Electronic Structure Engineering of Single-Atom Ru Sites via Co–N4 Sites for Bifunctional pH-Universal Water Splitting

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1. Introduction

Hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) are the two half-reactions of electrochemical water splitting, which is widely recognized as a promising method to produce green hydrogen via renewable energy sources.[3] Compared to OER in alkaline and HER in acids, OER in acidic and HER in alkaline are more challenging due to the additional step caused by water molecule dissociation.[2] Although tremendous efforts have been devoted to developing efficient electrocatalysts to overcome the energy barriers and accelerate the reaction kinetics of OER and/or HER, most of the reported electrocatalysts are only applicable for OER or HER under specific conditions (e.g., acid or alkaline).[3] Besides, the severe activity decay (for both OER and HER) significantly restricts their large-scale application. From a practical point of view, it is highly desirable to develop high-performance bifunctional electrocatalysts over a wide pH range for hydrogen production using proton exchange membrane (PEM) electrolyzers and alkaline water electrolyzers.

Platinum group metals (PGMs) are the benchmark catalysts for OER (e.g., Ru, Ir) and HER (e.g., Pt).[4] Ru-based catalyst exhibits better OER activity than Ir-based catalysts and is also a promising alternative to Pt for HER with significantly lower cost.[5] However, two issues need to be addressed in developing a Ru-based bifunctional electrocatalyst. First, the over-oxidation of RuO2 into soluble RuO4 moieties and the participation of lattice oxygen often results in poor OER stability.[6] Second, Ruthenium (Ru) is a promising substitute for the state-of-the-art Pt catalyst for alkaline HER due to its lower price and lower kinetic barrier for water adsorption/dissociation than Pt.[7] However, there have been some efforts to address these issues and simultaneously reduce the usage of Ru metal which are costly.

Single-atom catalysts (SACs) dispersed on nitrogen-doped carbon support have attracted significant attention owing to...
the distinct merits of atomically dispersed active sites and maximum atom utilization efficiency. However, SACs is intrinsically limited by the simplicity of their active sites. For complex reactions involving multiple intermediates like OER and HER, their single-site typically follow linear scaling relationships and exhibit either too strong or too weak bonding to one or more intermediates. The atomically dispersed catalysts with dual-sites have shown promise to improve catalytic performance through introducing more accessible active sites and optimizing electronic structures. For example, N-coordinated isolated diatomic Ni–Fe sites with unique electronic structure and geometry configuration exhibited high-performance for CO2 reduction in a wide potential than individual Ni–N–C and Fe–N–C. Atomically dispersed Mn–N moieties into Fe–N–C catalysts also show an enhanced activity of oxygen reduction reaction via improving the oxygen adsorption states and stretching the O–O bond length.

Herein, we show an atomically dispersed Ru–Co dual-sites catalyst to regulate the intermediate species affinity on the Ru surface, thereby enabling a highly active bifunctional catalyst for water splitting in both acidic and alkaline conditions. By pyrolyzing Ru/Co codoped UiO-66-NH2 and acid etching, RuN4 and CoN4 sites are isolated and well distributed on the nitrogen–carbon support (Ru/Co–N–C-800 °C). Benefiting from the unique atom-isolated structure and atomic-distance synergistic effect between Ru–N4 and Co–N4 moieties, the Ru/Co–N–C-800 °C shows exceptional catalytic performance for OER, HER, and overall water splitting, across a wide pH range.

2. Results and Discussion

2.1. Synthesis and Structural Characterization

The synthetic process of Ru/Co–N–C-800 °C is illustrated in Figure 1a. Briefly, the Zr6-based UiO-66-NH2 was first synthesized using RuCl3 and CoCl2 as metal precursors and 2-aminoterephthalic acid (H2BDC-NH2) as the N and C sources, which was acting as a host to encapsulate Ru3+ and Co2+ ions via a self-assembly process (denoted as RuCl3/CoCl2-Uio-66-NH2). The negatively charged –NH2 groups in the ligand can function as Lewis acidic sites to immobilize metal atoms, Ru and Co ions can coordinate with the nitrogen atoms, forming metal–N bonds. The color observed after adding RuCl3/CoCl2 change from yellow to light grey, indicating the strong electrostatic adsorption between Ru3+/Co2+ ions and the electron-rich –NH2 groups. During the self-assembly process and pyrolysis at 800 °C, the color of the obtained catalysts is confirmed by TEM, HR-TEM, and HAADF-STEM images (Figure 1e–g).

Figure 1. a) The illustration of the synthesis procedure of Ru/Co–N–C-800 °C. b) XRD patterns, c) Raman spectra, and d) N2 adsorption–desorption isotherm (inset is the pore size distribution) of Ru/Co–N–C-800 °C and Ru–N–C-800 °C. e) TEM, f) HR-TEM, and g) HAADF-STEM images of Ru/Co–N–C-800 °C.
the pyrolysis of RuCl₃/CoCl₂-UiO-66-NH₂ in Ar at 800 °C, Ru and Co sites were anchored on nitrogen-doped carbon (N–C) derived from H₂BDC-NH₂. Finally, the inert ZrO₂ was removed by acid etching to yield the nitrogen co-coordinated Ru/Co dual-sites catalyst (Ru/Co–N–C-800 °C).

After pyrolysis and acid etching, the X-ray diffraction (XRD) patterns show broad peaks of amorphous features in the absence of characteristic peaks for Ru or Co nanoparticles, implying that the skeleton of UiO-66-NH₂ was converted in situ into porous N-doped carbon (Figure 1b). Raman spectra exhibit the D₁ (1360 cm⁻¹) and G (1595 cm⁻¹) bands at Ru/Co–N–C-800 °C and Ru–N–C-800 °C, corresponding to the edge plane defects of graphite and defect-free sp²-hybridized carbon network respectively (Figure 1c). [14] The significantly increased I_D₁/I_G ratio for Ru/Co–N–C-800 °C (1.12), as compared to that of Ru–N–C-800 °C (1.05), suggests that more defects are produced due to the cocoordination between Ru and Co and the N doped carbon support, which is beneficial to improve the electron-transfer rate between the catalyst and reactants.[15] The specific surface area of Ru/Co–N–C-800 °C is 449 m² g⁻¹ as determined by N₂ adsorption/desorption, suggesting it is rich in micropores and mesopores (Figure 1d). The hierarchical microporous/mesoporous structure can increase the density of active sites and mass transport during the electrochemical reaction.[12]

Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) (Figure 1e; Figure S2, Supporting Information) reveal that Ru/Co–N–C-800 °C maintain the initial octahedral shape after carbonization and acid washing. The absence of discernable Ru and Co particles in the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images indicates that the Ru and Co are well dispersed on the N-doped carbon framework, which is in line with the XRD results. A series of characterizations including XRD, TEM, and X-ray photoelectron spectroscopy (XPS) was applied to confirm the successful removal of ZrO₂ (Figure S3, Supporting Information). Numerous nanopores (highlight in yellow) are observed on the catalyst surface (Figure 1f).[16] The isolated brighter dots (selectively highlighted in red) in the HAADF-STEM image verify the existence of the atomically dispersed metal sites on the N-doped carbon framework (Figure 1g). The elemental mapping shows that the Ru, Co, C, and N are homogeneously distributed on the carbon support (Figure S4, Supporting Information). The single-atom Ru–N–C-800 °C and Ru/Co nanoparticles (denoted as Ru/Co NPs/N–C-800 °C) catalysts were also synthesized by employing a similar method. The Ru atoms in Ru–N–C-800 °C are also distributed homogeneously on the N-doped carbon support without aggregation (Figure S5a,b, Supporting Information). By contrast, Ru/Co nanoparticles were obtained due to the aggregation of metal atoms at high temperatures in the absence of –NH₂ groups (Figure S5c,d, Supporting Information). The content of Ru and Co are quantified by inductively coupled plasma mass spectroscopic (ICP-MS) to be 0.36 and 0.15 wt%, respectively (Table S1, Supporting Information). Compared with the feed ratio of Ru/Co (1/1), the relatively larger density of Ru atoms than Co atoms in Ru/Co–N–C-800 °C is attributed to the removal of some unstable Co species during acid washing.

2.2. Analysis of Composition and Atomic Structure

The surface compositions and electronic structure are further investigated by XPS. The signals of Ru 3p and Co 2p are not detected due to their low concentrations and sensitivity limit of XPS (Figure S6a,b, Supporting Information). The N 1s spectra show that the feature of pyridinic (398.7 eV), metal–nitrogen (M–Nₓ) (399.5 eV), pyrrolic (401.0 eV), and graphitic–N (402.5 eV) species (Figure S6c,d, Supporting Information).[17] The dominant N species (pyridinic and pyrrolic N) located in a π conjugated system play an essential role in stabilizing metal atoms, in which p-electrons are effectively coordinated with Ru/Co atoms and modulate the electronic properties.[18] Besides, pyridinic nitrogen exhibits better water wettability and a strong affinity to water molecules, thus facilitating electron transfer in OER/HER process.[19]

The synchrotron-based X-ray absorption spectroscopy (XAS) characterization was carried out to provide a detailed understanding of the chemical state and coordination configurations of Ru and Co atoms. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements provide a more detailed understanding of the valance states and coordination states of the metal atom centers. As shown in the XANES spectra of Ru/Co–N–C-800 °C, the near-edge absorption energy of the Ru K-edge was positioned between those of the Ru foil and RuO₂ references, and close to that of RuCl₃, indicating the dominant valence state of Ru/Co–N–C-800 °C is around +3 (Figure 2a). Compared with commercial RuO₂ with highly symmetrical octahedral structures, a pre-edge peak of Ru/Co–N–C-800 °C near 22 114 eV is related to the transition of Ru 1s to the unoccupied Ru 4d level.[20] The unoccupied Ru 4d level is ascribed to the electrons transfers from Ru 4d state to N 2p state via strong Ru–N hybridization in the Ru–N₄ sites.[21] Moreover, the Ru K-edge absorption spectra of Ru/Co–N–C-800 °C show a significant shift to lower energy compared to Ru–N–C-800 °C, implying a decrease in the Ru valence state after introducing Co sites. Moreover, the adsorption threshold energies (E₀) of Ru obtained from the first derivative in Ru foil, RuCl₃, RuO₂, Ru/Co–N–C-800 °C, and Ru/Co–N–C-800 °C are 22 117.4, 22 125.4, 22 128.4, 22 126.8, and 22 125.6 eV, respectively (Figure S7a, Supporting Information). The smaller E₀ of Ru/Co–N–C-800 °C than that of the Ru–N–C-800 °C indicates a decreased oxidation state of Ru in Ru/Co–N–C-800 °C. The average valence state of Ru in Ru/Co–N–C-800 °C is +3.1, lower than that of Ru (±3.4) in Ru–N–C-800 °C, near to RuCl₃ (+3) (Figure S7b, Supporting Information). The modified electronic properties of Ru atoms is expected to facilitate water dissociation and modulate the binding strength of the adsorbed oxygen/hydrogen intermediate, thus endowing Ru/Co–N–C-800 °C with remarkable performance than Ru–N–C-800 °C.[22]

As shown in the Fourier-transformed (FT) k¹-weighted EXAFS spectra of Ru K-edge (Figure 2c), the dominant peak at z=1.48 Å (without phase correction) for Ru/Co–N–C-800 °C can be assigned to shell coordination of the nearest Ru–N/C bond, without the Ru–Ru peaks at z=2.3 Å, as shown in Ru foil.[23] Importantly, a significant increase in the length of Ru–N bond is detected after the introduction of foreign Co atoms, indicating a strong dipole hybridization of Ru–N coordination.
The formation of Ru/Co–N coordination can be confirmed by the soft XAS at N K-edge and C K-edge (Figure S8a,b, Supporting Information). Compared to the almost identical C K-edge spectra of Ru/Co–N–C-800 °C and N–C-800 °C, the significant variations in the peaks’ intensity of N K-edge spectra represents the strong interaction between N atoms and Ru/Co atoms through orbital hybridization.[21] The N 1s XPS measurement for Ru/Co–N–C-800 °C also demonstrates the formation of M–N\textsubscript{x} bonds (Figure S8c,d, Supporting Information). Also, the formation of Ru–O bonds in Ru/Co–N–C-800 °C catalyst can be excluded by the O K-edge spectrum and O 1s XPS measurements (as discussed in Figure S9 in the Supporting Information).

For Co K-edge spectra, the normalized Co adsorption spectrum in Ru/Co–N–C-800 °C is situated between Co foil and CoO, indicating the oxidation state of Co atoms in Ru/Co–N–C-800 °C. Ru/Co–N–C-800 °C shares similar characteristic features to cobalt (II) phthalocyanine (CoPc), indicating that Ru/Co–N–C-800 °C possesses comparable D\textsubscript{4h} symmetry as CoPc (Figure 2b).[23] A pre-edge peak (A) at ≈7709.6 eV can be assigned to the dipole-forbidden but quadrupole-allowed transition (1s→3d), referring to the 3d and 4p orbital hybridization of the Co central atoms.[24] Compared with CoPc, the reduced peak (B) intensity of 1s→4p transition in Ru/Co–N–C-800 °C acts as a fingerprint of square-planar Co–N\textsubscript{4} moieties, also confirming the distorted D\textsubscript{4h} symmetry of Co atom in Ru/Co–N–C-800 °C.[24] The adsorption threshold energies (E\textsubscript{0}) of Co obtained from the first derivative in Co foil, CoO, Co\textsubscript{3}O\textsubscript{4}, and Ru/Co–N–C-800 °C are 7708.3, 7721.0, 7728.1, and 7719.9 eV, respectively (Figure S7c, Supporting Information). The calculated average valence state of Co in Ru/Co–N–C-800 °C is +1.8, near to the CoO (Figure S7d, Supporting Information), confirming that the valence of Co in Ru/Co–N–C-800 °C is indeed between 0 and +2. The prominent peak at

\begin{figure}
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\caption{a) Ru K-edge and b) Co K-edge XANES spectra, and c,d) the corresponding Fourier transforms of EXAFS spectra of Ru/Co–N–C-800 °C and reference samples. Wavelet transform (WT) of e) Ru and f) Co in Ru/Co–N–C-800 °C. g,h) Ru K-edge and Co K-edge FT-EXAFS and the corresponding EXAFS fitting curves at R space for Ru/Co–N–C-800 °C. i) Proposed structural model of Ru/Co–N–C-800 °C.}
\end{figure}
≈1.39 Å in FT-EXAFS spectra of Co K-edge is attributed to the scattering interaction between the Co atoms and the nearest shell coordination of the Co–N bond (Figure 2d). The negligible peaks at ≈2.2 Å in the FT-EXAFS spectra of Ru and Co in Ru/Co–N–C-800 °C exclude the presence of M–M (M: Ru, Co) bonds, implying the isolated distribution of Ru and Co atoms.

The wavelet transforms (WT) of the k^3-weighted EXAFS spectra further confirm the above conclusion. The WT contour plot shows two intensity maxima at 5.7 and 10.2 Å⁻¹ in Ru foil and RuO₂ correspond to the Ru–O and Ru–Ru metallic bonds, respectively (Figure S10, Supporting Information).[25] The only dominant intensity at 4.3 Å⁻¹ in Ru/Co–N–C-800 °C is ascribed to the coordinated configuration of the Ru–N structure, where no Ru–Ru signal near 10.2 Å⁻¹ is detected (Figure 2e). Similarly, the WT contour maximum at 4.2 Å⁻¹ confirms the presence of Co–N bonds with the absence of Co–Co or Co–C bonds, compared with the WT contour plots of Co foil, CoPc, and CoO (Figure 2f; Figure S11, Supporting Information). The EXAFS fitting curves were carried out (Figure 2g;h; Figures S10a and S12, Supporting Information) and corresponding parameters were summarized (Table S2, Supporting Information). The fitting results reveal that the coordination is in the form of Ru–N₄ and Co–N₄ moieties with an average bond length of ≈2 Å. Together, the above results confirm the successful synthesis of atomically isolated Ru and Co single atoms on the N–C support, in which the electronic properties of Ru atoms are modified by Co atoms (Figure 2i).

3. Electrochemical Performance of OER

We first evaluated the OER performance of the as-prepared catalysts in N₂-saturated electrolytes using a three-electrode system. The OER performances in 0.5 m H₂SO₄ and 1 m KOH show the same trend: Ru/Co–N–C-800 °C > Ru–N–C-800 °C > commercial RuO₂ (Figure 3a). Specifically, Ru/Co–N–C-800 °C with dual-sites significantly improves OER activity with a lower onset potential of 1.40 V versus reversible hydrogen electrode (RHE) compared to Ru–N–C-800 °C (1.44 V vs RHE) in 0.5 m H₂SO₄, suggesting that the OER activity is significantly improved by introducing CoN₄ site in N-doped carbon support. The overpotential of Ru/Co–N–C-800 °C for delivering a current density of 10 mA cm⁻² are 232 and 276 mV in 0.5 m H₂SO₄ and 1 m KOH, respectively, much lower than those of Ru–N–C-800 °C (297 and 347 mV) and commercial RuO₂ (329 and 379 mV, Figure 3b), ranking Ru/Co–N–C-800 °C one of the most active noble metal-based catalysts in both acidic and alkaline media (Tables S3 and S4, Supporting Information). The Ru/Co NPs–N–C-800 °C catalyst shows a low current density of 3.4 mA cm⁻² at 1.5 V versus RHE in 0.5 m H₂SO₄, eightfold lower than Ru/Co–N–C-800 °C (27.6 mA cm⁻²) (Figure S13, Supporting Information). Besides, the inferior OER performance of Co–N–C-800 °C suggests that the active center in Ru/Co–N–C-800 °C is RuN₄ sites, and its electronic structure is efficiently regulated by introducing CoN₄ sites, thereby exhibiting an enhanced OER activity relative to Ru–N–C-800 °C. The carbonization temperature and ratios of Ru and Co are also found to affect OER performance (Figure S14, Supporting Information).

Figure 3. Electrocatalytic OER performance of Ru/Co–N–C-800 °C compared with Ru–N–C-800 °C, Co–N–C-800 °C, and commercial RuO₂. a) OER polarization curves were obtained at a scan rate of 5 mV s⁻¹ in N₂-saturated 0.5 m H₂SO₄ and 1 m KOH. b) Comparison of overpotential to achieve a current density of 10 mA cm⁻² and TOF value at 1.53 V versus RHE in 0.5 m H₂SO₄ and 1 m KOH. c) The chronopotentiometry of Ru/Co–N–C-800 °C and commercial RuO₂ in 0.5 m H₂SO₄ and 1 m KOH.
Information), possibly by influencing the dispersion of active sites and N-coordination number.[8a,26]

The turnover frequency (TOF) was calculated to understand the intrinsic activity of the catalysts based on the reported protocols.[27] Ru/Co–N–C-800 °C yields an ultrahigh TOF value of 9.20 s⁻¹ at 1.53 V versus RHE in 0.5 m H₂SO₄, which is 4.5 and 1840 times higher than Ru–N–C-800 °C (2.05 s⁻¹) and RuO₂ (0.005 s⁻¹), respectively (Figure 3b). Besides, the small Tafel slopes and small semicircle in electrochemical impedance spectroscopy (EIS) for Ru/Co–N–C-800 °C confirm its more favorable reaction kinetics and charge transfer efficiency (Figure S15, Supporting Information).[28] The Faradaic efficiency (FE) of Ru/Co–N–C-800 °C was determined to be 96%, indicating most of the charge transfer process was dominated by OER electrocatalysis (Figure S16, Supporting Information).

Apart from high catalytic activity, Ru/Co–N–C-800 °C also exhibits excellent durability over 20 h at 10 mA cm⁻² with noticeable activity degradation in 0.5 m H₂SO₄ and 1 m KOH (Figure 3c). By contrast, a sharp increase of overpotential for commercial RuO₂ is observed within 4 h, possibly due to the severe dissolution of RuO₂ in the electrolytes.[20] The well-overlapped LSV curves before and after CV tests and well-maintained current densities at a set potential in 0.5 m H₂SO₄ and 1 m KOH electrolytes reconfirm the remarkable electrocatalytic durability of Ru/Co–N–C-800 °C catalyst during the OER process (Figure S17, Supporting Information). After the OER stability test, the unchanged Raman spectrum and homogeneously distribution of Ru/Co atoms confirm the robustness of Ru/Co–N–C-800 °C (Figure S18, Supporting Information).

We also evaluated the OER performance of the as-prepared catalysts in neutral conditions. The required overpotential is 400 mV for Ru/Co–N–C-800 °C to realize a current density of 10 mA cm⁻², much lower than Ru–N–C-800 °C (424 mV) and commercial RuO₂ (461 mV) (Figure S19a, Supporting Information). Importantly, the mass activity of Ru/Co–N–C-800 °C at 1.7 V versus RHE is 413-times higher than commercial RuO₂ (Figure S19b, Supporting Information). Additionally, the applied potential to achieve 10 mA cm⁻² for Ru/Co–N–C-800 °C shows little increase during 20 h, implying its stable performance (Figure S19c, Supporting Information). The almost overlapped LSV curves before and after the stability test further approve the robust properties of Ru/Co–N–C-800 °C for OER in 1 m PBS (Figure S19d, Supporting Information). Together, the low overpotential, ultrahigh TOF values, and robust stability highlight Ru/Co–N–C-800 °C as an outstanding catalyst for OER over a wide pH range.

4. Electrochemical Performance of HER

Ru-based materials have been widely regarded as an attractive alternative to Pt-based catalysts for HER since they have similar metal–H bond strength.[29] We, therefore, investigated the HER performance of the as-prepared catalysts in 0.5 m H₂SO₄ and 1 m KOH, with commercial 20% Pt/C as a reference. As shown in Figure 4a and Figure S20a,c (Supporting Information), Ru/Co–N–C-800 °C initiates HER at nearly zero overpotential. The required overpotential to deliver a current density of 10 mA cm⁻² is merely 17 and 19 mV in 0.5 m H₂SO₄ and 1 m KOH, which are superior to the Ru–N–C-800 °C (44 and
32 mV, respectively) and Co–N–C-800 °C, and even outperform commercial Pt/C (33 and 23 mV, respectively) under same conditions. The Ru/Co–N–C-800 °C also has the smallest Tafel slopes of 23.3 and 27.8 mV dec⁻¹ in 0.5 m H₂SO₄ and 1 m KOH, respectively (Figure 4b), corresponding to the Volmer–Heyrovsky mechanism.[10] The TOF of Ru/Co–N–C-800 °C is more than ten times higher than the previously reported Ru-based catalysts (Figure S20b,d, Supporting Information). To the best of our knowledge, the HER performance of Ru/Co–N–C-800 °C surpasses most of the previously reported Ru-based HER catalysts in acid or alkaline conditions (Figure 4c; Tables S5 and S6, Supporting Information). Moreover, the chronoamperometric test at −100 mA cm⁻²geo highlights the exceptional stability of Ru/Co–N–C-800 in 0.5 m H₂SO₄ and 1 m KOH after 20 h of electrolysis (Figure 4d). In contrast, the severe activity decay for commercial Pt/C is observed, attributed to the dissolution of Pt surface atoms and agglomeration of Pt particles.[31] The Ru/Co–N–C-800 °C catalyst shows good HER performance in 1 m PBS, with an overpotential of 87 mV at a current density of 10 mA cm⁻²geo, which approaches that of the commercial Pt/C (58 mV), and is much better than that of Ru–N–C-800 °C (102 mV). The recorded chronopotentiometry curves at a constant current density of −50 mA cm⁻²geo manifest that the HER activity of Ru/Co–N–C-800 °C is well-maintained for 20 h (Figure S21, Supporting Information).

5. Discussion
To gain insight into the origin of the excellent OER performance of Ru/Co–N–C-800 °C, we probed the adsorption energy of the first produced oxygenated intermediate OH* based on the onset potential of methanol oxidation reaction (MOR) since OH* is electrophiles and prone to react with nucleophiles such as alcohol molecules (Figures S22 and S23, Supporting Information).[32] The lower MOR onset potential of Ru/Co–N–C-800 °C (1.17 V vs RHE) than Ru–N–C-800 °C reflects that the former possesses a higher surface coverage of OH* intermediates, which may be associated with energetically more favorable water molecule dissociation on Ru/Co dual sites. The high concentration of OH* intermediates is supposed to accelerate the formation of electrophilic O(II−δ)−species, which are more susceptible to nucleophilic attack by the water molecule, thereby improving OER performance.[13] The coverage of OH* shares a similar trend with the OER performance (Figure 5a). Compared with Ru–N–C-800 °C and commercial RuO₂, Ru/Co–N–C-800 °C

![Figure 5](image-url)

**Figure 5.** a) The relationship between OER performance and the concentration of OH intermediates for Ru/Co–N–C-800 °C, Ru–N–C-800 °C, and commercial RuO₂. b) OER free energy diagram for Ru/Co–N–C-800 °C and Ru–N–C-800 °C. Partial electronic density of states (PDOS) of c) Ru–N–C-800 °C and d) Ru/Co–N–C-800 °C. Differential charge density at the atomical Ru centers between Ru and neighboring C/N atoms in e) Ru–N–C-800 °C and f) Ru/Co–N–C-800 °C. Yellow and blue contours represent electron accumulation and depletion, respectively.
demonstrates a much smaller Tafel slope at a high potential region after adding CH₃OH, signifying much easier desorption of oxygenated intermediates.\(^\text{[34]}\) Interestingly, the OER performance and bonding strength of OH\(^{\circ}\) also share the same trend in 0.5 m H₂SO₄ and 1 m KOH: Ru/Co–N–C-800 °C > Ru–N–C-800 °C > RuO₂ (Figure S24, Supporting Information).

To understand the synergistic effect between isolated RuN4 and CoN4 dual sites on the electrochemical reactions, we took the OER and HER in acid as an example to conduct density functional theory (DFT) calculations and model the configurations of Ru/Co–N–C-800 °C catalyst (Figure S25a–d, Supporting Information). The strong water absorption ability is beneficial to the decomposition of water on the catalyst, which is the prerequisite step for OER in acids. The H₂O adsorption energy of Ru/Co–N–C-800 °C and Ru–N–C-800 °C are calculated based on the Ru site (Figure S25e, Supporting Information). The Ru/Co–N–C-800 °C shows a negligible energy barrier for water absorption, which is more favorable than Ru–N–C-800 °C. This result indicates that the surface states of Ru–N4 site can be regulated by introducing CoN4 sites, thus efficiently facilitating the water absorption and dissociation, which is in line with the higher OER activity.

The OER process usually involves four proton-electron transfer steps and three successive intermediates (OH\(^\circ\), O\(^\circ\), and OOH\(^\circ\), where the asterisk denotes the adsorption site). As shown in Figure 5b and Figure S26, Supporting Information, the Ru/Co–N–C-800 °C has the lower energy barrier for the rate-determining step (RDS) of the OOH\(^\circ\) intermediate formation (reducing from 2.06 to 2.01 eV). Moreover, the partial density of states (PDOS) results for Ru/Co–N–C-800 °C with CoN4 sites reveal that the d-band center shifts to a low-energy level relative to Ru–N–C-800 °C (Figure 5c,d). The negative shift of d-band center would increase the filling of as-hybridized antibonding orbitals ((d–σ)\(^\text{e}\)) and destabilize the interaction between the catalyst surface and the adsorbates, thus thermodynamically improving the binding ability of RuN4 sites with oxygen intermediates for better OER.\(^\text{[35]}\) Besides, the integrated PDOS results show that the Ru 4d and O 2p centers get closer in Ru/Co–N–C-800 °C compared with Ru–N–C-800 °C, indicating that the Ru/Co–N–C-800 °C with CoN4 sites exhibits a larger Ru–O covalency than Ru–N–C-800 °C (Table S7, Supporting Information). The enlarged Ru–O covalency can promote the electron transfer between the Ru sites and oxygenated adsorbates and decrease the binding strength of intermediates species on the surface of Ru/Co–N–C-800 °C, thereby boosting the OER rate.\(^\text{[36]}\) The additional calculations about electronic properties such as PDOSs of Ru atom in different models and the OER intermediates species are also investigated. As shown in Figure S27 (Supporting Information), all the d orbital of the Ru atom in Ru/Co–N–C-800 °C, involved with the initial reactants \(^\circ\)OH towards the final product O₂, shift towards the Fermi energy level with the modification of Co–N4 sites. This guarantees the efficient electron transfer and intermediate transformation during the OER process, indicating the enhanced catalytical activity of the Ru–N4 sites.\(^\text{[37]}\)

The Bader charges of the Ru atom were performed to give a quantitative comparison of the electron transfer with and without the CoN4 sites. In comparison to Ru–N–C-800 °C, the Ru sites in Ru/Co–N–C-800 °C with CoN4 sites gains an increased amount of electron (0.054 e\(^{\text{−}}\) per cell) from the adjacent C/N atoms, suggesting that more electron transfer occurs between neighboring C/N atoms and the isolated RuN4 sites, which is consistent with XAS results. Moreover, the differential charge density of Ru–N4 sites with CoN4 sites suggests that the C/N atoms act as an electron reservoir to donate electrons to Ru sites, thus efficiently enhancing the resistance to over-oxidation and corrosion of Ru–N4 (Figure 5e,f).\(^\text{[6b]}\)

Similarly, the Gibbs free energy of hydrogen adsorption (\(\Delta G_{\text{H*}}^{\text{ads}}\), * denotes an adsorption site) is a vital descriptor for appraising HER activity.\(^\text{[38]}\) An optimum HER electrocatalyst is suggested with a small \(\Delta G_{\text{H*}}^{\text{ads}}\) value. Ru/Co–N–C-800 °C catalyst presents a smaller \(\Delta G_{\text{H*}}^{\text{ads}}\) (−0.445 eV) than that of Ru–N–C-800 °C (−0.585 eV) in 0.5 m H₂SO₄, indicating that Ru/Co–N–C-800 °C possesses a better HER activity (Figure S25d, Supporting Information). Therefore, the correlations between HER activities and the calculated \(\Delta G_{\text{H*}}^{\text{ads}}\) values unveil that the incorporation of atomically CoN4 sites efficiently weakens the physiochemical interaction between Ru and H intermediate, thus promoting H adsorption/H₂ desorption and achieving a remarkable HER activity.

6. Application for Overall Water-Splitting and PEM Water Electrolyzer

Encouraged by the outstanding OER and HER activity of the Ru/Co–N–C-800 °C in a broad pH range, we further employ Ru/Co–N–C-800 °C as both the cathode and anode for overall water splitting. As shown in the polarization curve (Figure 6a), the cell voltage required for Ru/Co–N–C-800 °C is only 1.49 and 1.50 V to achieve a current density of 10 mA cm \(^{-2}\) in 0.5 m H₂SO₄, respectively, which is far lower than Pt/C|RuO₂ and outperform most reported electrocatalysts to date (Figure 6c; Tables S8 and S9, Supporting Information). Ru/Co–N–C-800 °C demonstrates remarkable stability in both acidic and alkaline, ranking it one of the best performing bifunctional electrocatalysts for overall water splitting over the broad pH range in terms of both activity and stability (Figure 6b). In contrast, due to the rapid dissolution of RuO₂, the applied potential of Pt/C|RuO₂ sharply increases to 1.75 V after only 2 h. Finally, we apply the Ru/Co–N–C-800 °C in a homemade proton exchange membrane (PEM) water electrolyzer device and achieve steady operation at a current density of 450 mA cm \(^{-2}\) for 330 h (Figure S28, Supporting Information), demonstrating the great potential of the catalyst for industrial applications.

7. Conclusions

An atomically dispersed Ru/Co dual-sites (Ru/Co–N–C-800 °C) catalyst is designed for bifunctional and pH-universal electrocatalyst towards OER, HER, and overall water-splitting in a wide pH range, which outperforms most of the electrocatalysts reported to date. Experimental results and theoretical calculations reveal that the main activity center of Ru/Co–N–C-800 °C is RuN4 sites, while CoN4 sites play a critical role in adjusting the electronic structure and bonding strength between oxygen/hydrogen intermediate species with RuN4.
sites. Theoretical calculations further reveal that the introduction of Co–N4 sites can increase the electron density of Ru–N4 sites, thereby improving the resistance of Ru–N4 to over-oxidation and corrosion. These findings provide a new perspective for the design and synthesis of bifunctional single-atom electrocatalysts with bi- or multimetallic active sites for energy-related conversions technologies such as water splitting, CO2 reduction and nitrogen reductions and beyond.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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electrochemical energy conversion, hydrogen, ruthenium cobalt, single-atom catalysts, water splitting

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