HOR measurements, the 0.1 M KOH electrolyte was bubbled with ultra-high purity (UHP) H_2 gas for 30 min to gain H_2 saturated 0.1 M KOH solution. Cyclic voltammetry (CV) curves were recorded between 0 and 1.0 V vs. reversible hydrogen electrode (RHE) in pre-made N_2 -saturated 0.1 M KOH electrolyte until the stable curves were obtained. HOR polarization curves were collected at a sweep rate of 10 mV s⁻¹ ranging from –0.05 to 0.5 V (vs. RHE) under 1600 r min⁻¹ of the rotating disk electrode (RDE) rotation rate. The stability was assessed by repeating the potential scan from 0 to 1.0 V (vs. RHE) for 1000 cycles at the scanning rate of 100 mV s⁻¹. Chronoamperometric characterization was performed at 50 mV vs. RHE for 20000 s.

The methods of the characterization techniques used and the details of the electrochemical tests have been outlined in the Supporting Information.

3. Results and discussion

3.1. Synthesis and structural analysis

The RuS₂-RuO₂@C heterostructure was synthesized using solvothermal and high-temperature annealing methods (Fig. 1a). Initially, a uniform suspension was created by sonicating RuCl₃ precursor and sulfur powder in a mixed solvent containing XC-72R through a simple solvothermal process. The resulting precursors were then annealed in nitrogen to produce the RuS₂-RuO₂@C heterostructure. XRD analysis of RuS₂-RuO₂@C indicated the presence of both RuO₂ (JCPDS: 43-1027) and RuS₂ (JCPDS: 19-1107) phases (Fig. 1b), confirming the successful formation of RuS₂-RuO₂@C heterostructure. The XRD pattern of XC-72R showed broad peaks around 24° and 43°, corresponding to the (0 0 2) and (1 0 1) crystal faces [21]. For comparison, Ru-RuO₂@C catalyst was prepared without sulphur source, revealing diffraction peaks consistent with Ru (JCPDS: 06-0663) and RuO₂ (JCPDS: 43-1027) (Fig. S1) [22,23].

The morphology of the materials was examined using TEM. Loading the catalyst onto the carbon black will result in the formation of a particulate structure. As shown in Fig. 1(c), the average particle size of RuS₂-RuO₂@C was about 9.26 nm, significantly smaller than the average size (13.52 nm) of Ru-RuO₂@C (Fig. S2). This indicated that dual anion-induced RuS₂-RuO₂@C heterostructure was beneficial for reducing the agglomeration phenomenon and enhancing the activity [24,25]. Fig. 1(d, e) displayed the lattice spacing of RuS₂-RuO₂@C, showing the interplanar spacing of 0.279 and 0.214 nm attributed to the $(2 \ 0 \ 0)$ and $(0 \ 0 \ 2)$ planes of RuS₂ and RuO₂, respectively [18,26]. Selected area electron diffraction (SAED) identified diffraction spots corresponding to RuS₂ (2 1 1), RuO_2 (100), and RuO_2 (311). This indicated the successful synthesis of the RuS₂-RuO₂@C composite and confirmed the existence of the S-Ru–O interface (Fig. 1f) [27]. Additionally, energy-dispersive X-ray spectroscopy (EDS) (Fig. S3) and elemental mappings



Fig. 1. (a) Schematic illustration of the preparation of RuS₂-RuO₂@C. (b) XRD patterns of RuS₂-RuO₂@C and XC-72R. (c) TEM image and the particle size distribution (inset) of RuS₂-RuO₂@C. (d, e) High-resolution TEM images, (f) SAED pattern, and (g) elemental mapping images of RuS₂-RuO₂@C.

(Fig. 1g) confirmed the presence of C, O, S, and Ru throughout the heterostructure.

To qualitatively detect the existence of sulfur vacancy in RuS₂-RuO₂@C, electron paramagnetic resonance (EPR) measurements were performed (Fig. 2a). The EPR spectrum of RuS₂-RuO₂@C presented an apparent paramagnetic absorption signal at g = 2.002, while $Ru-RuO_2@C$ did not display any significant fluctuations, revealing that sulfur vacancy trapped unpaired electrons in RuS₂-RuO₂@C [18]. XPS was conducted to investigate the elemental composition and surface chemical valence states of RuS₂-RuO₂@C. As depicted in Fig. S4, the highresolution S 2p spectrum of RuS₂-RuO₂@C divulged the contributions from S²⁻ (162.31 eV), S²⁻ (163.46 eV), and S–O (167.75 eV) [28]. Fig. 2(b) displayed the high-resolution Ru 3p spectrum of RuS₂-RuO₂@C with deconvoluted peaks at approximately 462.23 and 464.92 eV. corresponding to Ru–S and Ru–O bonds. indicating the formation of S-Ru-O bonds at the heterogeneous interfaces [22,29].

To thoroughly investigate the impact of heterogeneous interfaces on HOR activity, UPS was utilized to measure the work function (WF) of different materials [30]. As exhibited in Fig. 2(c), the WF trend was RuS_2 - $RuO_2@C$ (4.35 eV) > Ru- $RuO_2@C$ (2.81 eV). This indicated that the surface valence state of RuS₂-RuO₂@C was more positive compared to Ru-RuO₂@C, suggesting that RuS₂-RuO₂@C possessed a greater number of empty *d*-orbitals than Ru-RuO₂@C [30]. Consequently, the RuS₂-RuO₂@C was expected to improve the oxidation capacity of the catalyst and hydroxyl adsorption, thus accelerating the crucial Volmer step [1,31].

To identify the electronic structure and coordination environment of catalysts, the Ru K-edge X-ray absorption near-edge structure (XANES) and EXAFS measurements were carried out. As revealed in Fig. 2(d), the average valence state of Ru in RuS₂-RuO₂@C lied between 0 and +4. The local environment surrounding Ru was examined using k^3 -weighted EXAFS Fourier transform magnitude in *R*-space, as illustrated in Fig. 2(e). Two characteristic peaks at 1.48 and 1.81 Å for reference samples RuO₂ and RuS₂ were indexed to Ru-O and Ru-S bonds, respectively [18,20]. RuS₂-RuO₂@C displayed an evident broad peak around 1.72 Å. attributable to Ru–S/Ru–O bonds. Further curve fitting was conducted to ascertain specific structural parameters around the Ru atoms (Fig. 2f, g), with the results provided in Table S1. In RuS₂-RuO₂@C heterogeneous catalyst, the calculated coordination numbers for Ru-O and Ru-S were 1.0 and 4.0, respectively, offering strong evidence for the existence of S-Ru-O interfaces [32]. Diversely, the



Fig. 2. (a) EPR spectra of RuS₂-RuO₂@C and Ru-RuO₂@C. (b) High resolution XPS of Ru 3*p* in RuS₂-RuO₂@C. (c) UPS spectra with inset work functions of the different catalysts. (d) Ru *K*-edge XANES and (e) EXAFS spectra of RuS₂-RuO₂@C and Ru-RuO₂@C. Corresponding EXAFS fitting curves of (f) RuS₂-RuO₂@C and (g) Ru-RuO₂@C at *R* space. (h) Ru *K*-edge WT-EXAFS of RuS₂-RuO₂@C, Ru-RuO₂@C, RuO₂, and RuS₂.

coordination numbers for Ru–O and Ru–Ru in Ru-RuO₂@C were found to be 2.4 and 5.9, respectively. The coexistence of the double anion (O and S) in RuS₂-RuO₂@C significantly weakened the Ru–O coordination compared to Ru-RuO₂@C, which aided in inhibiting Ru solubility and enhancing stability during catalytic process [33]. To further validate these findings, wavelet transform (WT) analyses were examined on the Ru EXAFS data. The WT signal at the Ru *K*-edge for RuS₂-RuO₂@C exhibited peak intensity around 4.97 Å⁻¹ (Fig. 2h and Fig. S5), further indicating the formation of a heterogeneous S–Ru–O interface, consistent with the XPS results.

3.2. Electrochemical HOR performance

The electrocatalytic peculiarity of the catalysts was evaluated via the RDE technique in H₂-saturated 0.1 M KOH electrolyte. Initially, by performing systematic experiments in which the temperature and Ru concentration were varied, we investigated the impact of diverse reaction conditions on the catalytic performance of RuS₂-RuO₂@C. We determined that the material prepared from RuS₂-RuO₂@C at the optimal synthesis temperature of 400 °C exhibits the best HOR activity, with a Ru content of 3.59 wt% (Fig. S6 and Table S2). To in-depth analyze hydrogen adsorption/desorption behaviors, CV curves were recorded in N2-saturated 0.1 M KOH solution. Previous research had indicated that the underpotentially deposited hydrogen (H_{upd}) peaks correlated directly with HBE, with a stronger HBE observed as the hydrogen desorption peak potential increased [34,35]. However, a stronger HBE was primarily responsible for the slower kinetics of the HOR [36]. As depicted in Fig. S7, compared to Pt/C and Ru-RuO₂@C, RuS_2 -RuO₂@C exhibited a more negative H_{upd} peak potential. This indicates that the HBE on RuS2-RuO2@C is weaker. According to the bifunctional theory, this weakened HBE promotes the Volmer step in the alkaline HOR [1]. Linear scanning voltammetry (LSV) was performed in H₂-saturated 0.1 M KOH to obtain HOR polarization curves for various catalysts. As shown in Fig. 3(a), RuS₂-RuO₂@C displayed markedly superior HOR activity compared to other control catalysts. Control experiments carried out in electrolytes saturated with N₂ verified that the anodic current was negligible (Fig. S8). This finding strongly attests to the fact that the anodic current predominantly originated from the oxidation of H₂. Furthermore, we evaluated the HOR polarization curves of RuS₂-RuO₂@C with respect to different rotation speeds. It was observed that as the rotation rate increased, so did the limiting current density. This phenomenon was a clear indication that the process is governed by H₂ mass-transport (Fig. 3b) [37]. According to Koutecky-Levich equation (Eq. (S2)), the calculated slope of RuS₂- $RuO_2@C$ was 4.63 cm² mA⁻¹ s^{-1/2}, closely aligning with the theoretical value of 4.87 cm² mA⁻¹ s^{-1/2}, consistent with two-electron transfer principles [12]. To explore the catalytic mechanism of HOR, Tafel slopes were determined by plotting kinetic current density (j_k) against overpotential for the synthesized catalysts. The asymmetrical behavior observed in the Tafel plot indicated that RuS₂-RuO₂@C adhered to the Heyrovsky-Volmer mechanism, with the Volmer step identified as the rate-determining step (RDS) (Fig. 3c) [38]. As depicted in Fig. 3(d), the geometric j_0 values for the samples were derived from the micro-polarization region (from -5 to 5 mV). As anticipated, RuS₂-RuO₂@C achieved a j_0 of 2.96 mA cm⁻², underscoring its remarkable inherent activity (Fig. 3e and Table S3). Recently, it was reported that S is a pivotal site for enhancing HOR activity through S-site blocking experiments [18]. Therefore, we verified this through an S-site blocking experiment. By introducing Zn^{2+} ions, Zn^{2+} ions were bonded to the surface S sites, blocking the adsorbed substances, especially H. As expected, after introducing Zn²⁺ ions, the catalytic activity of RuS₂-RuO₂@C decreased significantly, indicating that the S sites

played a promoting role in enhancing its catalytic activity (Fig. 3f). Notably, the mass activity of RuS₂-RuO₂@C reached 2.61 mA μ g⁻¹_{Ru}, and the j_0 reached 2.96 mA cm⁻², which significantly exceeded the currently reported catalysts (Fig. 3g). Moreover, we had summarized the HOR performance parameters of the studied catalysts (Tables S4 and S5). Subsequently, we conducted accelerated durability experiments using chronoamperometry (*j*-*t*) measurements in H₂-saturated 0.1 M KOH electrolyte. Fig. 3(h) revealed that RuS₂-RuO₂@C exhibited only minimal current density degradation, starkly contrasting with the commercial Pt/C and Ru-RuO₂@C, highlighting the remarkable stability of RuS₂-RuO₂@C.

3.3. Theoretical study

Apart from hydrogen adsorption species, the adsorbed hydroxyl group (OH*) serves as another crucial indicator for modulating catalytic activity [34]. The behavior of OH* can be assessed using CO stripping techniques, as the presence of OH* facilitates CO oxidation. A more negative CO stripping peak value signifies a stronger OH* adsorption on the surface of electrocatalyst [34,39]. As shown in Fig. 4(a), the CO-stripping peak for RuS₂-RuO₂@C (0.72 V) was more negative than that of Ru-RuO2@C (0.79 V), RuS2@C (0.84 V), and RuO₂@C (0.86 V), indicating a stronger binding affinity for OH_{ads} in RuS₂-RuO₂@C. Furthermore, hydroxyl adsorption on catalysts can be also investigated using zeta potential measurements [40]. As illustrated in Fig. 4(b), RuS₂-RuO₂@C demonstrated optimized OH adsorption, with a more negative potential of -23.59 mV compared to Ru-RuO₂@C (-15.19 mV), RuS₂@C (-7.32 mV), and RuO₂@C (-3.27 mV). Collectively, the CO-stripping and zeta potential analyses revealed that the strengthened hydroxyl binding energy (OHBE) of RuS₂-RuO₂@C can accelerate the rate-limiting Volmer step, thereby improving HOR catalysis.

To gain insight into the mechanism underlying the enhanced HOR activity of the RuS₂-RuO₂@C heterostructure, DFT calculations were conducted. In this study, the interfaces based on the crystallographic orientations of RuO₂ (1 0 1) and RuS₂ (3 1 1) were constructed to simulate the RuS2-RuO2@C heterostructure. Fig. S9 presented the four theoretical models of RuS2-RuO2@C, Ru-RuO₂@C, RuS₂@C, and RuO₂@C. The differential charge density analysis of RuS₂-RuO₂@C revealed significant charge depletion around RuO₂, while charge accumulation was observed around RuS₂, highlighting the strong electronic interaction between the RuO₂ and RuS₂ components (Fig. 4c). The density of states (DOS) was employed to investigate the electronic characteristics of the four samples. When compared with Ru-RuO₂@C. RuS₂@C. and RuO₂@C. RuS₂-RuO₂@C demonstrated a greater DOS occupancy in the vicinity of the Fermi level. This indicates that RuS2-RuO2@C has better electrical conductivity, a stronger electron transport ability, and more rapid reaction kinetics (Fig. 4d) [19]. Based on the *d*-band theory, the binding strength of the adsorbed intermediates could be indicated by the position of the *d*-band center [19]. The *d*-band centers for RuS₂-RuO₂@C, Ru-RuO₂@C, RuS₂@C, and RuO₂@C were found to be -1.51, -1.54, -1.56, and -1.69 eV, respectively. In RuS₂-RuO₂@C, the upward movement of the dband center signified a more robust interaction occurring between the catalyst and the intermediates. This stronger interaction was beneficial for reducing the potential energy barrier, thereby enhancing the catalytic efficiency of the HOR [12].

Given that H^{*} and OH^{*} are two key reaction intermediates in the HOR process, we performed an evaluation of the HBE and OHBE on different catalysts. Fig. 4(e) and Figs. S10 and S11 illustrated the preferred adsorption sites for H and OH on RuS₂-RuO₂@C, Ru-RuO₂@C, RuS₂@C, and RuO₂@C. In comparison, the HBE value for RuS₂-RuO₂@C was -0.27 eV, which was closer to zero than the values of Ru-RuO₂@C (-0.41 eV), RuS₂@C (-0.43 eV), and RuO₂@C

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Fig. 3. (a) HOR polarization curves. (b) HOR polarization curves for RuS_2 - $RuO_2@C$ at various rotation speeds. Inset in (b) shows corresponding Koutecky-Levich plots at 50 mV. (c) Tafel plots of the kinetic current density. (d) Linear fitting curves in the micro-polarization region (from -5 to 5 mV). (e) j_k and j_0 of different studied catalysts. (f) HOR polarization curves of RuS_2 - $RuO_2@C$ before and after soaking in 1 mM $Zn(NO_3)_2$ solution for 30 s. (g) j_0 and MA compared to other recently reported alkaline HOR electrocatalysts (Tables S4 and S5 provide each value and the relevant references). (h) Chronoamperometry (*j*-*t*) responses of RuS_2 - $RuO_2@C$, Ru- $RuO_2@C$, and commercial Pt/C at 50 mV.

(-0.51 eV), indicating a favorable HOR process. Additionally, the OHBE values for Ru-RuO2@C, RuS2@C, and RuO2@C were 0.03, 0.06, and 0.40 eV, respectively, indicating insufficient hydroxyl adsorption capability that impeded the HOR process. In contrast, RuS₂-RuO₂@C exhibited an OHBE value of -0.09 eV, demonstrating a stronger OH adsorption capacity, which promoted the capture of OH* on the surface, so the Volmer step in the alkaline HOR process was expedited through a bifunctional mechanism [19]. Subsequently, the free energy profiles and reaction pathways for HOR on RuS₂-RuO₂@C, Ru-RuO₂@C, RuS₂@C, and RuO₂@C were calculated (Fig. 4f). The findings indicated that for RuS₂-RuO₂@C. the steps of H*+OH* and water formation were endothermic, whereas water adsorption was exothermic. This was in line with the steps seen in Ru-RuO₂@C, RuS₂@C, and RuO₂@C. Consequently, the H* + OH* step became the rate-determining step (RDS) for all four catalysts. Among these catalysts, RuS₂-RuO₂@C showed the lowest energy barrier, measured to be 0.27 eV. This can be ascribed to its strengthened OHBE. As a result, the outstanding HOR performance of RuS₂-RuO₂@C was mainly attributed to the optimized OHBE and

a decreased RDS energy. These results implied that the interfacial synergy between the RuS_2 and RuO_2 components was of great significance in regulating the adsorption of H and OH, thus promoting the kinetics of the HOR, as depicted in Fig. 4(g).

3.4. In situ ATR-SEIRAS analysis

To further explore the H adsorption behavior during the reaction and the impact of interfacial water on the catalyst surface, we utilized in situ ATR-SEIRAS (Fig. 5a–d). The v_{O-H} peaks corresponded to weakly hydrogen-bonded water on the Ru surface (3600 cm⁻¹) and triangular water (3400 cm⁻¹) [15,41]. However, the water situated on either side of the triangular region can be classified as strongly hydrogen-bonded (HB) water [42]. Previous reports have indicated that a high concentration of strongly HB water contributes to a lower energy barrier for the protoncoupled electron transfer (PCET) process, facilitated by the hydrogen-bond network in interfacial water [42]. Consequently, strongly HB water is essential for enhancing the activity of the



Fig. 4. (a) CO stripping curves of RuS₂-RuO₂@C, Ru-RuO₂@C, RuS₂@C, and RuO₂@C, (b) Zeta potential of RuS₂-RuO₂@C, Ru-RuO₂@C, RuS₂@C, and RuO₂@C. (c) Charge-density distribution of the RuS₂-RuO₂@C model (the blue, red, and violet balls represent O, Ru, and S atoms respectively). (d) DOS plots. (e) Calculated HBEs and OHBEs value on RuS₂-RuO₂@C, Ru-RuO₂@C, RuS₂@C, and RuO₂@C models. (f) The reaction pathways of RuS₂-RuO₂@C, Ru-RuO₂@C, RuS₂@C, and RuO₂@C for alkaline HOR. (g) Mechanism diagram of RuS₂-RuO₂@C for the alkaline HOR processes.

HOR process. Notably, RuS₂-RuO₂@C exhibited a pronounced signal peak around 3400 cm⁻¹, while Ru-RuO₂@C, RuS₂@C, and RuO₂@C did not show a similar peak at this position. These findings manifested that the S-Ru-O interface formed in RuS₂-RuO₂@C effectively promoted the accumulation of water molecules and progressively expedited the hydrogen bond network, thereby facilitating reaction kinetics and boosting HOR catalytic activity [18,42,43].

4. Conclusions

In summary, we successfully synthesized a heterogeneous catalyst ($RuS_2-RuO_2@C$) featuring a rich S–Ru-O interface using a dual anion-induced strategy. The presence of asymmetric S–Ru-O interfaces in $RuS_2-RuO_2@C$ was confirmed through XPS and EXAFS spectroscopy. DFT calculations revealed that the synergistic effect of RuS_2 and RuO_2 , along with the abundant S–Ru-O interfaces, optimized the electronic structure by shifting the *d*-band center closer to the Fermi level. This modulation regulated the adsorption strength of intermediates and reduced the reaction energy barrier during alkaline HOR. ATR-SEIRAS characterization further demonstrated that the asymmetric S–Ru-O interface enhanced the hydrogen bonding network connectivity, thereby accelerating the desorption of H_2O_{ad} and facilitating Volmer kinetics. As a result, $RuS_2-RuO_2@C$ exhibited superior alkaline HOR catalytic performance compared to RuS₂@C, RuO₂@C, and Ru-RuO₂@C, achieving mass activity and exchange current density of 2.61 mA μg_{Ru}^{-1} and 2.96 mA cm⁻², respectively. These findings suggest that the incorporation of asymmetric interfaces in Ru-based catalysts holds great potential for significantly enhancing HOR performance. However, scaling RuS₂-RuO₂@C for fuel cells faces durability, CO tolerance, cost, and integration challenges. While beyond our current research, future efforts will focus on stability optimization, CO-resistant modifications, cost-effective synthesis, and membrane electrode assembly (MEA) integration strategies.

CRediT authorship contribution statement

Chenggong Niu: Writing – original draft, Conceptualization. **Yi Liu:** Methodology. **Shuqing Zhou:** Investigation. **Heyang Liu:** Data curation. **Linyu Chen:** Data curation. **Jingya Guo:** Writing – review & editing. **Tayirjan Taylor Isimjan:** Writing – review & editing. **Xiulin Yang:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Fig. 5. Interfacial water signals for ATR-SEIRAS of (a) RuS₂-RuO₂@C, (b) Ru-RuO₂@C, (c) RuS₂@C, and (d) RuO₂@C.

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Appendix A. Supplementary material

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References

- [1] J.-T. Ren, L. Chen, H.-Y. Wang, Y. Feng, Z.-Y. Yuan, Energy Environ. Sci. 17 (2024) 3960–4009.
- [2] P. Han, L. Wu, J. Yue, Y. Zhang, Y. Jin, H. Jia, W. Luo, Angew. Chem. Int. Ed. 64 (2024) e202419320.
- [3] L. Wei, W. Yan, Z. Huang, R. Li, Q. Kong, W.-H. Huang, C.-W. Pao, Z. Hu, H. Lin, N. Chen, Y. Xu, H. Geng, X. Huang, Energy Environ. Sci. 17 (2024) 5922–5930.
 [4] L. Su, H. Wu, S. Zhang, C. Cui, S. Zhou, H. Pang, Adv. Mater. 37 (2024) 2414628.
- [4] L. Su, H. Wu, S. Zhang, C. Cui, S. Zhou, H. Pang, Adv. Mater. 37 (2024) 2414628.
 [5] X. Song, Q. Yang, K. Zou, Z. Xie, J. Wang, W. Ding, Adv. Funct. Mater. 35 (2024)
- 2414570.
- [6] L. Su, D. Gong, N. Yao, Y. Li, Z. Li, W. Luo, Adv. Funct. Mater. 31 (2021) 2106156.
 [7] L. An, X. Zhao, T. Zhao, D. Wang, Energy Environ. Sci. 14 (2021) 2620–2638.
- [7] L. AL, X. Zhao, F. Zhao, D. Wang, Energy Environ. Sci. 14 (2021) 2020-2036.
 [8] J. Durst, A. Siebel, C. Simon, F. Hasché, J. Herranz, H.A. Gasteiger, Energy Environ. Sci. 7 (2014) 2255–2260.
- [9] W. Sheng, M. Myint, J.G. Chen, Y. Yan, Energy Environ. Sci. 6 (2013) 1509.

- [10] P. Han, L. Wu, Y. Zhang, J. Yue, Y. Jin, H. Jia, W. Luo, Angew. Chem. Int. Ed. 64 (2024) e202419320.
- [11] Y. Guo, W. He, X. Tan, Y. Xiao, B. Du, C. Wang, H. Cui, Y. Li, C. Wang, Adv. Funct. Mater. 35 (2024) 2412142.
- [12] Y. Liu, L. Cheng, S. Zhou, C. Niu, T.T. Isimjan, X. Yang, Appl. Catal. B Environ. Energy 362 (2025) 124709.
- [13] Z. Cui, Z. Ren, C. Ma, B. Chen, G. Chen, R. Lu, W. Zhu, T. Gan, Z. Wang, Z. Zhuang, Y. Han, Angew. Chem. Int. Ed. 63 (2024) e202404761.
- [14] J. Park, H. Kim, S. Kim, S.Y. Yi, H. Min, D. Choi, S. Lee, J. Kim, J. Lee, Adv. Mater. 36 (2024) 2308899.
- [15] L. Wei, Y. Dong, W. Yan, Y. Zhang, C. Zhan, W.-H. Huang, C.-W. Pao, Z. Hu, H. Lin, Y. Xu, H. Geng, X. Huang, Angew. Chem. Int. Ed. 64 (2024) e202420177.
- [16] L. Chen, C. Li, M. Liu, Z. Dai, H. Wang, X. Zhou, Q. Zhao, Y. Cong, Adv. Sci. 11 (2024) 2410881.
- [17] P. Han, X. Yang, L. Wu, H. Jia, J. Chen, W. Shi, G. Cheng, W. Luo, Adv. Mater. 36 (2024) 2304496.
- [18] C. Yang, J. Yue, G. Wang, W. Luo, Angew. Chem. Int. Ed. 63 (2024) e202401453.
- [19] Y. Liu, L. Cheng, S. Zhou, Y. Yang, C. Niu, T.T. Isimjan, B. Wang, X. Yang, J. Energy Chem. 94 (2024) 332–339.
- [20] X. Zhang, L. Xia, G. Zhao, B. Zhang, Y. Chen, J. Chen, M. Gao, Y. Jiang, Y. Liu, H. Pan, W. Sun, Adv. Mater. 35 (2023) 2208821.
- [21] Y. Xia, W. Wu, H. Wang, S. Rao, F. Zhang, G. Zou, Nanotechnology 31 (2020) 145401.
- [22] Y. Chen, Y. Liu, L. Li, T. Sakthive, Z. Guo, Z. Dai, Adv. Funct. Mater. 34 (2024) 2406587.
- [23] H. Shi, Y. Yang, P. Meng, J. Yang, W. Zheng, P. Wang, Y. Zhang, X. Chen, Z. Cheng, C. Zong, D. Wang, Q. Chen, J. Am. Chem. Soc. 146 (2024) 16619–16629.
- [24] S. Zhou, Q. Yang, Y. Liu, L. Cheng, T. Taylor Isimjan, J. Tian, X. Yang, J. Catal. 433 (2024) 115491.
- [25] H. Li, X. Hu, L. Wang, L. Shi, T.T. Isimjan, X. Yang, Chem. Eng. J. 481 (2024) 148547.
- [26] D. Zhang, M. Li, X. Yong, H. Song, G.I.N. Waterhouse, Y. Yi, B. Xue, D. Zhang, B. Liu, S. Lu, Nat. Commun. 14 (2023) 2517.

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- [27] Y. Wang, X. Lei, B. Zhang, B. Bai, P. Das, T. Azam, J. Xiao, Z.-S. Wu, Angew. Chem. Int. Ed. 63 (2024) e202316903.
- [28] X. Li, Z. Kou, S. Xi, W. Zang, T. Yang, L. Zhang, J. Wang, Nano Energy 78 (2020) 105230.
- [29] P. Li, W. Li, Y. Huang, J. Li, Q. Huang, S. Zhao, S. Tian, Nanoscale 14 (2022) 6258–6267.
- [30] L. Su, X. Fan, Y. Jin, H. Cong, W. Luo, Small 19 (2023) 2207603.
 [31] Y.-S. Feng, Y.-N. Li, P. Wang, Z.-P. Guo, F.-F. Cao, H. Ye, Angew. Chem. Int. Ed. 62
- (2023) e202310132. [32] H. Yu, M. Hu, C. Chen, C. Hu, Q. Li, F. Hu, S. Peng, J. Ma, Angew. Chem. Int. Ed. 62
- (2023) e202314569.
- [33] W. Gou, S. Zhang, Y. Wang, X. Tan, L. Liao, Z. Qi, M. Xie, Y. Ma, Y. Su, Y. Qu, Energy Environ. Sci. 17 (2024) 6755.
- [34] H. Luo, K. Wang, F. Lin, F. Lv, J. Zhou, W. Zhang, D. Wang, W. Zhang, Q. Zhang, L. Gu, M. Luo, S. Guo, Adv. Mater. 35 (2023) 2211854.
- [35] M. Huang, H. Yang, X. Xia, C. Peng, Appl. Catal. B Environ. Energy 358 (2024) 124422.

- [36] B. Qin, H. Yu, X. Gao, D. Yao, X. Sun, W. Song, B. Yi, Z. Shao, J. Mater. Chem. A 6 (2018) 20374–20382.
- [37] Y. Han, L. Zhao, W. Cheng, M. Wang, L. Yang, Y. Lin, K. Xu, Adv. Funct. Mater. 34 (2024) 2407060.
- [38] X. Tian, P. Zhao, W. Sheng, Adv. Mater. 31 (2019) 1808066.
- [40] L. Su, Y. Zhao, Y. Jin, Z. Liu, H. Cui, W. Luo, Adv. Funct. Mater. 32 (2022) 2113047.
- [41] K. Sun, X. Wu, Z. Zhuang, L. Liu, J. Fang, L. Zeng, J. Ma, S. Liu, J. Li, R. Dai, X. Tan, K. Yu, D. Liu, W.-C. Cheong, A. Huang, Y. Liu, Y. Pan, H. Xiao, C. Chen, Nat. Commun. 13 (2022) 6260.
- [42] Y. Jin, X. Fan, W. Cheng, Y. Zhou, L. Xiao, W. Luo, Angew. Chem. Int. Ed. 63 (2024) e202406888.
- [43] H. Zhao, D. Chen, R. Yu, J. Jiao, W. Zeng, J. Zhu, X. Mu, Y. Yao, D. Wu, Y. Zhang, J. Wu, S. Mu, Nano Energy 121 (2024) 109247.