



## Electronic regulation via d-p coupling between ruthenium nanoclusters and ReS<sub>2</sub> nanosheets for enhanced green hydrogen production performance

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Hydrogen is widely regarded as a key future energy carrier due to its high energy density and carbon-free utilization. Among various hydrogen production pathways, electrocatalytic water splitting has been matured into a scalable method for green hydrogen production [1]. Especially, converting intermittent electricity from solar or wind power into storable hydrogen offers a sustainable solution to harness fluctuating energy, enhancing grid stability and increasing renewable energy utilization [2]. Green hydrogen plays a vital role in chemical manufacturing and metallurgy, serving as a clean feedstock or reducing agent [3]. To date, platinum (Pt)-based materials remain the benchmark as commercial catalysts for acidic hydrogen evolution reaction (HER). However, Pt's high cost and scarcity severely limit its application in large-scale implementation in industrial water electrolysis [4]. Beyond Pt-based catalysts, current research has also focused on other precious metal catalysts for HER, including ruthenium (Ru)-based and palladium (Pd)-based systems [5]. Non-precious alternatives span transition metal phosphides [6], transition metal sulfides [7], alloy catalysts [8,9], and single-atom catalysts [10,11]. While these materials offer significantly lower costs, they generally exhibit inferior HER performance compared to Pt-based catalysts [12].

Two-dimensional transition metal dichalcogenides (TMDs) possess high specific surface area and abundant active sites, making them promising as HER catalysts [13–15]. Strategies such as phase transformation, defect engineering, and heterostructure construction have been employed to modulate the electronic structure of TMD, thereby optimizing  $\Delta G_{H^+}$  for HER [16,17]. Among TMDs, MoS<sub>2</sub> has been extensively studied and demonstrated promising applications in the electrocatalytic HER [18,19]. For example, the inert basal facet of monolayer MoS<sub>2</sub> can be activated through the introduction of Frenkel defects, leading to enhanced HER activity with an overpotential of 164 mV at 10 mA cm<sup>-2</sup> and a Tafel slope of 36 mV dec<sup>-1</sup>, which significantly outperforms both pristine MoS<sub>2</sub> and Pt single-

atom-doped MoS<sub>2</sub> [20]. In addition, dendritic MoS<sub>2</sub>@Co<sub>9</sub>S<sub>8</sub>/C heterostructures grown on carbon nanofibers exhibit superior electrocatalytic performance compared to pristine MoS<sub>2</sub>, demonstrating a Tafel slope of 98 mV dec<sup>-1</sup> in acidic HER [21]. However, the conductive 1T' phase of MoS<sub>2</sub> is metastable and readily transforms into the semiconductive 2H phase, which has low electronic conductivity and consequently degrades its electrocatalytic performance. Compared with MoS<sub>2</sub>, ReS<sub>2</sub> offers the advantage of an intrinsic 1T' structure with good conductivity [22], which remains stable during the catalytic process without undergoing phase transition [23]. Furthermore, ReS<sub>2</sub> exhibits outstanding stability. After 10,000 cyclic voltammetry (CV) cycles, the overpotential of fluorine-doped ReS<sub>2</sub> (ReS<sub>2</sub>-F<sub>5.93</sub>) at a current density of 10 mA cm<sup>-2</sup> increased by only 22 mV, whereas the overpotential of the reference Pt/C catalyst increased by approximately 54 mV [7], highlighting its potential for high-current electrocatalytic applications [24]. However, in water electrolysis, the inherently inert surface of ReS<sub>2</sub> renders water molecule adsorption as the critical rate-limiting step [25]. Its insufficient affinity for water severely impedes the subsequent catalytic decomposition processes [26,27].

Our design strategy involves the incorporation of catalytically active sites to promote water molecule adsorption, thereby significantly improving the HER performance of ReS<sub>2</sub> toward efficient green hydrogen production. We select Ru as a catalytic element owing to its lower cost relative to Pt and Ir, while still maintaining excellent water adsorption and dissociation performance [16]. Further calculation results reveal that uniformly loading zero-valent Ru nanoparticle clusters onto the nanosheet optimizes hydrogen adsorption free energy, ultimately enhancing catalytic activity (Fig. 1a) [28]. This improvement is primarily driven by the modulation of p-d orbital interactions. The core achievement of this work lies in the successful preparation of Ru-loading ReS<sub>2</sub> nanosheets through a solid-phase lithiation and confined ion exchange strategy [29,30]. Experimental validation confirmed that the introduced Ru substantially improves

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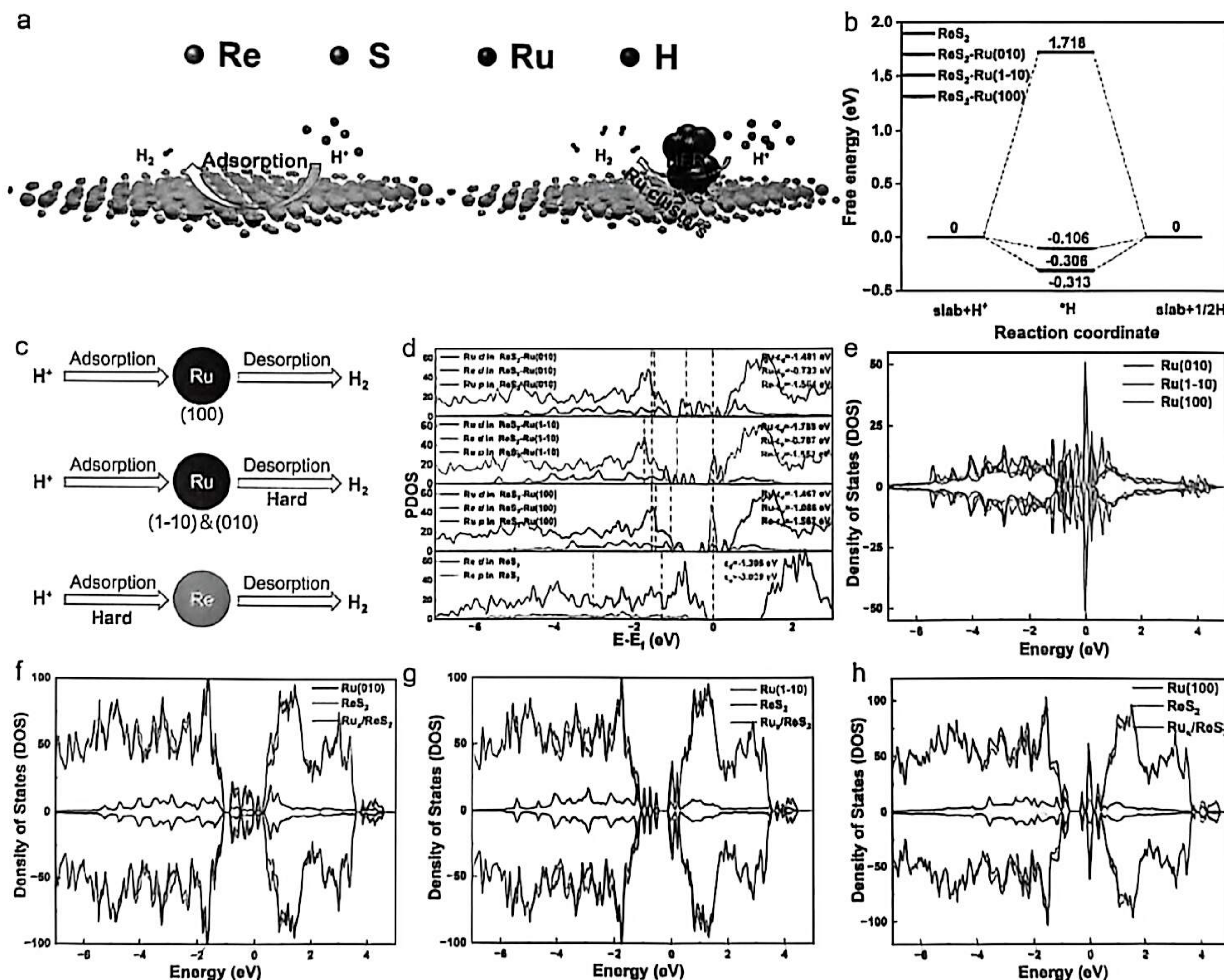
the acidic HER activity of  $\text{ReS}_2$  nanosheets, manifested in significantly lowered overpotentials and Tafel slopes. This modification also endows the catalyst with outstanding high-current-density hydrogen evolution performance, exhibiting no obvious degradation over 100 h of continuous cycling, demonstrating its potential for efficient water electrolysis applications with low precious metal consumption.

To investigate the origin of the exceptional HER catalytic activity of  $\text{Ru}_x/\text{ReS}_2$ , we performed density functional theory (DFT) calculations. HER catalytic activity is primarily determined by the adsorption free energy of  $\text{H}^*$  ( $\Delta G_{\text{H}^*}$ ) [31]. An ideal catalyst should exhibit  $\Delta G_{\text{H}^*}$  properties that simultaneously promote  $\text{H}^*$  intermediate adsorption and  $\text{H}_2$  molecular desorption [32]. To elucidate whether differences in catalytic activity stem from electronic properties, we employed band center theory [33].

To validate the effect of S, Re and Ru elements for HER, we calculated  $\Delta G_{\text{H}^*}$  for Ru, S, and Re sites across all three heterostructure systems. For the Ru (100) facet, the  $\Delta G_{\text{H}^*}$  on the active sites of Ru, Re, and S is  $-0.106$ ,  $0.604$ , and  $1.579$  eV, respectively. For the Ru (1-10) facet, these values are  $-0.306$ ,  $0.812$ , and

$2.868$  eV, respectively. For the Ru (010) facet, they are  $-0.313$ ,  $2.226$ , and  $2.238$  eV, respectively. As shown in Fig. S1, the Ru site consistently exhibits negative  $\Delta G_{\text{H}^*}$  values, while S and Re sites display positive  $\Delta G_{\text{H}^*}$  values in all systems, indicating that Ru is the most stable adsorption site for  $\text{H}^*$ . Furthermore, among all considered sites,  $\Delta G_{\text{H}^*}$  at the Ru site was closest to zero, confirming Ru as the active center for HER within these heterostructures.

The illustration shown in Fig. 1a displays DFT calculation results, with Ru clusters acting as the active centers for HER. Based on these calculation results, Gibbs free energy profiles of  $\Delta G_{\text{H}^*}$  were plotted (Fig. 1b). The calculation results first confirm that the pristine  $\text{ReS}_2$  basal facet possesses a  $\Delta G_{\text{H}^*}$  value as high as  $1.718$  eV (Fig. 1b), indicating an extremely high energy barrier for hydrogen adsorption. This explains its inherent inertness toward HER. After loading Ru nanoparticles, the active sites shifted to the Ru surface. The calculated  $\Delta G_{\text{H}^*}$  values for the (100), (010), and (1-10) facets of Ru are  $-0.106$ ,  $-0.313$ , and  $-0.306$  eV, respectively. Although all facets show significant improvement compared to  $\text{ReS}_2$ , the Ru (100) facet exhibits the  $\Delta G_{\text{H}^*}$  value closest to zero. This indicates that this facet achieves



**Figure 1** DFT calculation of  $\text{Ru}_x/\text{ReS}_2$  for HER activity enhancement. (a) Schematic illustration of the HER process on  $\text{ReS}_2$  and  $\text{Ru}_x/\text{ReS}_2$  nanosheet. (b) Gibbs free energy profiles for hydrogen adsorption on  $\text{ReS}_2$  and the Ru (1-10), (010), and (100) facets active sites. (c) Simulation diagram comparing the ease of water absorption and desorption. (d) PDOS and band center for Re and Ru in the  $\text{ReS}_2$  and  $\text{Ru}_x/\text{ReS}_2$  system. (e) Total DOS for Ru nanoparticles with different facets. Ru clusters,  $\text{ReS}_2$ , and  $\text{Ru}_x/\text{ReS}_2$  of  $\text{Ru}_x/\text{ReS}_2$  system with (f) Ru (010) facet, (g) Ru (1-10) facet and (h) Ru (100) facet.

the optimal balance between hydrogen adsorption and  $\text{H}_2$  desorption, thereby yielding the highest HER activity. Based on theoretical calculation results, the adsorption and desorption processes of simulated hydrogen ions ( $\text{H}^+$ ) on active sites are visualized in Fig. 1c. The Ru (100) facet exhibits an optimal  $\Delta G_{\text{H}^+}$  value, achieving excellent adsorption-desorption equilibrium. In contrast, the Ru (1-10) and (010) facets present challenges with hydrogen desorption, while Re features a high energy barrier that hinders reaction occurrence.

To further study the influence of electronic structure on HER performance, we calculated the projected density of states (PDOS) of key elements (Fig. 1d). In the pristine  $\text{ReS}_2$  basal facet, the p-band center of Re is farther away from the Fermi level than its d-band center, enabling Ru d orbitals to participate in  $\text{H}^+$  adsorption. However, the d-band center of the Re atom is relatively far from the Fermi level, resulting in weak interaction with the H 1s orbital. This manifests as a highly positive  $\Delta G_{\text{H}^+}$  value and low HER activity. Crucially, the formation of the  $\text{Ru}_x/\text{ReS}_2$  interface induces significant electronic modulation. As shown in Fig. 1d, Ru doping shifts the d-band center of  $\text{ReS}_2$  down by approximately 0.25 eV. For Ru nanoparticles, we calculated the positions of the d-band center relative to the p-band center on different facets. Comparisons reveal that the p-band center of Ru is closer to the Fermi level than the d-band center of Ru, suggesting that the p orbitals of Ru—which are often neglected in transition metal catalysis—may also contribute to  $\text{H}^+$  adsorption. Similar d-p orbital coupling effects have been recently reported in Ru-based systems, supporting the plausibility of p-orbital participation [34–36]. On the (100) facet, the p-band center of Ru is farther from the Fermi level but closer than the d-band center of Re in  $\text{ReS}_2$ . This structure favors  $\text{H}^+$  adsorption-desorption equilibrium, yielding the  $\Delta G_{\text{H}^+}$  value closest to 0 eV. Although Ru (010) and (1-10) facets exhibit upward shifts in p-band centers toward the Fermi level, computational results indicate that the p-band centers of Ru are also relatively distant from the d-band center of Re, resulting in an excessive strengthening of  $\text{H}^+$  binding. This manifests as more negative  $\Delta G_{\text{H}^+}$  values, resulting in active site poisoning and hindering  $\text{H}_2$  release.

Analysis of the DOS of Ru nanoparticle clusters reveals that, as shown in Fig. 1e, the (100) facet contributes most significantly to the Fermi level at 0 eV for Ru across three distinct facets. Consequently, this facet serves as the optimal reactive site for the HER. Then, the DOS for Ru clusters,  $\text{ReS}_2$ , and  $\text{Ru}_x/\text{ReS}_2$  systems with three distinct Ru crystal facets are analyzed in Fig. 1f–h, respectively. After Ru loading onto the  $\text{ReS}_2$  basal facet, the DOS values increased compared to those of isolated Ru nanoparticles, indicating that the  $\text{ReS}_2$  basal facet can enhance the electron activity within the Ru. Comparing the Fermi level in the 0 eV region clearly shows that the Ru (100) facet contributes more than the other two facets. This further explains why the Ru (100) facet exhibits the best HER activity in the PDOS.

Collectively, the  $\text{Ru}_x/\text{ReS}_2$  catalyst exhibits exceptionally high HER activity in this computational study, primarily attributed to the dominant exposure of the Ru (100) facet. Through interfacial interactions with the  $\text{ReS}_2$  support, this facet fully exploits the interaction between the p-band center of Ru and the d-band center of Re, thereby achieving an optimal  $\text{H}_2$  adsorption free energy.

To validate the effect of the  $\text{Ru}_x/\text{ReS}_2$  catalyst for HER, we experimentally prepared the materials. Fig. 2a illustrates the

synthesis process, which can be divided into two steps. First, bulk  $\text{ReS}_2$  is exfoliated into  $\text{ReS}_2$  nanosheets via solid-phase lithiation followed by liquid-phase exfoliation. Subsequently, solid-phase lithiation is performed again to obtain Li-intercalated  $\text{ReS}_2$  nanosheets. Finally, through an *in-situ* controlled reduction strategy, the high hydration energy of hydrated metal chlorides enables the exchange of Ru ions with Li ions intercalated between  $\text{ReS}_2$  layers. For solvent selection, ultra-dry *N*-methyl-2-pyrrolidone (NMP) was used here [37]. The ultradry NMP not only facilitates the dispersion of Li-intercalated  $\text{ReS}_2$  nanosheets but also suppresses side reactions with  $\text{H}_2\text{O}$ . During ion exchange, Li ions are replaced by Ru ions and subsequently removed as soluble  $\text{LiCl}$ . Due to the highly reductive nature of the lithiated  $1\text{T}'$   $\text{ReS}_2$ , Ru ions are reduced to zero-valent metal particles. As a result, uniformly distributed Ru nanoclusters are obtained on  $\text{ReS}_2$  nanosheets, denoted as  $\text{Ru}_x/\text{ReS}_2$ . By adjusting the molar ratio of  $\text{Li}_x\text{ReS}_2$  nanosheets to  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ , five types of  $\text{Ru}_x/\text{ReS}_2$  nanosheets with Ru intercalation ratios of 3:1, 3:2, 1:1, 1:2, and 1:3 ( $x$  represents Ru's actual load capacity) were synthesized. The X-ray diffraction (XRD) patterns of these five samples and  $\text{ReS}_2$  are shown in Fig. S2. Fig. 2b presents the XRD patterns of  $\text{ReS}_2$ ,  $\text{Li}_x\text{ReS}_2$ , and  $\text{Ru}_x/\text{ReS}_2$ . Both Li-intercalated and Ru-loaded samples exhibit a sharp diffraction peak near  $14.5^\circ$ , corresponding to the (002) facet.  $\text{Ru}_x/\text{ReS}_2$  additionally displays a new diffraction peak near  $28^\circ$ , not observed in  $\text{Li}_x\text{ReS}_2$  or bulk  $\text{ReS}_2$ , which is attributed to metal Ru. Scanning electron microscopy (SEM) images of  $\text{Ru}_x/\text{ReS}_2$  nanosheet on copper mesh are shown in Fig. 2c and Fig. S3, indicating that the nanosheets possess a relatively thin structure. Table S1 details the elemental content of each sample, with results determined via energy-dispersive spectroscopy (EDS). As the Ru loading increases, the resulting catalysts are designated as  $\text{Ru}_{0.0468}/\text{ReS}_2$ ,  $\text{Ru}_{0.0533}/\text{ReS}_2$ ,  $\text{Ru}_{0.0829}/\text{ReS}_2$ ,  $\text{Ru}_{0.0945}/\text{ReS}_2$  and  $\text{Ru}_{0.1152}/\text{ReS}_2$ . Fig. 2d shows an atomic force microscopy (AFM) image revealing that the thickness of  $\text{Ru}_x/\text{ReS}_2$  nanosheets is approximately 5.8 nm, consistent with an ultrathin morphology.

Transmission electron microscopy (TEM) was used to examine the crystal structure of  $\text{Ru}_x/\text{ReS}_2$  nanosheets. Fig. 2e presents a low-magnification image of  $\text{ReS}_2$ , showing that after solid-state lithiation and exfoliation, the material forms an ultrathin layer with several stacked nanosheets observable at the edges. TEM images and EDS spectra of bulk  $\text{ReS}_2$  are provided in Fig. S4. The unique layered structure of these nanosheets ensures that subsequent Ru particles can be loaded and form nanoclusters in the interlayer spaces. High-resolution TEM (HRTEM) was used to examine the atomic lattice structure of  $\text{ReS}_2$ . The HRTEM image shown in Fig. 2f displays distinct zipper-like stripes within the lattice. Analysis of the interplanar spacings indicates that the measured distances of 0.559 and 0.481 nm correspond to the (100) and (1-10) facets, respectively, in agreement with the  $\text{ReS}_2$  lattice parameters. The inset selective area electron diffraction (SAED) pattern confirms the high crystallinity of bulk  $\text{ReS}_2$ . Fig. 2g shows that the well-ordered lattice of the original  $\text{ReS}_2$  is disrupted after ion exchange, yet the exfoliated material predominantly retains the  $\text{ReS}_2$  lattice. The lattice fringes exhibit a distinct zipper-like pattern with an interplanar spacing of 0.617 nm, corresponding to the  $\text{ReS}_2$  (002) facet. In contrast, the disordered regions of the lattice fringes show an interplanar spacing of 0.237 nm, corresponding to the Ru (100) facet. Its SAED pattern indicates reduced crystallinity after ion-exchange loading, possibly due to sample oxidation. However, the sym-

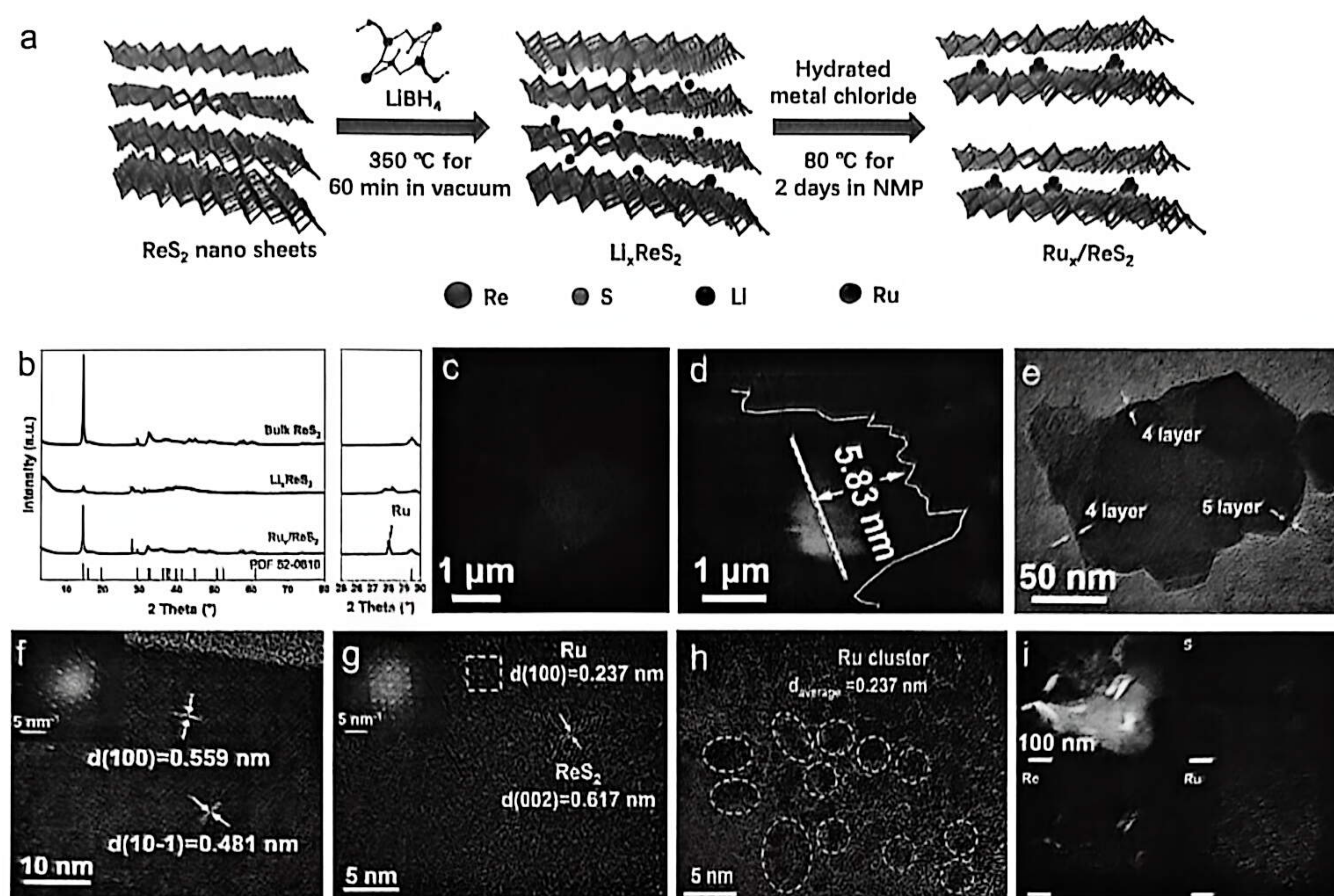


Figure 2 Structural and morphological characterizations of  $\text{Ru}_x/\text{ReS}_2$  nanosheets. (a) Schematic illustration of Ru nanoclusters uniformly distributed on  $\text{ReS}_2$  nanosheets. (b) XRD patterns of bulk  $\text{ReS}_2$ ,  $\text{Li}_x\text{ReS}_2$ , and  $\text{Ru}_x/\text{ReS}_2$ . (c) SEM image of  $\text{Ru}_x/\text{ReS}_2$  nanosheets. (d) AFM image of  $\text{Ru}_x/\text{ReS}_2$  nanosheets. (e) TEM image of  $\text{ReS}_2$  nanosheets. HRTEM images and corresponding SAED patterns of (f)  $\text{ReS}_2$  and (g)  $\text{Ru}_x/\text{ReS}_2$  nanosheets. (h) HRTEM image of  $\text{Ru}_x/\text{ReS}_2$  nanosheets showing the Ru cluster. (i) TEM image and EDS mappings of  $\text{Ru}_x/\text{ReS}_2$  nanosheets.

metrical electron diffraction pattern confirms that the exfoliated nanosheets exhibit highly crystalline properties. Several regions distinct from the  $\text{ReS}_2$  lattice are highlighted in Fig. 2h. In these areas, Ru nanoparticles possess an average interplanar spacing of 0.237 nm, corresponding to the (100) facet of Ru. EDS spectra (Fig. S5) and statistical analysis (Fig. S6) confirm that Ru forms uniformly dispersed clusters on the  $\text{ReS}_2$  nanosheet surface. For the  $\text{Ru}_x/\text{ReS}_2$  sample with a Ru:Re ratio of 3:1, the Ru content is determined to be 11.53% (Fig. S5f). EDS spectra further confirm a homogeneous distribution of Ru across the nanosheets, consistent with the brighter regions observed in Fig. 2i, corresponding to Ru-decorated  $\text{ReS}_2$ .

To establish the intrinsic relationship between the structure and properties of the material, we employed a combination of characterization techniques. As shown in Fig. S7a, Raman spectra show that bulk  $\text{ReS}_2$  exhibits the 1T' phase. Following the insertion of Li and Ru, the positions of the primary Raman vibrational peaks remained unchanged, with only variations in peak intensity observed. This confirms that the sample maintains high reducibility prior to ion exchange due to its distorted structure containing the 1T' phase. After Ru insertion, a new peak appears at  $275\text{ cm}^{-1}$ , corresponding to the Ru–S bond vibration, arising from the strong chemical adsorption between high-surface-energy zero-valent Ru atoms/clusters and exposed or interlayer S atoms in  $\text{ReS}_2$  [38,39]. To confirm the reduction of Ru ions after intercalation between nanolayers, X-ray photoelectron spectroscopy (XPS) was performed to analyze elec-

tronic valence states. Comparing results before ion exchange (Fig. S7b, c) with those after exchange (Fig. S7e, f) shows that both Re and S binding energies shift by approximately 1 eV toward higher values. This indicates that after Ru ions exchange with Li ions, electrons transfer from the  $\text{ReS}_2$  layer to the Ru ions due to the electron-deficient nature of  $\text{Ru}^{3+}$ , thereby stabilizing the entire system. Concurrently, the Ru ions gain electrons and are reduced to zero-valent metallic particles, as confirmed by the Ru 3p orbital electron spectra in Fig. S7d. Fitting calculations based on peak areas indicate that  $\text{Ru}^0$  roughly accounts for 85.7% of all Ru elements. The remaining portion may be due to incomplete reduction of some Ru ions or their subsequent oxidation in air. These oxidized Ru species primarily exist in the  $\text{Ru}^{3+}$  form and may slightly alter the local electronic environment, but their low abundance (~14.3%) relative to the dominant metallic  $\text{Ru}^0$  ensures that they do not govern the HER activity. The XPS spectra of Ru 3d (Fig. S8) also indicate that  $\text{Ru}^0$  accounts for around 79.4% of all Ru elements, which means nanoparticles loaded onto the nanosheets primarily exist as zero-valent metal in the interlayer space.

Subsequently, the electrocatalytic HER performance of  $\text{Ru}_x/\text{ReS}_2$  was investigated. Linear sweep voltammetry (LSV) results are shown in Fig. 3a. At a current density of  $10\text{ mA cm}^{-2}$ , the overpotentials decrease from 348 mV (pure  $\text{ReS}_2$ ) to 133, 114, 36, 72, and finally 32 mV ( $\text{Ru}_{0.1152}/\text{ReS}_2$ ), with corresponding Tafel slopes reduced from 383 to 68, 61, 44, 60, and  $15\text{ mV dec}^{-1}$ , respectively—outperforming commercial Pt/C

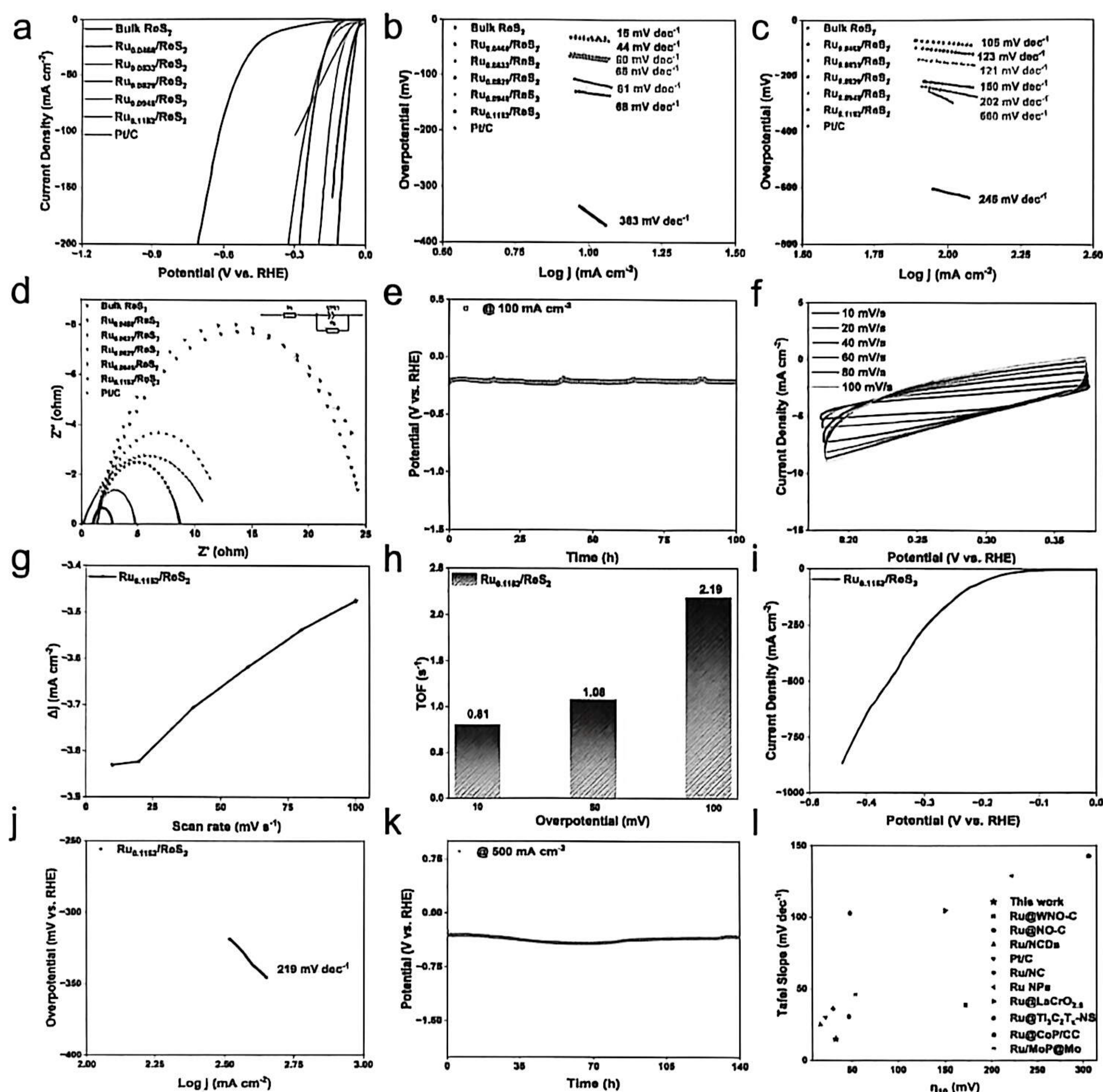


Figure 3 HER performance characterization of  $\text{Ru}_x/\text{ReS}_2$  catalysts. (a) LSV curves of the bulk  $\text{ReS}_2$ ,  $\text{Ru}_x/\text{ReS}_2$ , and Pt/C reference catalysts. Tafel plots of the bulk  $\text{ReS}_2$ ,  $\text{Ru}_x/\text{ReS}_2$ , and Pt/C reference catalysts at (b) 10 and (c) 100  $\text{mA cm}^{-2}$ , respectively. (d) Nyquist plots of the bulk  $\text{ReS}_2$ ,  $\text{Ru}_x/\text{ReS}_2$ , and Pt/C reference catalysts. Inset is the corresponding EIS simulation model. (e) Long-term stability of the  $\text{Ru}_{0.1152}/\text{ReS}_2$  catalyst at 100  $\text{mA cm}^{-2}$ . (f) ECSA of  $\text{Ru}_{0.1152}/\text{ReS}_2$  obtained by CV at different scan rates. (g) Calculated  $C_{dl}$  value of  $\text{Ru}_{0.1152}/\text{ReS}_2$ . (h) Comparison of the TOF values for  $\text{Ru}_{0.1152}/\text{ReS}_2$  at different overpotentials. The TOF was derived from the ECSA. (i) LSV curve of the  $\text{Ru}_{0.1152}/\text{ReS}_2$  catalyst at large current densities. (j) Tafel plots of the  $\text{Ru}_{0.1152}/\text{ReS}_2$  catalyst at 500  $\text{mA cm}^{-2}$ . (k) Long-term stability of the  $\text{Ru}_{0.1152}/\text{ReS}_2$  catalyst at 500  $\text{mA cm}^{-2}$ . (l) Comparison of the Tafel slopes and overpotentials at 10  $\text{mA cm}^{-2}$  for the  $\text{Ru}_{0.1152}/\text{ReS}_2$  catalyst with those of previously reported high-activity acidic HER catalysts. The potential window used for  $C_{dl}$  measurements was 0.1–0.2 V vs. RHE without faradaic processes occurring. All experiments were conducted in 0.5 M  $\text{H}_2\text{SO}_4$  at room temperature.

(70 mV, 60  $\text{mV dec}^{-1}$ ) under the same conditions. At 100  $\text{mA cm}^{-2}$ , the trend persists, with the optimal  $\text{Ru}_{0.1152}/\text{ReS}_2$  sample exhibiting the lowest overpotential of 82 mV and a Tafel slope of 105  $\text{mV dec}^{-1}$ , compared to 286 mV and 560  $\text{mV dec}^{-1}$  for Pt/C. Concurrently, the material's impedance decreases with increasing Ru doping ratio, as reflected in the Nyquist plot shown in Fig. 3d. To exclude possible interference from Pt species (e.g., dissolution or redeposition from the Pt electrode), we performed control experiments using a carbon rod electrode

(Fig. S9). The results show that the overpotential difference was less than 5 mV, indicating a negligible effect. At 100 and 500  $\text{mA cm}^{-2}$ , the overpotentials of the  $\text{Ru}_{0.1152}/\text{ReS}_2$  catalyst are 82 and 360 mV, respectively (Fig. 3c, i), with corresponding Tafel slopes of 105 and 219  $\text{mV dec}^{-1}$ , indicating promising high-current performance. Further long-term stability of the optimal catalyst was evaluated at high currents of 100 and 500  $\text{mA cm}^{-2}$  (Fig. 3e, k). The  $\text{Ru}_{0.1152}/\text{ReS}_2$  catalyst shows negligible voltage decay after 100 h of continuous operation at

100 mA cm<sup>-2</sup> and maintains stable performance over 140 h at 500 mA cm<sup>-2</sup>. Based on XPS analysis, Fig. S10a reveals an increase in the O content compared to the sample before stability testing (Fig. S11), suggesting the oxidation of certain species in the sample. Figs S10b, c and S7 (the XPS spectra of the pristine sample) show that the Re 4f and S 2p peak positions remain essentially unchanged, indicating that the catalyst support remains unoxidized. Fitting of the O 1s spectrum in Fig. S10d shows peaks corresponding to oxide species, which are likely attributable to RuO<sub>2</sub> or higher-valence ruthenium oxides. Comparison of Figs S10e and S11f reveals a partial transformation of Ru from the initial metallic state (0) to higher oxidation states, such as +4 and +6. Although the proportion of metallic Ru decreases, it remains predominant. Quantitative fitting indicates that metallic Ru still accounts for 48.7% and 44.3% of the total Ru content, further confirming the stability of the catalyst. Here, Co<sub>x</sub>/ReS<sub>2</sub> and Ni<sub>x</sub>/ReS<sub>2</sub> nanosheets were synthesized and evaluated for acidic HER, showing promising activity as shown in Fig. S12.

To investigate the origin of the exceptional performance of the Ru<sub>0.1152</sub>/ReS<sub>2</sub> catalyst, we quantitatively evaluated its electrochemically active surface area (ECSA) and intrinsic catalytic activity. The ECSA is directly correlated with the double-layer capacitance (*C<sub>dl</sub>*), with results shown in Fig. 3f. By measuring the capacitance current in the non-Faradaic region under different scan conditions via CV, we calculated a *C<sub>dl</sub>* value as high as 4.2 mF cm<sup>-2</sup> for the Ru<sub>0.1152</sub>/ReS<sub>2</sub> catalyst. Fig. 3g shows the *C<sub>dl</sub>* plot calculated via linear fitting. Based on this, its ECSA was estimated to be approximately 105, indicating that the catalyst's true electrochemical active surface area is 105 times that of its geometric surface area. This exceptionally large ECSA is primarily attributed to the unique nanosheet structure of Ru<sub>x</sub>/ReS<sub>2</sub> and the increased exposed edge sites following successful intercalation. These features provide abundant external active sites for electrochemical reactions, a prerequisite for achieving highly efficient catalysis. However, high ECSA reflects only the quantity of active sites. To evaluate the quality or intrinsic catalytic efficiency per site, we further calculated the turnover frequency (TOF). As shown in Fig. 3h, the TOF value of the catalyst increases sharply with increasing overpotential (*η*). Notably, the TOF exceeds 1.08 s<sup>-1</sup> at a low overpotential of *η* = 50 mV. When the overpotential increases to 100 mV, the TOF further climbs to 2.19 s<sup>-1</sup>. These results clearly demonstrate that the catalyst not only possesses abundant active sites but also exhibits extremely high intrinsic activity at each site. A TOF value exceeding 1 s<sup>-1</sup> at such a low overpotential indicates highly efficient adsorption, desorption, and conversion of reactants at the active sites. Compared with Ru-based catalysts reported in the past decades [40–45], the present work demonstrates significant performance advantages, as shown in Fig. 3l.

In summary, we have successfully constructed a highly efficient and stable acidic HER electrocatalyst by anchoring Ru nanoclusters onto 1T'-ReS<sub>2</sub> nanosheets. This unique structure, achieved through solid-state lithiation and localized ion exchange, endows the Ru<sub>x</sub>/ReS<sub>2</sub> catalyst with exceptional catalytic performance, including ultra-low overpotentials and outstanding durability at high current densities. Importantly, DFT calculations reveal that its outstanding activity stems from atomic-level mechanisms involving critical electronic structure regulation at the heterointerface. This primarily involves the downward shift of the p-band center on the exposed Ru (100)

facet, synergistically interacting with the modulated Re d-band center within the ReS<sub>2</sub> support. This synergistic electronic regulation via d-p coupling between Ru nanoclusters and ReS<sub>2</sub> nanosheets drives the Δ*G<sub>H\*</sub>* toward thermally neutral values, thereby optimizing overall HER kinetics. This work not only delivers an exceptional catalyst but also elucidates fundamental mechanisms of interfacial orbital interactions, paving new pathways for designing next-generation energy conversion catalysts through precise tuning of p-band and d-band centers.

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**Author contributions** Wang L designed the experiments, synthesized the materials, conducted the electrochemical measurements, and wrote the original draft. Guo R and Liu M assisted with material synthesis and Raman characterization. Chen Z, Li G, Lin H and Chen J assisted with SEM and TEM characterization. Wang C and Wang D assisted with XPS and AFM characterization. Guo M and Zhu X assisted with material characterization. Zheng Z performed the theoretical calculations. Huang K helped with theoretical calculations and result analysis. Yu Y, Wang JJ, Yu H and Zhao W guided the electrochemical testing and data analysis. Mi J and Tian Z polished the manuscript. Zhang L supervised the whole experiments, revised and polished the manuscript. All authors contributed to the general discussion.

**Conflict of interest** The authors declare that they have no conflict of interest.

**Supplementary information** Supplementary materials are available in the online version of the paper.



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钌纳米簇与二硫化铼纳米片d-p耦合的电子调控以增强绿色析氢性能

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**摘要** 采用非贵金属载体负载纳米颗粒, 是降低电催化析氢反应催化剂成本、实现工程化应用的有效策略。然而, 常见的二维材料载体在催化过程中会发生相变, 由导体性质的1T'相转变为半导体性质的2H相, 导致催化性能下降。本文报道了采用固态锂化与离子交换策略, 制备稳定的1T'相二硫化铼(ReS<sub>2</sub>)载体, 构筑了异质结催化剂, 并将其应用于绿色电催化制氢领域。该催化剂具有钌(Ru)纳米簇均匀锚定在1T'-ReS<sub>2</sub>纳米片(Ru<sub>x</sub>/ReS<sub>2</sub>)上的特征, 且在酸性介质中展现出卓越的析氢性能: 在10 mA cm<sup>-2</sup>电流密度下实现32 mV的低过电位, 15 mV dec<sup>-1</sup>的低塔菲尔斜率, 并在100和500 mA cm<sup>-2</sup>的高电流密度下保持超过100小时的优异稳定性, 性能无显著衰减。密度泛函理论计算揭示: 通过与ReS<sub>2</sub>的界面相互作用, Ru(100)晶面充分利用了Ru纳米簇与ReS<sub>2</sub>纳米片的d-p能带耦合的相互作用, 从而实现了仅-0.106 eV的最优氢吸附自由能, 为优异的析氢性能作出贡献。本研究强调了界面p-d轨道相互作用的关键作用, 为设计高性能、低贵金属含量的电催化剂提供了新策略。