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Interfacial engineering-induced electronic state modulation in Ru/MoS₂ heterostructures for efficient hydrogen evolution reaction†

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In traditional binary heterojunction catalysts, mismatched energy band structures lead to higher electron transfer barriers. By reducing the work function difference via a ternary Ru–RuS₂/MoS₂ heterostructure, we developed a HER catalyst with remarkable activity (17 mV@10 mA cm⁻²) and excellent stability (300 h@500 mA cm⁻²).

Alkaline water electrolysis serves as an efficient method for hydrogen production. The development of efficient and durable electrocatalysts to improve the kinetics of the hydrogen evolution reaction (HER) is essential for the large-scale production of green hydrogen.¹ To date, Pt-based catalysts are effective but limited by high cost and scarcity.² MoS₂, with its active metallic edges, is a promising Pt alternative for HER.³ Nevertheless, the application of MoS₂ as a catalyst in HER is restricted by its limited density of active sites and poor electrical conductivity.⁴

Strategies like phase engineering,⁵ defect engineering,⁶ doping,⁷ and heterostructure construction⁸ have been explored. Among these approaches, metal (such as Pb, Ru, Co, *etc.*) doping has been extensively validated as an effective strategy to significantly enhance the HER catalytic activity of MoS₂. As one of the most cost-effective noble metals, Ru has demonstrated significant advantages in the field of water splitting.^{9,10} However, direct contact between metals and wide-bandgap semiconductors often introduces significant impedance. In recent years, the effective design and construction of heterostructures have been demonstrated to facilitate the directional transport of electrons as a

solution to this issue. For example, Huang *et al.* developed a metallic heterostructure, Mo₂S₃@NiMo₃S₄, with excellent electron transfer, fast reaction kinetics, and strong structural stability, achieving overpotentials of 173 mV for OER and 32 mV for HER at 10 mA cm⁻².⁹ Nonetheless, the work function disparity between metallic nanoparticles and MoS₂ obstructs electron transfer, leading to increased energy losses and reduced catalytic efficiency. Although some studies have attempted to address this challenge, further exploration of effective strategies is still required to enhance catalytic performance.

Herein, we constructed a Ru–RuS₂/MoS₂ heterostructure, where RuS₂ serves as a “cross-interfacial electron bridge” between narrow-bandgap Ru and wide-bandgap MoS₂. This interfacial design reduces ohmic impedance and enhances electron transfer. Ru–RuS₂/MoS₂ delivers outstanding HER performance with a low overpotential of 17 mV (10 mA cm⁻²) and stability for over 300 h (500 mA cm⁻²). Density functional theory (DFT) results indicate that the incorporation of RuS₂ reduces the bandgap of Ru–MoS₂, facilitates the directional transfer of electrons from Ru sites to MoS₂, and lowers the dissociation energy of *H₂O as well as the adsorption energy of *H. This simultaneously enhances water dissociation and hydrogen desorption, thereby significantly accelerating the HER process.

As depicted in Fig. 1a, the synthesis of Ru–RuS₂/MoS₂ follows a four-step process (Experimental Section for details ESI†). The Ru–MoS₂ was synthesized by the same method. The XRD pattern of Ru–RuS₂/MoS₂ (Fig. 1b) reveals characteristic peaks at 27.519°, 31.881°, 45.710°, and 54.186°, corresponding to the (111), (200), (220), and (311) planes of RuS₂ (PDF#97-004-1996). Additionally, peaks at 14.125°, 32.911°, 39.512°, and 58.764° are associated with the (002), (100), (103), and (110) planes of MoS₂ (PDF#97-003-1067). These observations preliminarily indicate the formation of a RuS₂/MoS₂ heterojunction structure in Ru–RuS₂/MoS₂. Furthermore, Raman spectroscopy was conducted on MoS₂, Ru–MoS₂, and Ru–RuS₂/MoS₂ samples (Fig. S1, ESI†). Raman spectroscopy analysis demonstrated that, in addition to the A_{1g} and E_{2g} modes of MoS₂, the Ru–RuS₂/MoS₂ exhibited a

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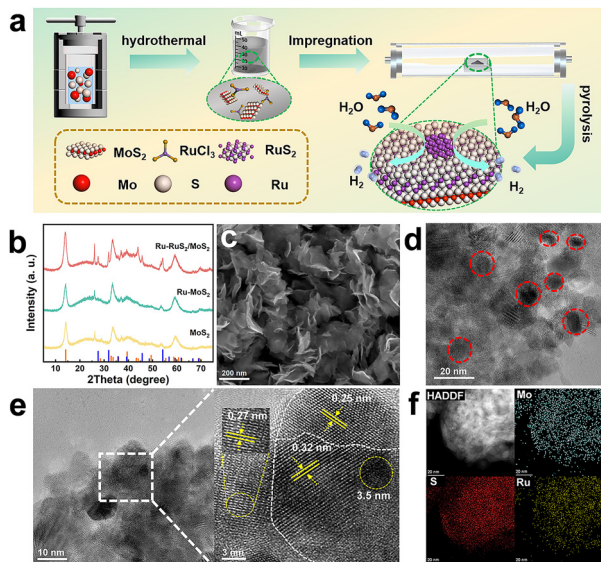


Fig. 1 Characterization of the structure and morphology of catalysts. (a) The synthesis process schematic diagram of Ru–RuS₂/MoS₂; (b) XRD pattern of MoS₂, Ru–MoS₂ and Ru–RuS₂/MoS₂; (c) SEM image; (d) TEM image, (e) HRTEM (inset high-magnified HRTEM image) and (f) elemental mapping images of Mo, S, Ru for the Ru–RuS₂/MoS₂.

weak peak at 386 cm⁻¹, corresponding to RuS₂.¹¹ This observation further confirms the formation of RuS₂ structures in the target sample. SEM (Fig. 1c) shows a nanoflower-like structure in Ru–RuS₂/MoS₂, enhancing stability and active site density for better catalysis.¹² Moreover, SEM images at higher magnifications (Fig. S3, ESI[†]) reveal spherical structures attached to the nanoflowers, which preliminarily confirm the successful formation of Ru nanoclusters. TEM images reveal that Ru–RuS₂/MoS₂ exhibits a sheet-like distribution. Lattice fringes indicate the stacking of distinct nanosheets. Additionally, dark spots, which are uniformly distributed throughout the material, confirm the presence of Ru nanoclusters (Fig. 1d). The structure suggests a MoS₂–RuS₂ heterojunction with uniform Ru nanoclusters. To further investigate the nanostructure of Ru–RuS₂/MoS₂, high-resolution transmission electron microscopy (HRTEM) was employed for detailed analysis (Fig. 1e). In the magnified HRTEM images, lattice fringes with interplanar spacings of 0.25 nm, 0.27 nm, and 0.32 nm are observed, which correspond to the (102) and (100) planes of MoS₂ and the (111) plane of RuS₂, respectively. The results support the aforementioned hypothesis and confirm the successful formation of the heterointerfaces. In addition, high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and corresponding elemental mapping uncover the homogeneous distribution of Mo, S, and Ru elements within the Ru–RuS₂/MoS₂ heterostructure (Fig. 1f). AFM (Fig. S4, ESI[†]) shows a consistent MoS₂ layered structure (~3.5 nm thickness) in all samples.

XPS was used to analyze electronic properties and valence states (Fig. S5, ESI[†]). The results indicate that the formation of RuS₂ induces a higher oxidation state of Ru in Ru–RuS₂/MoS₂.¹³ Meanwhile, the electron transfer from the Ru nanoclusters to MoS₂ is also evidenced.¹⁴ Moreover, the characteristic peaks of

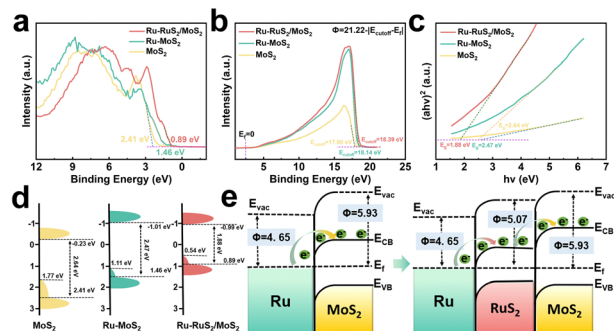


Fig. 2 Characterization of valence states and electronic structure. (a) VB-XPS spectra, (b) UPS spectra and (c) UV-VIS spectra of MoS₂, Ru–MoS₂ and Ru–RuS₂/MoS₂; (d) energy band diagram of MoS₂, Ru–MoS₂ and Ru–RuS₂/MoS₂; (e) schematic diagram of band structures (E_f = Fermi level, E_{vac} = vacuum energy).

Ru⁰ 3p_{1/2} (484.4 eV) and Ru⁰ 3p_{3/2} (462.2 eV) reflect the presence of Ru nanoclusters. It is well established that the electrical conductivity of semiconductors is determined by the band gap within their energy band structure, with the transition of electrons between the valence band and the conduction band dictating their conductive properties.¹⁵ To further investigate the impact of RuS₂ on electron conduction, we initially employed X-ray photoelectron spectroscopy valence band (VB-XPS) to analyze the VB positions of MoS₂, Ru–MoS₂, and Ru–RuS₂/MoS₂ (Fig. 2a). In contrast to MoS₂ (2.41 eV) and Ru–MoS₂ (1.46 eV), the valence band position of Ru–RuS₂/MoS₂ (0.89 eV) is significantly closer to the Fermi level. The lower valence band position confirms RuS₂'s role as a “cross-interfacial electron bridge” optimizing the catalyst's electronic structure. To examine the effect of work function difference ($\Delta\Phi$) on electron transfer,¹⁶ UPS was employed to determine the (Φ) values of MoS₂, Ru–MoS₂, and Ru–RuS₂/MoS₂. The corresponding results reveal that compared to the higher work function (Φ) values for MoS₂ (3.32 eV) and Ru–MoS₂ (3.08 eV), the Ru–RuS₂/MoS₂ possesses the lowest Φ value of 2.83 eV. A lower work function indicates a reduced energy requirement for electron emission, which in turn lowers the energy barrier, facilitates charge transfer, and enhances conductivity.¹⁷ Simultaneously, UV-VIS analysis reveals the smallest band gap (1.88 eV) for Ru–RuS₂/MoS₂, supporting its high conductivity (Fig. 2c). This further corroborates the enhanced conductivity of Ru–RuS₂/MoS₂. DFT calculations also determine that the work function (Φ) of RuS₂ is 5.07 eV, which is lower than that of MoS₂ (Φ = 5.93 eV) but higher than that of Ru (Φ = 4.65 eV) (Fig. S6, ESI[†]). This satisfies the prerequisite for the formation of an interfacial energy barrier and supports the theoretical feasibility of RuS₂ acting as the “cross-interfacial electron bridge” to facilitate electron transfer from Ru to MoS₂ (Fig. 2d). After electronic modification, a significant optimization of the band structure was observed. The band diagrams of MoS₂, Ru–MoS₂, and Ru–RuS₂/MoS₂ were derived from VB-XPS and UV-VIS, as shown in Fig. 2e. Band diagrams reveal that RuS₂ shifts the valence band closer to the Fermi level and reduces the band gap, enhancing conductivity. The above findings demonstrate that

the introduction of RuS₂ effectively reduces the material's intrinsic ohmic impedance and enhances electron transfer from the metal to the wide-bandgap semiconductor.

We conducted electrochemical tests to verify the role of RuS₂ as a “cross-interfacial electron bridge” that enhances Ru to MoS₂ electron transfer and evaluated the catalytic HER performance of Ru–RuS₂/MoS₂. At a current density of 10 mA cm⁻², Ru–RuS₂/MoS₂ exhibited the lowest overpotential ($\eta_{10} = 17$ mV) (Fig. 3a and b and Fig. S7, ESI[†]), demonstrating its superior electron transfer capabilities. The heterostructure displayed a significantly lower Tafel slope of 75.9 mV dec⁻¹ (Fig. 3c), indicating exceptional reaction kinetics. Moreover, the Tafel slope indicates that the Heyrovsky step is the rate-limiting process in HER.¹⁸ We hypothesize that this phenomenon may be attributed to the heterostructure formed between MoS₂ and RuS₂, which facilitates electron transfer from Ru to the MoS₂ surface.

Additionally, Ru–RuS₂/MoS₂ has the highest electrochemical double-layer capacitance (C_{dl}) measurement of 19.99 mF cm⁻² (Fig. 3d and Fig. S9, ESI[†]), and even after normalizing by the ECSA value, Ru–RuS₂/MoS₂ continues to show the highest current density (J_{ECSA}) (Fig. S10, ESI[†]), indicating it possesses a high density of active sites to participate in the HER process and rapid reaction kinetics. EIS reveals Ru–RuS₂/MoS₂ has the smallest semicircle (Fig. 3e), suggesting minimal charge transfer resistance.¹⁹ Catalyst stability is essential for practical applications, which was appraised by chronopotentiometric test. As expected in Fig. 3f, the Ru–RuS₂/MoS₂ demonstrates stable operation for 300 h at 500 mA cm⁻² in 1 M KOH, while still maintaining its morphology and structure (Fig. S11, ESI[†]). Meanwhile, the faraday efficiency of Ru–RuS₂/MoS₂ is 96.7%. Compared to most recently reported Ru-based and MoS₂-based catalysts, this catalyst exhibits the lowest overpotential (Fig. 3g

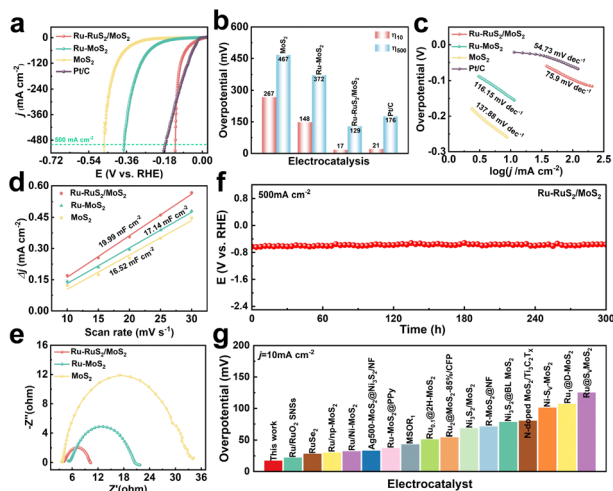


Fig. 3 HER performance in 1 M KOH. (a) LSV curves, (b) overpotentials at current densities of 10 mA cm⁻² and 500 mA cm⁻², and (c) Tafel slopes of MoS₂, Ru–MoS₂, Ru–RuS₂/MoS₂, and commercial Pt/C; (d) electrochemical double-layer capacitance (C_{dl}), (e) electrochemical impedance spectroscopy (EIS); (f) stability testing of the Ru–RuS₂/MoS₂ catalyst; (g) comparison chart of overpotential at a current density of 10 mA cm⁻².

and Table S1, ESI[†]). These results underscore that Ru–RuS₂/MoS₂ exhibits impressive HER activity and robust stability in alkaline electrolytes.

In situ techniques were employed to evaluate the adsorption behavior on the catalyst surface. First, electrochemical *in situ* impedance spectroscopy was analyzed using Nyquist plots to assess the conductivity of MoS₂, Ru–MoS₂, and Ru–RuS₂/MoS₂ (Fig. S13, ESI[†]). The data were fitted using a dual parallel circuit model, where R_2 represents hydrogen adsorption resistance (Fig. S14, ESI[†]).²⁰ The R_2 was fitted to the overpotential (Fig. 4a), revealing that Ru–RuS₂/MoS₂ has smaller hydrogen adsorption resistance than Ru–MoS₂, confirming improved hydrogen adsorption and transfer. The Bode plots were applied to further understand the reaction kinetics of HER on MoS₂, Ru–MoS₂, and Ru–RuS₂/MoS₂ (Fig. S15, ESI[†]). The Bode plot illustrates the variations of phase peak angles (θ) and peak frequency (f_{max}) under different applied voltages, as shown in Fig. 4b. Notably, Ru–RuS₂/MoS₂ exhibits a smaller phase angle (θ) in the low-frequency region and overall higher peak frequencies (f_{max}), indicating that the incorporation of RuS₂ facilitates charge transfer.²¹ In order to substantiate the previously discussed conclusions, *in situ* Raman analysis in 1 M KOH verifies that Ru–RuS₂/MoS₂ enhances *H₂O dissociation. In Fig. S16, ESI[†], the broad peak observed between 3200 cm⁻¹ and 3400 cm⁻¹ is attributed to the adsorption of *H₂O.²² As the potential decreases from 0.20 V to 0 V vs. RHE, the intensity of the H₂O adsorption peaks for MoS₂, Ru–MoS₂, and Ru–RuS₂/MoS₂ shows no significant change. However, when the potential is further reduced from 0 V to –0.1 V vs. RHE, an obviously weakened adsorption peak of *H₂O is observed for both Ru–MoS₂ and Ru–RuS₂/MoS₂. The relationship between normalized Raman intensity and potential is illustrated in Fig. 4c. It is evident that, compared to MoS₂ and Ru–MoS₂, the *H₂O adsorption peak for Ru–RuS₂/MoS₂ exhibits more pronounced changes during the dissociation phase (from 0 V to –0.1 V vs. RHE). This suggests that the incorporation of RuS₂ enhances the dissociation of *H₂O.²³

To further demonstrate the positive role of the “cross-interfacial electron bridge” (RuS₂) in facilitating electron transfer from Ru to MoS₂, DFT calculations were conducted. The MoS₂ (001), RuS₂ (200), and Ru (101) surfaces were selected as the optimized models for the Ru–RuS₂/MoS₂ heterostructure (Fig. S17, ESI[†]).²⁴ The electron transfer behavior was unveiled through differential charge density calculations (Fig. 5a), and the charge density of the Ru–MoS₂ and Ru–RuS₂/MoS₂ models

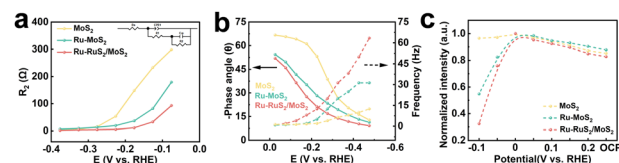


Fig. 4 Electrochemical *in situ* testing (a) Comparison of hydrogen adsorption resistance (R_2) at different voltages; (b) phase peak angles and peak frequencies in the range of –0.026 to –0.476 V (vs. RHE); and (c) plot of normalized Raman intensity of the water adsorption peak versus potential for MoS₂, Ru–MoS₂, and Ru–RuS₂/MoS₂.

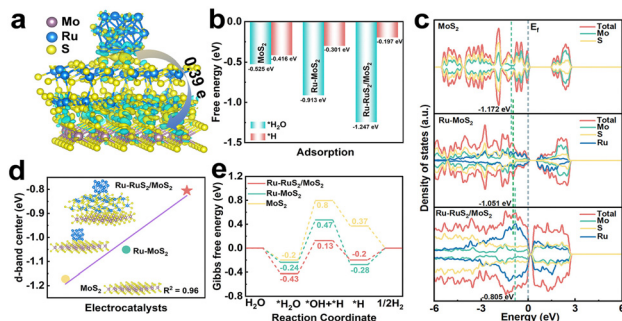


Fig. 5 DFT calculations for MoS₂, Ru-MoS₂, and Ru-RuS₂/MoS₂. (a) Charge density difference plot; (b) free energy of *H₂O and *H adsorption; (c) DOS diagram (density of states diagram); (d) trend chart of d-band center values; (e) HER processes models.

was analyzed using visualized two-dimensional slices (Fig. S19, ESI[†]). Evidently, RuS₂ induces local charge redistribution, resulting in electron migration from Ru to MoS₂. These electron-deficient Ru sites on the surface can serve as active centers for the appropriate adsorption of various reaction intermediates.²⁵ Moreover, based on the adsorption structures of *H₂O, *OH, and *H on MoS₂, Ru-MoS₂, and Ru-RuS₂/MoS₂ as well as the corresponding adsorption energies (Fig. 5b and Fig. S20–S22, ESI[†]), the Ru clusters in Ru-RuS₂/MoS₂ are considered as the active sites for the adsorption of *OH, while the adsorption site for *H is the adjacent S atom on RuS₂, which is suitable for HER process. This suggests that Ru-RuS₂/MoS₂ enhances water activation and *H release, improving HER efficiency. Additionally, an analysis of the density of states (DOS) diagrams and d-band center positions for MoS₂, Ru-MoS₂, and Ru-RuS₂/MoS₂ (Fig. 5c and d) was conducted. The construction of the heterostructure reduced the bandgap of the catalyst, with the d-band center of Ru-RuS₂/MoS₂ (−0.805 eV) being closer to the Fermi level ($E_f = 0$ eV). The d-band centers of the three catalysts demonstrate an exceptional linear fit quality ($R^2 = 0.96$).²⁶ A more positive value of the d-band center would reduce the filling of antibonding orbitals, decreasing the interaction between the active sites and the adsorbates. This reduction in antibonding orbital filling in Ru-RuS₂/MoS₂ would yield enhanced σ and π bonds with adsorbed *H₂O, thus facilitating the HER process.²⁷ Furthermore, water dissociation is the rate-determining step in the MoS₂, Ru-MoS₂, and Ru-RuS₂/MoS₂ models (Fig. 5e). The lower water dissociation energy of Ru-RuS₂/MoS₂ indicates that the heterostructure enhances the catalyst's activity and efficiency in HER, as it facilitates a faster supply of the reactive species required for the reaction. According to the hydrogen binding energy (HBE) theory, the Gibbs free energy of *H on Ru-RuS₂/MoS₂ is closer to zero, indicating enhanced HER activity (Fig. 5e).²⁸

In conclusion, RuS₂ acts as an electron bridge, improving band alignment, reducing charge transfer resistance, and enabling efficient HER. *In situ* characterization and DFT calculations reveal that the introduction of RuS₂ facilitates the redistribution of localized charge within the catalyst, significantly improving its ability to dissociate *H₂O and promote *H desorption. The Ru-RuS₂/MoS₂ catalyst exhibits an exceptionally low overpotential of merely 17 mV at a current density of 10 mA cm^{−2} for the alkaline HER. Moreover, it demonstrates outstanding stability, maintaining performance for over 300 h at a high current density of 500 mA cm^{−2}. This work highlights an effective interfacial design for improving HER performance.

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Data availability

The data supporting this article have been included as part of the ESI.[†]

Conflicts of interest

There are no conflicts to declare.

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