

Interface-Engineered Ru/WS₂/g-C₃N₄ Mott–Schottky Heterostructure for Efficient OER and Rechargeable Zn–Air Batteries

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Abstract

Progress in metal–air batteries largely relies on efficient electrocatalysts that can drive the oxygen evolution reaction (OER). However, Ru-based electrocatalysts still face limitations in performance and stability due to slow OER kinetics, which are linked to strong adsorption of oxygen intermediates and limited control over interfacial charge transfer. Here, Ru species and WS₂ nanosheets were integrated into a conductive g-C₃N₄ framework to create a Ru/WS₂/g-C₃N₄ heterostructure that functions as an active catalyst. Structural and surface characterization confirmed the formation of the heterostructure and revealed strong electronic interactions among Ru, S, C, and N, facilitating charge redistribution and boosting catalytic activity. The catalyst achieves an overpotential of 209 mV at 10 mA cm⁻² and a Tafel slope of 84.2 mV dec⁻¹, reflecting improved OER performance due to the combined contributions of Ru sites, WS₂ conductivity, and the π -conjugated g-C₃N₄ framework. The Ru/WS₂/g-C₃N₄ electrode delivered an open-circuit voltage of 1.48 V, along with specific capacity of 811 mAh g⁻¹ and maximum power density of 161 mW cm⁻², and stable operation for 200 hours. The well-integrated heterointerface, which supported effective charge transfer and stabilized the active catalytic sites over time, was credited with the improved performance. These results show that Ru/WS₂/g-C₃N₄ is an effective catalyst for high-performance Zn–air batteries and OER-driven energy conversion.

1. Introduction

Global demand for sustainable energy conversion and storage solutions has increased due to the unrelenting rise in fossil fuel consumption and the ensuing environmental problems. Because of its extraordinarily high gravimetric energy density, carbon-free emissions, and environmentally benign character, hydrogen has attracted a lot of attention among several clean energy carriers [1–3]. Electrochemical water splitting is considered a promising way to produce hydrogen, as it can be both cost-effective and environmentally friendly compared to conventional methods [4].

During electrochemical water splitting, hydrogen is generated at the cathode through hydrogen evolution reaction (HER), while oxygen is produced at the anode via oxygen evolution reaction (OER) [5]. The inherently sluggish kinetics of these reactions require large overpotentials to overcome thermodynamic energy barriers, thereby compromising overall energy efficiency. Apart from water splitting, Zn–air batteries have emerged as promising energy storage technologies, owing to their high theoretical energy density, environmentally friendly characteristics, and intrinsic safety [6, 7]. As in water splitting, charging in Zn–air batteries involve the OER, which is limited by sluggish reaction kinetics [8, 9]. Thus, designing efficient and durable OER catalysts is crucial for advancing both water splitting and Zn–air battery technologies.

OER and HER usually take place mostly at the interface or on the surface of electrocatalysts. As a result, the density of exposed active sites and the intrinsic activity of each site are the two main parameters that determine the total catalytic efficiency. To date, Pt-based catalysts have been recognized as the

benchmark for HER, whereas Ir-based materials are considered the state-of-the-art for OER. However, the scarcity of Pt and Ir, along with their high cost, and limited bifunctionality severely restrict large-scale deployment. Moreover, Pt-group catalysts often suffer from poor long-term durability under operational conditions, further hindering their practical applicability in integrated energy conversion and storage systems [10–12]. Achieving efficient HER/OER performance, therefore, requires electrocatalysts that exhibit both a high density of accessible active sites and well-optimized electronic structures. These feature lower reaction energy barriers and accelerate the multistep electron-transfer processes inherent to both reactions. The electronic structure governs these processes by dictating the adsorption and desorption behavior of reaction intermediates; therefore, precise control of surface composition, morphology, and interfacial characteristics is essential during catalyst design. In this regard, the number of active sites and intrinsic catalytic activity of electrocatalysts have been successfully increased by rational nanostructure engineering using techniques like alloying, heterostructure creation, or hybridization.

Although several earth-abundant transition metal-based catalysts have shown promise as substitutes for noble metal electrocatalysts [13, 14], their catalytic activity and durability still fall short of commercial benchmarks. In this regard, Ru has emerged as an attractive alternative owing to its relatively low cost compared with Pt and Ir. Interestingly, the electronic configuration of Ru closely mirrors those of Pt and Ir, imparting comparable catalytic characteristics while offering a more economic option [15]. Consequently, Ru-based electrocatalysts are increasingly regarded as among the most practical and efficient alternatives to conventional Pt- and Ir-based catalysts. However, although metallic Ru demonstrates outstanding catalytic activity toward HER, its OER performance remains limited because of strong adsorption of oxygenated intermediates and surface oxidation under anodic potentials, which lead to catalyst degradation [16, 17]. To address these limitations, coupling Ru with transition metal oxides, phosphides, sulfides, nitrides, and carbonaceous materials has been explored as an effective strategy to modulate its electronic structure and stabilize active surfaces during OER. For instance, Ru/CeO₂ [18], Ru/NiCoP [19], Ru/Fe₂O₃ [20], Ru/S,N-doped carbon matrix (NSCSs) [21], Ru/IrO_x [22], Ru–MoCoP [23], and Ru/MoS₂ [24] composites have all exhibited notable improvements in OER activity. These studies highlight that designing well-defined metal–semiconductor interfaces provides a promising avenue to further optimize the electronic structure of Ru-based catalysts, thereby advancing OER performance and expanding their potential for high-efficiency Zn–air battery applications.

In this context, introducing a Mott–Schottky (M–S) junction represents a powerful approach to regulate interfacial electron distribution, optimize band alignment, and accelerate reaction kinetics within electrocatalysts. Constructing a well-defined hybrid architecture based on an M–S heterojunction effectively tailors electron distribution. Owing to the difference in work functions between the metal and semiconductor (or metal oxide) components, their Fermi energy levels tend to align at the interface, resulting in the formation of an internal electric field. The Schottky barrier in the M–S heterojunction blocks electron backflow and promotes directional electron transfer across the junction, thereby establishing an interfacial potential barrier that facilitates charge separation and rearrangement [25–27].

Consequently, such interfacial electronic modulation not only accelerates charge transport but also optimizes the adsorption energy of reaction intermediates, thereby enhancing the overall electrocatalytic efficiency.

In order to achieve exceptional OER activity and rechargeable Zn–air battery performance, we offer in this study a straightforward yet efficient method for engineering a Ru-decorated WS₂ (Ru/WS₂) M–S heterojunction enclosed within graphitic carbon nitride (g-C₃N₄). Although WS₂ is widely recognized for its outstanding HER activity and is more extensively reported in the literature alongside its analogues, such as MoS₂, its potential for OER has been largely overlooked because of its semiconducting nature and poor electrical conductivity [28, 29]. By coupling metallic Ru with WS₂, a well-defined metal–semiconductor junction is formed, promoting a built-in electric field that facilitates directional charge transfer and tunes the electronic structure [30, 31] to enhance OER kinetics. Furthermore, g-C₃N₄ encapsulation not only improves interfacial electron transport but also protects the Ru surface from oxidation and ensures long-term structural stability under anodic conditions [32–34]. Therefore, the effective platform for accelerating charge migration, increasing active-site utilization, and attaining high catalytic efficiency is provided by the synergistic integration of Ru, WS₂, and g-C₃N₄. This offers new insights into the logical design of sophisticated Ru-based heterostructures for sustainable energy conversion and storage.

2. Results and Discussion

2.1 Morphological and Structural Characterization

As illustrated in Fig. S1, bulk g-C₃N₄ was first obtained via thermal polycondensation of dicyandiamide, whereas WS₂ was synthesized through a solvothermal route. Subsequently, Ru species were introduced onto WS₂, followed by integration with g-C₃N₄ through sonication and thermal treatment to construct the ternary Ru/WS₂/g-C₃N₄ heterostructure. This assembly ensures intimate interfacial contact among the three components and induces strong electronic interactions. As depicted in Fig. 1, the interfacial coupling leads to Fermi level equilibration, accompanied by band bending and the formation of a built-in electric field, which drives directional electron transfer from g-C₃N₄ through WS₂ toward Ru. In this configuration, WS₂ serves as an efficient electron mediator, while Ru acts as an electron-enriched active center, resulting in pronounced charge redistribution across the heterostructure. By encouraging the adsorption and transformation of important intermediates (*OH, *O, and *OOH) at the Ru active sites, this improved electrical structure speeds up the oxygen evolution reaction and eventually produces O₂. The synergistic integration of Ru, WS₂, and g-C₃N₄ was expected to promote favorable reaction kinetics and enable stable performance when applied in rechargeable Zn–air batteries.

The morphological and structural features of the prepared g-C₃N₄ and Ru/WS₂/g-C₃N₄ electrocatalysts were examined using FE-SEM analysis (Fig. 2). The SEM micrographs of pristine g-C₃N₄ (Figs. 2a and b) revealed a loosely stacked, sheet-like morphology composed of thin, wrinkled nanosheets aggregated

into a porous network. The layers appeared partially exfoliated, forming an interconnected three-dimensional (3D) architecture with abundant interflake voids and lamellar nanosheets exhibiting rough surface textures. The open, rippled framework suggests a high surface area and numerous defect sites, which can provide favorable anchoring points for the subsequent deposition of metallic or semiconductor species.

By contrast, the Ru/WS₂/g-C₃N₄ (Figs. 2c and d) exhibited a distinctly transformed microstructure after hybridization. The sheets became thicker, more compact, and exhibited a denser hierarchical texture compared with g-C₃N₄. The roughened surface and increased structural complexity indicate strong interfacial interactions among the constituents. The formation of such a hybrid heterostructure likely enhanced electrical connectivity and would provide additional catalytic sites through the combined contributions of metallic Ru, semiconducting WS₂ layers, and g-C₃N₄ matrix. Overall, the morphological evolution from loosely wrinkled g-C₃N₄ nanosheets to a densely packed Ru/WS₂/g-C₃N₄ heterostructure confirmed the formation of a well-integrated catalyst system with enhanced surface roughness, a higher density of active interfaces, and improved charge-transport pathways, which were essential for high-performance electrocatalysis. The corresponding EDX mapping analysis of Ru/WS₂/g-C₃N₄ confirmed the presence of C, N, O, Ru, W and S elements (Fig. 2e).

Figure 2f shows the HRTEM images of the Ru/WS₂/g-C₃N₄ heterostructure. The low-magnification TEM micrograph revealed a crumpled, layered morphology characteristic of WS₂ nanosheets intimately integrated with g-C₃N₄, while Ru nanoparticles were homogeneously distributed without noticeable aggregation, indicating strong interfacial coupling within the composite. The high-magnification TEM micrograph (Fig. 2g) clearly resolved distinct lattice fringes originating from the individual components. The spacing of 0.274 nm was matched to the interplanar distance of WS₂ (100), while a spacing of 0.205 nm corresponded to the (101) crystal plane of Ru [35, 36], confirming the crystalline nature of the anchored Ru nanoparticles. Additionally, lattice fringes with an interplanar spacing of 0.324 nm were observed, which can be assigned to the (002) plane of g-C₃N₄ [37], demonstrated the preserved crystallinity of the carbon nitride framework. As shown in Fig. 2h, the SAED pattern exhibited well-defined concentric diffraction rings, which were indexed to WS₂ (100), Ru (101), and g-C₃N₄ (002) planes, further confirming the polycrystalline nature and successful integration of all constituent phases. The clear lattice continuity and coexistence of multiple crystalline domains highlight the formation of a tightly coupled Ru/WS₂/g-C₃N₄ heterostructure, which is favorable for efficient interfacial charge transport [38].

XRD analysis was used to investigate the Ru/WS₂/g-C₃N₄ composite's phase composition and crystal structure. Figure 3a shows a distinct diffraction peak near 27.5°, which can be assigned to the (002) plane of g-C₃N₄ and is related to the stacking of conjugated layers in its graphitic framework. For comparison, pristine g-C₃N₄ shows two distinct peaks at around 13.1° and 27.5°, assigned to the (100) in-plane ordering and (002) interlayer stacking, respectively. This peak is consistent with the standard pattern of g-C₃N₄ (JCPDS No. 87-1526) [39].

Furthermore, a diffraction peak observed at 13.3° is assigned to the (002) plane of hexagonal WS_2 , confirming the layered structure of WS_2 . Other characteristic peaks appearing at approximately 32.62° , 38.49° , and 59.3° related to the (100), (103), and (110) crystal planes of WS_2 , respectively, which align with the standard hexagonal WS_2 pattern (JCPDS No. 87-2417) [40]. These peaks verify the successful formation of crystalline WS_2 in the composite. Furthermore, a weak diffraction feature detected near 44.07° is attributed to the overlapping reflections of WS_2 (006) and metallic Ru (101) (JCPDS No. 006-0663) [41], indicating the incorporation of Ru species into the $\text{WS}_2/\text{g-C}_3\text{N}_4$ framework. The relatively low intensity of the Ru-related reflection suggests that Ru nanoparticles are highly dispersed or present in small quantities, which is typical for supported noble-metal catalysts. Overall, the XRD results confirm the successful integration of WS_2 and Ru onto the $\text{g-C}_3\text{N}_4$ matrix, forming the $\text{Ru/WS}_2/\text{g-C}_3\text{N}_4$ heterostructure without detectable impurity phases.

The electrocatalyst's valence states and surface elemental content were ascertained using XPS analysis. The survey spectrum confirmed the presence of C and N from $\text{g-C}_3\text{N}_4$ along with Ru, W, and S from the incorporated Ru and WS_2 components, demonstrating the successful construction of the ternary composite (Fig. S2). In the high-resolution C 1s spectrum (Fig. 3b), three characteristic peaks at 284.9, 288.2, and 293.5 eV are attributed to graphitic sp^2 C–C, sp^2 -hybridized N–C = N of the heptazine units, and the π – π^* shake-up satellite of the conjugated aromatic system [42], respectively. For comparison, the C 1s spectrum of pristine $\text{g-C}_3\text{N}_4$ (Fig. S3a) exhibited similar characteristic features, confirming the intrinsic chemical structure of the carbon framework. Notably, the N–C = N peak shifted slightly after hybridization, suggesting that the electronic environment of the carbon framework was altered because of interaction with Ru and WS_2 .

The N 1s spectrum was deconvoluted into peaks at 398.4 eV (C–N = C), 399.2 eV (N–(C)₃), and 400.9 eV (C–N–H) (Fig. 3c) [42, 43]. Compared with pristine $\text{g-C}_3\text{N}_4$ (Fig. S3b), the C–N = C and N–(C)₃ peaks exhibited a slight positive shift in binding energy, indicating electron redistribution at the interface. This shift implies that electrons were partially transferred from the $\text{g-C}_3\text{N}_4$ matrix toward the Ru and WS_2 species, thereby establishing strong electronic coupling among the three components. Such interfacial charge transfer is essential for improving conductivity and catalytic activity.

The Ru 3p spectrum revealed the coexistence of Ru^{3+} and Ru^{4+} species (Fig. 3d), indicating that Ru was present in mixed valence states. The presence of these oxidized Ru species is particularly beneficial for OER, as higher valence Ru centers can facilitate the adsorption and transformation of oxygen-containing intermediates. Meanwhile, the W 4f spectrum (Fig. 3e) exhibited characteristic W^{4+} doublets corresponding to WS_2 , and the S 2p spectrum (Fig. 3f) displayed typical S^{2-} peaks without significant oxidation signals, confirming the structural integrity of WS_2 in the composite [44]. Slight binding energy variations in the W 4f region further supported the existence of interfacial electronic interactions in the heterostructure.

Overall, the observed binding energy shifts in the C 1s, N 1s, and W 4f spectra clearly indicate strong electronic coupling and charge redistribution among Ru, WS₂, and g-C₃N₄. This synergistic interaction modulated the electronic configuration of the active sites, which could optimize the adsorption strength of OER intermediates (*OH, *O, *OOH) and accelerate reaction kinetics in basic solutions. For Zn–air battery applications, such improved electronic conductivity and bifunctional oxygen activity enhance oxygen evolution and oxygen reduction processes at the air cathode, ultimately contributing to superior catalytic performance and stability.

Furthermore, the specific surface areas of g-C₃N₄ and Ru/WS₂/g-C₃N₄ have been evaluated by nitrogen adsorption–desorption measurements at 77 K using the BET method (Figs. S3c and d). Prior to analysis, both the samples have degassed at 200°C for over 12 h to ensure the removal of physisorbed species. The g-C₃N₄ showed a BET surface area of 15.75 m² g^{−1}, as determined from the linear region of the adsorption isotherm, whereas the Langmuir surface area was 12.79 m² g^{−1}. By comparison, Ru/WS₂/g-C₃N₄ demonstrated a significantly higher BET surface area of 24.10 m² g^{−1}, with a corresponding Langmuir surface area of 30.46 m² g^{−1}. This substantial increase in surface area upon g-C₃N₄ functionalization was attributed to the introduction of additional mesoporous structure and improved dispersion of active sites [45, 46]. The higher specific surface area of Ru/WS₂/g-C₃N₄ is expected to facilitate enhanced electrolyte accessibility, promote mass transport, and expose a greater number of catalytic centers, thereby contributing directly to enhanced electrochemical activity.

2.2 OER Activity of electrocatalysts

The OER performance of various electrocatalysts (Ru/WS₂/g-C₃N₄/NF, Ru/WS₂/NF, g-C₃N₄/NF, and RuO₂/NF) was evaluated using LSV curves (Fig. 4a). Among these, Ru/WS₂/g-C₃N₄/NF showed the best OER activity, requiring the lowest overpotential of 209 mV to achieve 10 mA cm^{−2} current density, compared with Ru/WS₂/NF (260 mV), g-C₃N₄ (350 mV), and RuO₂/NF (307 mV). The Ru/WS₂/g-C₃N₄/NF sample achieved a higher current density at a lower overpotential, indicating that g-C₃N₄ incorporation into Ru/WS₂ effectively enhanced catalytic performance for OER.

The Tafel plots derived from the LSV data further highlight the improved kinetic behavior of the Ru/WS₂/g-C₃N₄/NF catalyst (Fig. 4b). Ru/WS₂/g-C₃N₄/NF exhibited a Tafel slope of 84.2 mV dec^{−1}, which was substantially lower than those of g-C₃N₄/NF (146.1 mV dec^{−1}), RuO₂/NF (132.9 mV dec^{−1}) and Ru/WS₂/NF (122.1 mV dec^{−1}), demonstrating faster reaction kinetics and lower energy barriers for OER. The reduced Tafel slope for Ru/WS₂/g-C₃N₄/NF was attributed to the synergistic effect of g-C₃N₄ integration, which likely promoted more efficient charge transfer and increased the density of active sites compared with single-component Ru/WS₂ [47, 48]. EIS was performed to investigate the reaction kinetics further and obtain a better understanding of the interfacial behavior between the electrode and electrolyte. The Nyquist plots of Ru/WS₂/g-C₃N₄/NF (Fig. 4c) revealed a markedly lower charge-transfer resistance (R_{ct}) of 6.57 Ω cm^{−2}, compared with Ru/WS₂/NF (8.01 Ω cm^{−2}) and bare NF (13.41 Ω cm^{−2}),

indicating faster charge-transfer dynamics [49]. The corresponding equivalent circuit models are presented in Fig. S4.

The durability and stability of Ru/WS₂/g-C₃N₄/NF were further assessed using chronopotentiometry at a constant current density of 10 mA cm⁻² for approximately 100 h; the results are shown in Fig. 4d. The Ru/WS₂/g-C₃N₄/NF electrode exhibited a minimal potential deviation of 79 mV (1.4384–1.4463 V_{RHE}), whereas Ru/WS₂/NF showed a larger deviation of 133 mV (1.4934–1.5067 V_{RHE}). These results clearly demonstrated the superior stability and durability of Ru/WS₂/g-C₃N₄/NF toward OER compared with Ru/WS₂/NF.

To further evaluate the catalytic efficiency of the developed electrocatalysts, the ECSA was estimated from CV in the nonfaradaic region over scan rates of 10 to 100 mV s⁻¹ by evaluating the C_{dl} (Figs. 4e and f). The Ru/WS₂/g-C₃N₄/NF electrode exhibited the highest C_{dl} value (0.01906 mF), exceeding that of Ru/WS₂/NF (0.01462 mF). A higher C_{dl} corresponds to the increased ECSA, which is well known to enhance the intrinsic catalytic activity of electrocatalysts. Accordingly, the ECSA of Ru/WS₂/g-C₃N₄/NF was calculated to be 0.4765 cm² (Fig. 4h), notably larger than that of Ru/WS₂/NF (0.3655 cm²) (Fig. 4g), confirming the superior electrochemical activity of the Ru/WS₂/g-C₃N₄/NF electrode [49]. On comparing the overpotential of Ru/WS₂/g-C₃N₄ catalyst with previously reported catalysts [50–64] the catalyst demonstrates a competitive and relatively lower overpotential, as illustrated in Fig. 4i, indicating its superior OER performance among state-of-the-art electrocatalysts. This enhanced activity can be attributed to the synergistic interaction between Ru, WS₂, and g-C₃N₄, which promotes efficient charge transfer and optimizes the adsorption/desorption behavior of reaction intermediates.

2.3 Rechargeable Zn–Air Battery Performance of Ru/WS₂/g-C₃N₄

To assess the electrocatalytic performance of the Ru/WS₂/g-C₃N₄ heterostructure for energy conversion, a rechargeable Zn–Air Battery was assembled using zinc foil as the anode, 6 M KOH containing 0.2 M Zn(CH₃COO)₂ as the electrolyte, and Ru/WS₂/g-C₃N₄ coated on carbon cloth as the air cathode [65] (Fig. 5a). The assembled cell exhibited an open-circuit voltage (OCV) of 1.48 V (Fig. 5b) and maintained stable output over 12 h of continuous operation, indicating strong catalytic activity and minimal self-discharge. The OCV was monitored using a digital multimeter (Fig. 5c) confirmed consistent voltage retention, demonstrating superior electrode–electrolyte compatibility and efficient electron transport within the Ru/WS₂/g-C₃N₄ heterostructure.

The galvanostatic discharge profile (Fig. 5d) showed a high specific capacity of 811 mAh g⁻¹ at a current density of 10 mA cm⁻², normalized to the mass of consumed Zn, which approached the theoretical value (820 mAh g⁻¹) [66]. This result indicates efficient Zn utilization and reversible oxygen electrochemistry, with the specific capacity exceeding those of multiple reported noble-metal and

transition-metal-based catalysts. The polarization and power density plots (Fig. 5e) showed a maximum power density of 161 mW cm^{-2} , demonstrating rapid oxygen reduction/oxygen evolution kinetics and excellent catalytic efficiency. In addition, the rate capability of the assembled Zn–air battery was investigated by applying stepwise current densities between 10 and 50 mA cm^{-2} (Fig. 5f). As the current density increased, the discharge–charge voltage gap gradually widened because of increased polarization effects. When the current density was set back to 10 mA cm^{-2} , the voltage profile almost returned to its original form, indicating good stability and fast reaction kinetics of the Ru/WS₂/g-C₃N₄ catalyst.

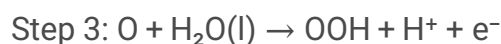
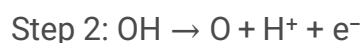
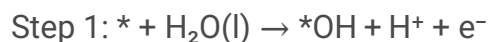
The durability of the rechargeable Zn–air battery was evaluated by continuous charge–discharge cycling at 10 mA cm^{-2} (Fig. 5g). The device maintained stable charge and discharge voltage profiles for approximately 200 h, indicating excellent durability and electrochemical reversibility of the Ru/WS₂/g-C₃N₄ catalyst during prolonged cycling. From the cycling profiles, the average discharge and charge voltages were determined to be approximately 1.12 and 1.93 V, respectively, corresponding to a voltage gap of 0.81 V. Accordingly, the energy efficiency of the rechargeable Zn–air battery was calculated as approximately 58%, confirming the effective bifunctional catalytic activity of the Ru/WS₂/g-C₃N₄ electrocatalyst for reversible oxygen reactions.

The overall electrochemical performance was assessed using a radar plot (Fig. 5h) [67–69, 11, 70–72], comparing this work with previously reported electrocatalysts for Zn–air batteries. The developed system exhibited improved OCV, specific capacity, and power density, reflecting efficient catalytic activity and fast reaction kinetics. However, the cycling stability was relatively lower, indicating limitations in long-term durability. Overall, the results demonstrated strong energy and power performance, while suggesting that further improvements in stability are needed for practical applications.

The Ru/WS₂/g-C₃N₄-based Zn–air battery delivers strong electrochemical performance, including a high OCV of 1.48 V, a specific capacity of 811 mAh g^{-1} at 10 mA cm^{-2} , a power density of 161 mW cm^{-2} , and stable cycling over 200 h. These results suggest that Ru/WS₂/g-C₃N₄ is an efficient and durable bifunctional electrocatalyst for high-performance rechargeable Zn–air batteries.

2.4 DFT Studies

The OER free energies were evaluated using the computational hydrogen electrode (CHE) method proposed by Nørskov et al. [73]. The four-electron alkaline OER mechanism proceeds through the following elementary steps:



Step 4: $\text{OOH} \rightarrow + \text{O}_2(\text{g}) + \text{H}^+ + \text{e}^-$

The Gibbs free energy change for each step was calculated as:

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S - eU, (\text{S5})$$

where, ΔE is the DFT-computed reaction energy, ΔZPE and $T\Delta S$ are the zero-point energy and entropic corrections at $T = 298.15 \text{ K}$, and U is the electrode potential. The ZPE and entropy corrections were adopted from established literature values: $\Delta \text{ZPE} - T\Delta S = + 0.29 \text{ eV}$ for OH , $+ 0.02 \text{ eV}$ for O , and $+ 0.31 \text{ eV}$ for $^*\text{OOH}$. The O_2 energy was derived indirectly using the experimental total OER free energy of 4.92 eV ($= 4 \times 1.23 \text{ eV}$) to circumvent the well-known overestimation of O_2 binding energy in generalized gradient approximation (GGA)-level DFT. The theoretical OER overpotential was determined as:

$$\eta = \max(\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4)/e - 1.23 \text{ V} (\text{S6})$$

The d-band center (ϵ_d) was computed as the initial moment of the occupied Ru 4d projected density of states (PDOS) concerning to the Fermi level. The constructed $\text{Ru}/\text{WS}_2/\text{g-C}_3\text{N}_4$ model is shown in Fig. 6a. The adsorption free energies of the key intermediates were determined as $\Delta G(^*\text{OH}) = - 0.17 \text{ eV}$, $\Delta G(^*\text{O}) = 0.23 \text{ eV}$, and $\Delta G(^*\text{OOH}) = 2.80 \text{ eV}$. The corresponding free-energy diagram revealed the highest energy barrier of 2.57 eV for the $\text{O} \rightarrow \text{OOH}$ transformation, identifying it as the rate-determining step (RDS). Figure 6b showed the theoretical overpotential for the Ru/WS_2 catalyst which is found to be $\eta = 1.34 \text{ V}$. The negative ΔG_1 value indicates the spontaneous formation of $^*\text{OH}$ from H_2O on the Ru site, whereas the moderate ΔG_2 value suggests favorable dehydrogenation from $^*\text{OH}$ to $^*\text{O}$. However, the strong stabilization of the $^*\text{O}$ intermediate increased the energy barrier for $^*\text{OOH}$ formation, which constituted the primary kinetic limitation of OER process.

In order to elucidate further, the electronic role of the support, the electronic structure of the $\text{Ru}/\text{WS}_2/\text{g-C}_3\text{N}_4$ heterostructure was analyzed using PDOS (Fig. 6c). The results showed that Ru 4d orbitals dominated the states near the Fermi level, confirming that the Ru atom behaved as the primary catalytic center. The calculated Ru d-band center (ϵ_d) was $- 1.36 \text{ eV}$, which governed the adsorption strength of oxygen intermediates according to d-band theory. Significant orbital hybridization between Ru 4d and W 5d states, together with the overlap between Ru 4d and N 2p orbitals, indicated strong electronic coupling across the heterostructure. Löwdin charge analysis revealed a charge transfer of approximately 0.20 e from Ru to the WS_2 layer, whereas the nitrogen atoms of $\text{g-C}_3\text{N}_4$ exhibited induced spin polarization, confirming interfacial charge redistribution. These results demonstrated that the $\text{g-C}_3\text{N}_4$ support electronically modulated the Ru active site through the pathway $\text{g-C}_3\text{N}_4 \rightarrow \text{WS}_2 \rightarrow \text{Ru}$, thereby tuning the adsorption behavior of OER intermediates and influencing the overall catalytic activity.

3. Conclusion

In summary, we successfully developed a $\text{Ru}/\text{WS}_2/\text{g-C}_3\text{N}_4$ heterostructure as the most efficient bifunctional electrocatalyst for OER and rechargeable Zn–air battery applications. Structural and surface

analyses confirmed the successful integration of Ru and WS₂ within the g-C₃N₄ framework, forming a strongly coupled heterointerface that promoted effective electronic interaction among the constituent elements. This unique architecture enabled enhanced charge transport, abundant accessible active sites with the help of optimized adsorption of oxygen intermediates. Consequently, the Ru/WS₂/g-C₃N₄ electrode delivered excellent activity towards OER, with a low overpotential of 209 mV at 10 mA cm⁻², a small Tafel slope of 84.2 mV dec⁻¹, and reduced charge-transfer resistance compared with reference catalysts.

When applied as the air cathode in a rechargeable Zn–air battery, the catalyst exhibited a high OCV of 1.48 V and large specific capacity of 811 mAh g⁻¹ along with the maximum power density of 161 mW cm⁻², and stable operation for 200 h. The enhanced performance was mainly attributed to the synergistic interaction between Ru active sites, conductive WS₂ layers, and the electron-rich g-C₃N₄ network, which collectively facilitated rapid electron transport and stabilized catalytic centers during long-term operation. Density functional theory calculations revealed that Ru served as the primary active site, whereas the g-C₃N₄-WS₂ support modulated oxygen intermediate adsorption to facilitate OER. These findings establish the Ru/WS₂/g-C₃N₄ heterostructure as the most promising candidate for advanced oxygen electrocatalysis and practical metal–air battery systems.

Declarations

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Authors’ contributions:

List the descriptions of their diverse contributions to the published work. Such as, **Thirumalaisamy Suryaprabha**: Writing-original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Chandrasekaran Pitchai**: Writing-original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Chunghyeon Choi**: Visualization, Formal analysis, Data curation. **Thirumalaisamy Krithika**: Software, Resources, Investigation, Data curation. **Mahalakshmi Vedanarayanan**: Writing - review & editing, Visualization,

Validation. **Sooman Lim:** Writing - review & editing, Visualization, Validation, Methodology. **Chih-Ming Chen:** Writing - review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Byungil Hwang:** Writing - review & editing, Visualization, Validation, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization.

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Figures

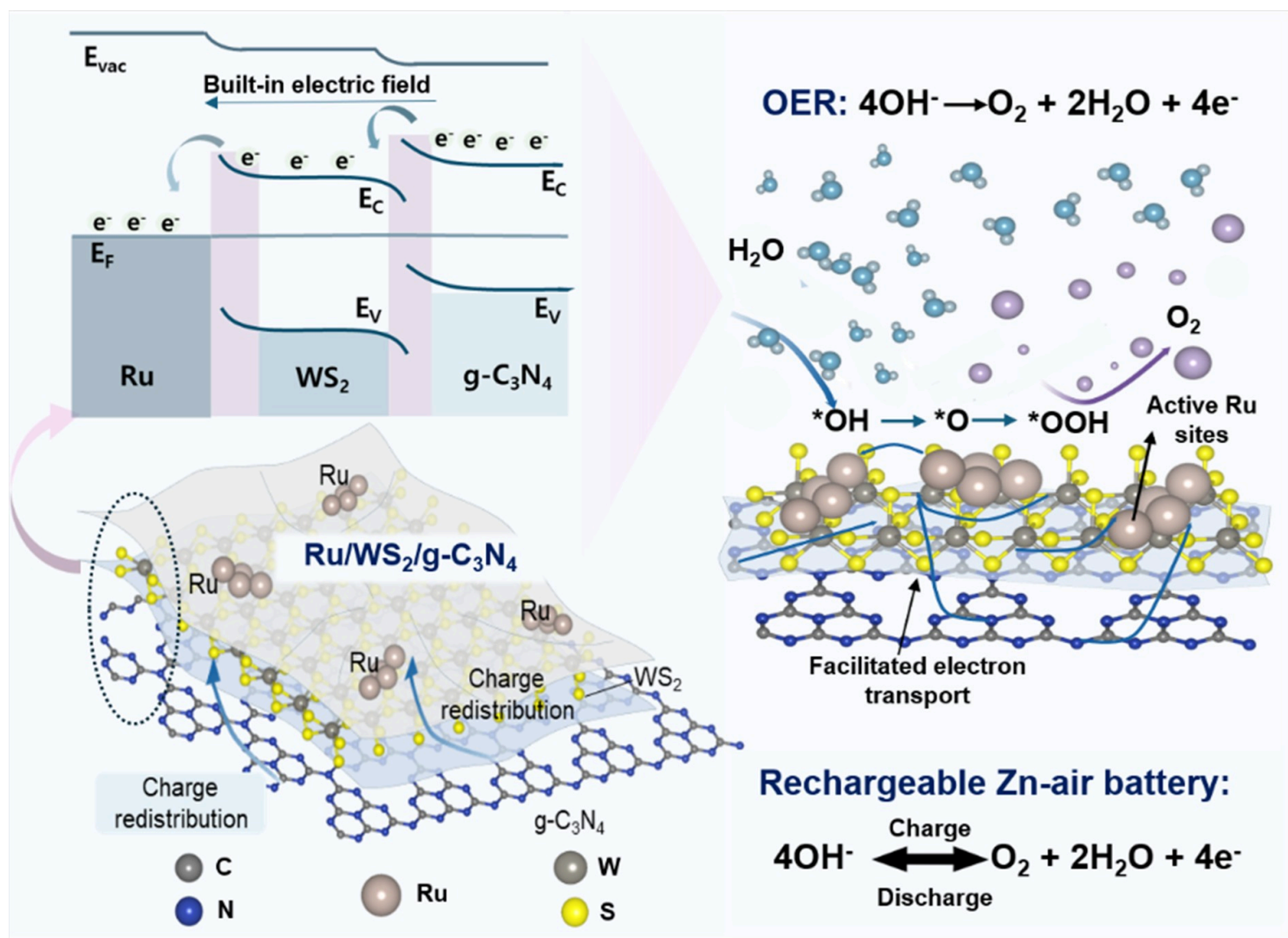


Figure 1

Schematic representation of the Ru/WS₂/g-C₃N₄ ternary heterostructure. (Top Left) Electronic band alignment showing the built-in electric field and electron flow. (Bottom Left) Structural model highlighting charge redistribution and facilitated electron transport. (Right) Proposed OER mechanism on active Ru sites and the working principle of the material within a rechargeable Zn–Air Battery.

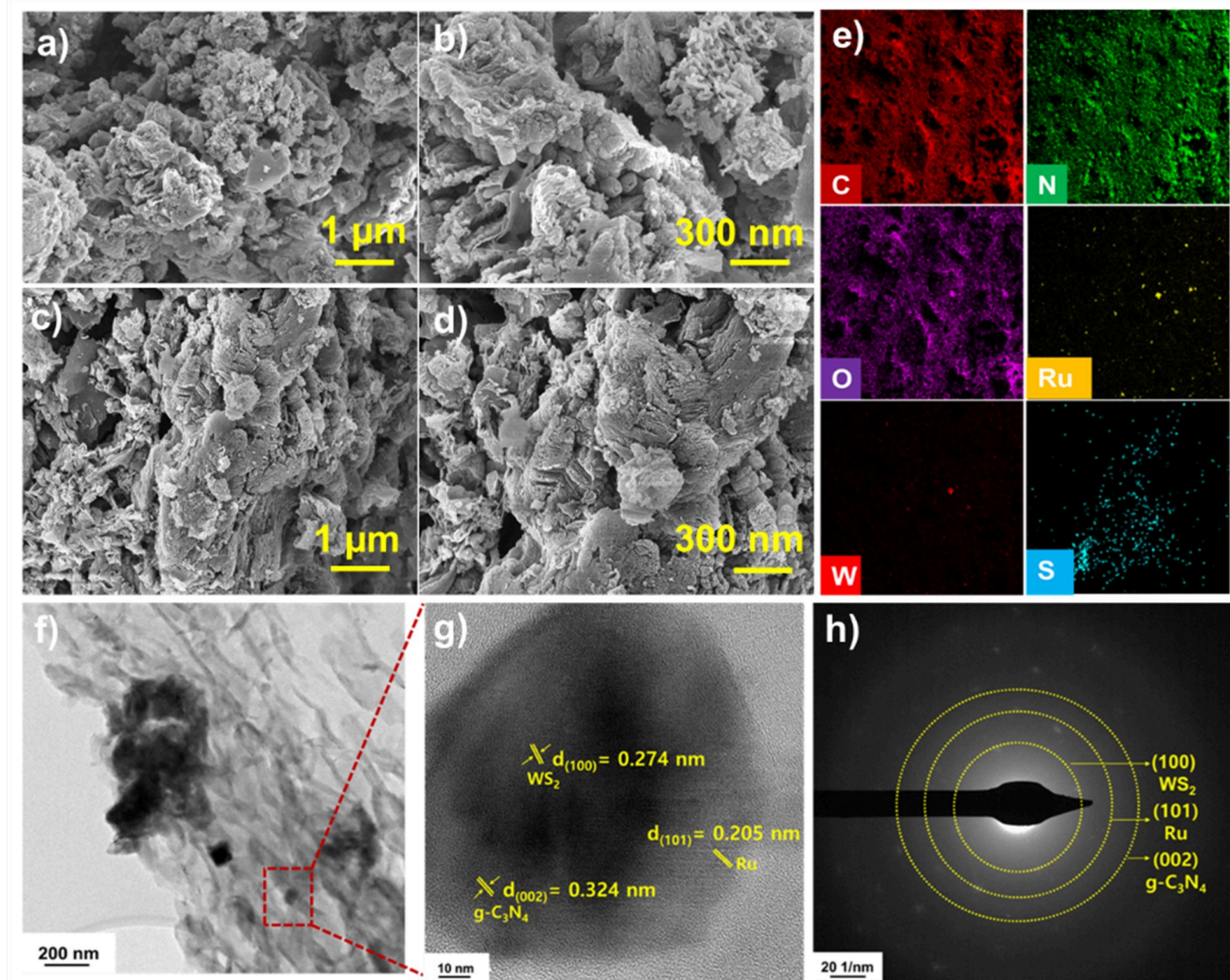


Figure 2

Low- and high-magnification SEM micrographs of (a, b) pristine g-C₃N₄ and (c, d) Ru/WS₂/g-C₃N₄. (e) EDX mapping images of Ru/WS₂/g-C₃N₄. (f, g) TEM micrographs and (h) corresponding SAED pattern of Ru/WS₂/g-C₃N₄.

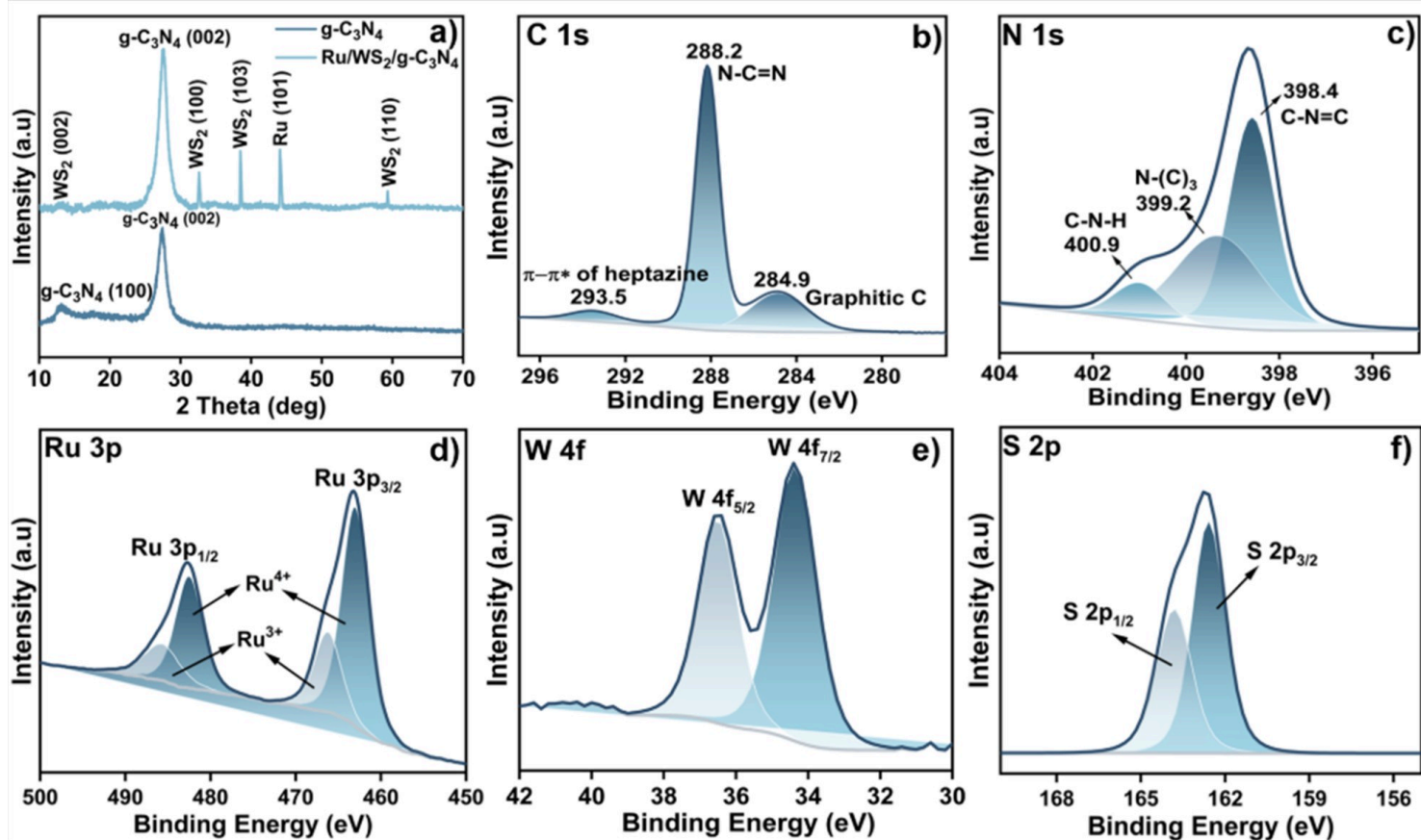


Figure 3

(a) XRD pattern of Ru/WS₂/g-C₃N₄. XPS analysis: (b) survey spectrum of pristine g-C₃N₄ and Ru/WS₂/g-C₃N₄; high-resolution spectra of (c) C 1s, (d) N 1s, (e) Ru 3p, (f) W 4f, and (g) S 2p.

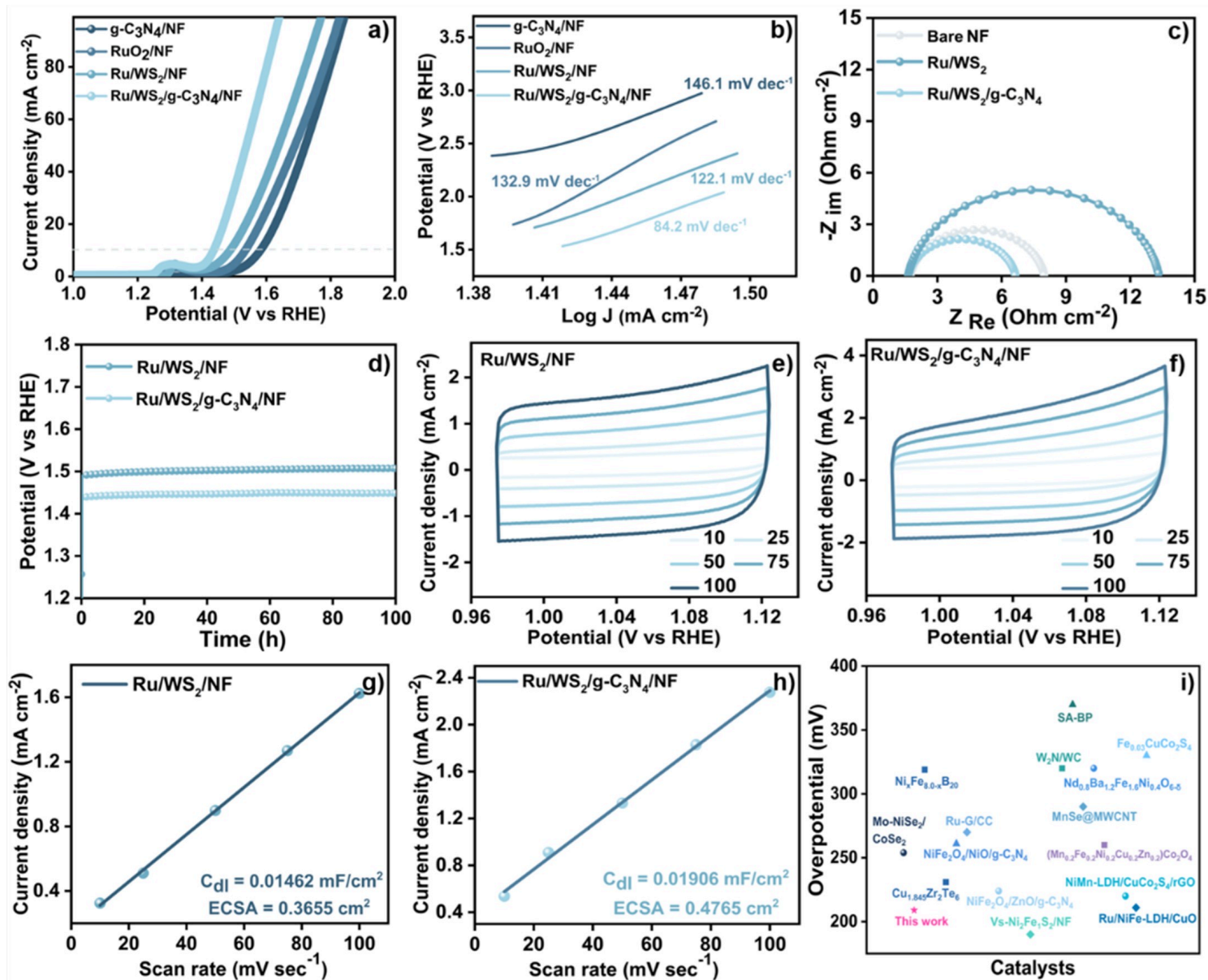


Figure 4

OER performance measurements: (a) LSV curves. (b) Tafel slopes of the as-prepared electrocatalysts. (c) EIS spectra, (d) chronopotentiometric analysis, (e, f) CV curves, (g, h) linear relationships between current density and scan rate for Ru/WS₂ and Ru/WS₂/g-C₃N₄ electrocatalysts, and (i) Overpotential comparison of reported electrocatalysts for overall water splitting.

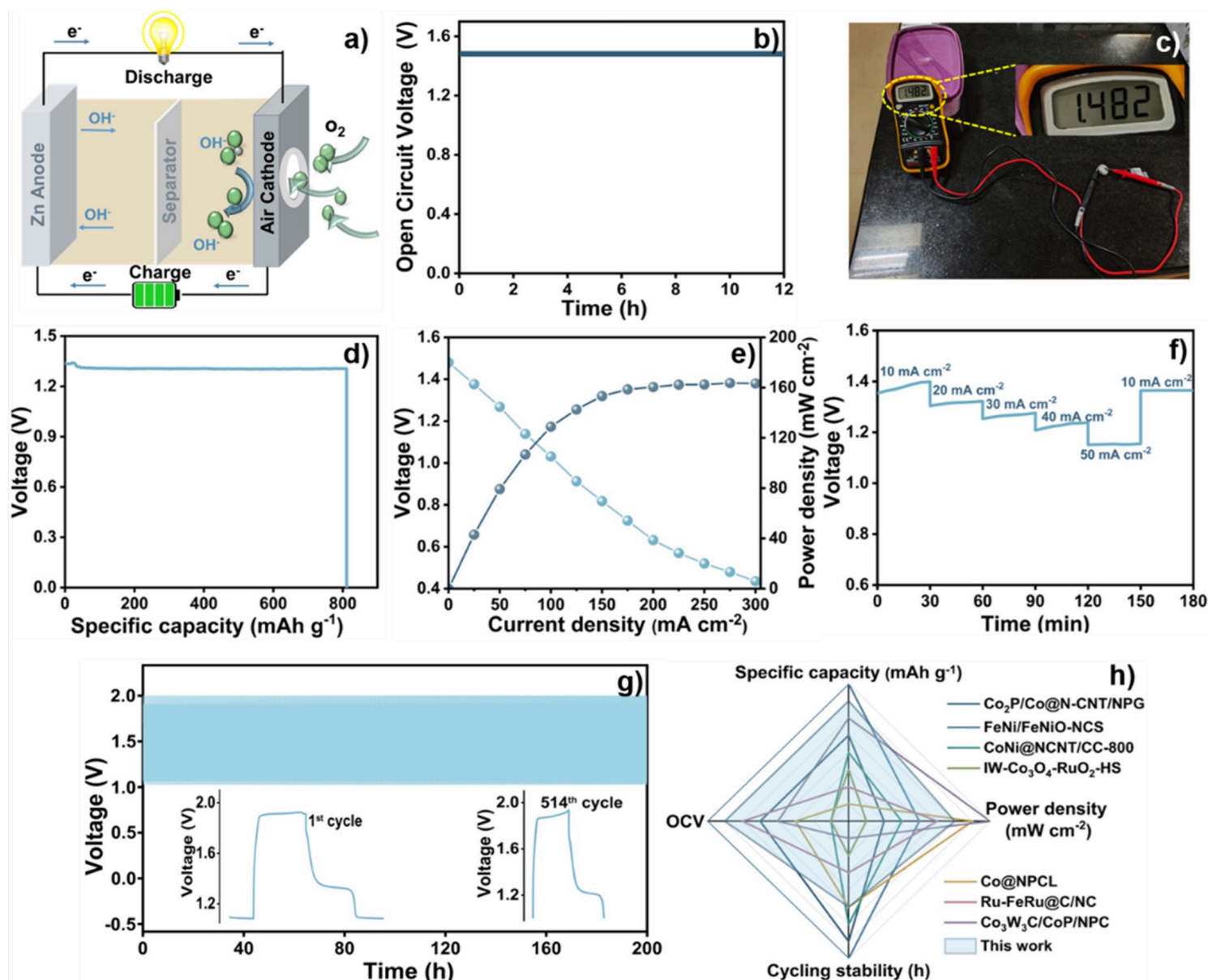


Figure 5

Electrochemical performance of the Ru/WS₂/g-C₃N₄ catalyst in a Zn–air battery. (a) Schematic of the assembled Zn–air battery configuration. (b) OCV profile of the Zn–air battery with the Ru/WS₂/g-C₃N₄ air cathode. (c) Digital photograph of the OCV measurement using a multimeter. (d) Galvanostatic discharge curve and corresponding specific capacity of the assembled Zn–air battery. (e) Polarization curves and corresponding power density plots of the Zn–air battery. (f) Rate performance of the Zn–air battery at different current densities. (g) Long-term charge–discharge cycling performance at a constant current density (inset: representative charge–discharge profiles at the 1st and 514th cycles). (h) Radar plot comparing the electrochemical performance of this work with reported electrocatalysts in the literature.

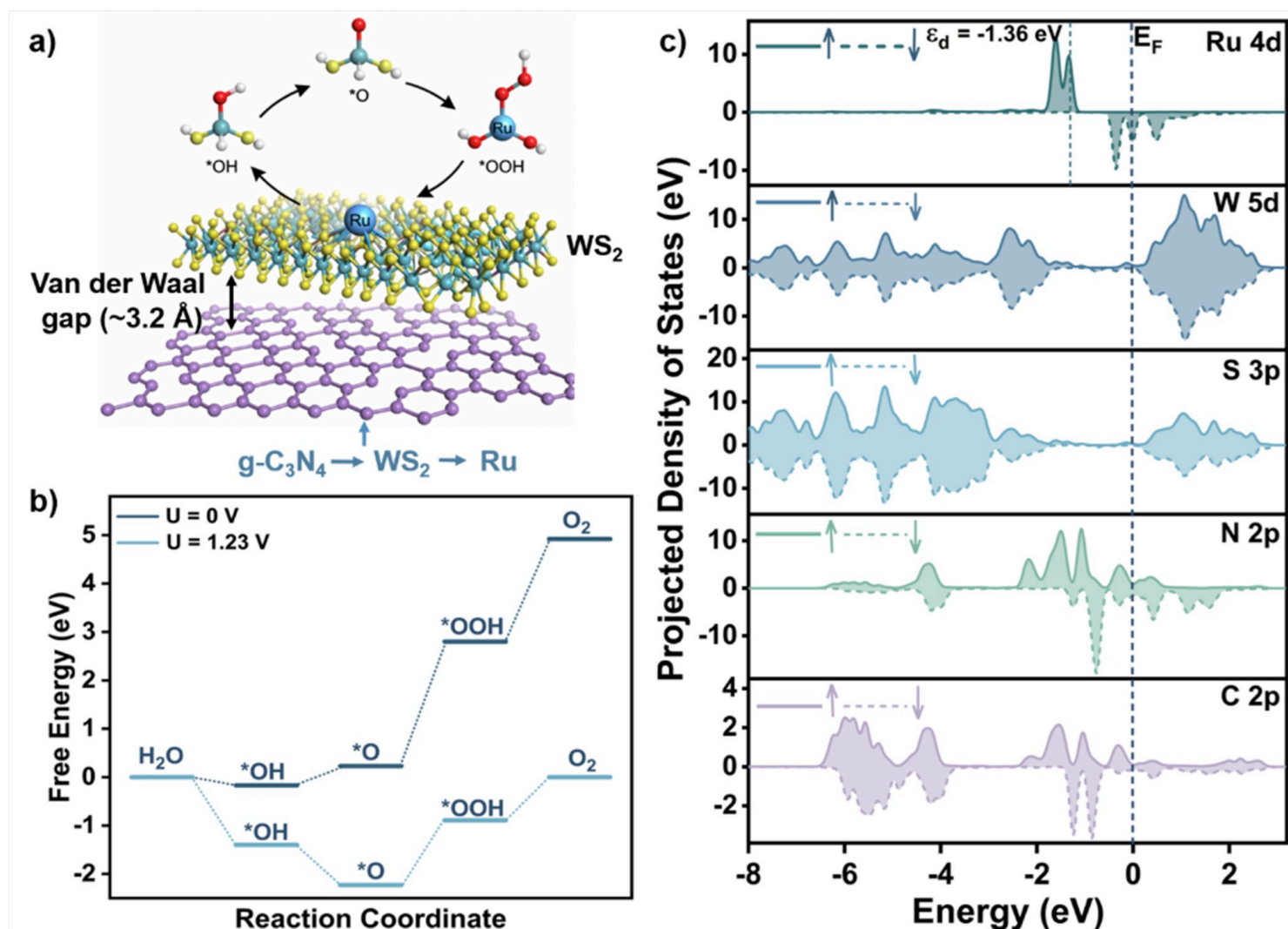


Figure 6

DFT calculations and electronic structure analysis of the Ru/WS₂/g-C₃N₄ catalyst. (a) Structural model of the Ru/WS₂/g-C₃N₄ heterostructure with the schematic four-step OER mechanism on the single-atom Ru active site. (b) Gibbs free-energy diagram for the OER on Ru/WS₂ at U = 0 V (black) and U = 1.23 V (red). RDS was O → OOH (Step 3), with a theoretical overpotential $\eta = 1.34$ V. (c) PDOS of the Ru/WS₂/g-C₃N₄ heterostructure, showing Ru 4d, W 5d, S 3p, N 2p, and C 2p orbital contributions. Solid and dashed lines represent spin-up ($\uparrow$) and spin-down ($\downarrow$) channels, respectively. Ru d-band center is marked at $\epsilon_d = -1.36$ eV (red dotted line). The vertical dashed line corresponds to the Fermi level ($E_F = 0$ eV).

Supplementary Files

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