

RESEARCH ARTICLE

Excellent Overall Water Splitting Catalyst of Single Phase 6H Triple Perovskite $\text{Ba}_3\text{Co}(\text{Co}_{0.25}\text{Ru}_{0.75})_2\text{O}_9$ at 1 A cm^{-2} for 1000 h

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Received: 18 January 2026 | **Revised:** 27 May 2026 | **Accepted:** 29 June 2026

Keywords: ampere-level stability | in situ XAS | overall water splitting | single-phase perovskite oxide | synergistic effect

ABSTRACT

Developing efficient bifunctional electrocatalysts for overall water splitting (OWS) remains a critical challenge due to the divergent reaction mechanisms required for oxygen and hydrogen evolution reactions (OER and HER), especially in a single-phase material. Here, we present a novel self-adaptive 6H triple perovskite oxide, $\text{Ba}_3\text{Co}(\text{Co}_{0.25}\text{Ru}_{0.75})_2\text{O}_9$ (BCCRO), as a highly active and durable alkaline OWS catalyst. BCCRO exhibits low overpotentials of 178 and 32 mV for the OER and HER at 10 mA cm^{-2} in 1.0 M KOH, respectively. A symmetric electrolyzer maintains stable performance for 1000 h at 1 A cm^{-2} . Operando X-ray absorption spectroscopy reveals its dynamic surface restructuring processes: under OER conditions, Co^{3+} and Ru^{5+} are oxidized to Co^{4+} and Ru^{6+} , while during HER, they transform into metallic CoRu nanoparticles. Density functional theory calculations indicate that its high activity of OWS originates from synergy between high valence Ru^{6+} and Co^{4+} for OER, and between metallic Co and Ru for HER. This study presents a rare single-phase oxide catalyst that achieves exceptional OWS performance through operando adaptation, providing a transformative framework for developing practical water-splitting technologies.

1 | Introduction

Hydrogen is an ideal energy carrier for a sustainable future owing to its high energy density and zero carbon emissions upon utilization [1]. However, its large-scale adoption is primarily hindered by high production costs, especially energy consumption. One promising solution is renewable electricity-driven electrocatalytic water splitting, which offers a sustainable and cost-competitive route to hydrogen [2]. Water electrolysis consists of two coupled half-reactions: the hydrogen evolution

(HER) and oxygen evolution (OER) reactions [3, 4]. The sluggish kinetics inherent to both HER and OER, arising from multi-step proton-coupled electron transfer, demand high overpotentials that severely diminish the efficiency and economic viability of water splitting [5, 6]. Consequently, highly efficient electrocatalysts are urgent to lower the reaction barriers for these reactions [7, 8].

Electrocatalytic water splitting typically requires different catalysts for each half-reaction, with Pt-based materials and Ir-/Ru-

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based oxides being the benchmark catalysts for HER and OER, respectively [9, 10]. However, the use of separate catalysts for the cathode and anode increases system complexity and cost [11]. More critically, under the harsh operating conditions of water electrolysis (e.g., extreme pH, high potentials), catalysts inevitably degrade through leaching or structural transformation. This can cause cross-contamination between electrodes, ultimately reducing system reliability [11]. The high cost, scarcity, and operational instability of conventional catalysts dramatically hinder the large-scale implementation of overall water splitting (OWS) [12, 13]. Addressing these limitations motivates the development of efficient bifunctional electrocatalysts that integrate HER and OER activities within a single material.

The pursuit of high-efficiency OWS catalysts has driven the development of sophisticated catalyst architectures. These designs aim to increase geometric surface area, modulate the electronic structure of active sites, and fine-tune the adsorption energies of key reaction intermediates (e.g., *O, *OOH, *H). Apart from classical heterostructures [14–16] and layered double hydroxides (LDHs) [17], the research landscape now encompasses diverse advanced configurations such as high-entropy alloys (HEAs) [18], metal–organic frameworks (MOFs) [4], nanofiber architectures [19], and single-atom catalysts (SACs) [20]. However, each strategy suffers from inherent limitations that impede practical application. These include synthesis complexity and interfacial issues in heterostructures [21], low conductivity in LDHs [17], ill-defined structure–property relationships in HEAs [18], poor stability and conductivity in MOFs [4], scalability and mechanical fragility in nanofibers [19], as well as stability and scalability challenges for SACs [20]. Consequently, the scalability and widespread implementation of these sophisticated designs remain limited. Recent efforts have demonstrated that single-phase catalysts can achieve bifunctional activity for OWS. For example, $\text{Ni}_{0.33}\text{Co}_{0.67}\text{MoS}_4$ nanosheets on carbon fiber cloth served as a bifunctional electrocatalyst with a cell voltage of 1.55 V at 10 mA cm^{-2} in 1.0 M KOH [22]. A quadruple perovskite $\text{CaCu}_3\text{Co}_2\text{Ru}_2\text{O}_{12}$ (CCCRO) achieved cell voltages of 1.536 V at 10 mA cm^{-2} and 1.629 V at 100 mA cm^{-2} in alkaline conditions, along with 500 h of operational stability at 100 mA cm^{-2} [23]. Additionally, FeCoNiLaPd high-entropy alloys achieved overpotentials of 279 and 278 mV at 100 mA cm^{-2} for OER and HER, respectively, with notable stability (>900 h) at high current densities [24]. However, their activities at industrial current densities remain insufficient, and the dynamic structural adaptation process under operating conditions has been rarely captured.

Moreover, designing superior bifunctional catalysts is inherently challenging because the optimal electronic structures for the active sites in HER and OER are fundamentally divergent. This inherent conflict creates a compelling need for self-adaptive catalysts that can dynamically reconfigure their active interfaces under operating conditions. Notably, as the most cost-effective platinum group metal, Ru-based materials have demonstrated significant activity for both HER and OER, making them promising candidates for next-generation bifunctional OWS catalysts [12, 19, 25–28]. For instance, metallic Ru and RuO_2 are known for their superior intrinsic activity toward HER and OER, respectively. Furthermore, Ru is more abundant and cost-effective than the benchmark Pt and Ir/IrO₂, offering an economic advantage

for large-scale applications. The key challenge, therefore, is to design such a self-adaptive Ru-based catalyst that can efficiently accommodate both reactions within a single material, ideally by dynamically tuning its active interfaces under operating conditions.

Perovskite-type oxides, particularly double perovskites ($\text{AA}'\text{BB}'\text{O}_6$) and triple perovskites ($\text{A}_3\text{BB}'_2\text{O}_9$), are attracting significant interest as electrocatalysts owing to their tunable electronic structures, high conductivity, and robust stability [29, 30]. As demonstrated previously [31–35], the strategic combination of 3d and 4d transition metals at the B-site enables precise electronic optimization, leading to significantly enhanced catalytic activity. Guided by this principle and the inherent bifunctionality of Ru, we designed a novel single-phase triple perovskite oxide, $\text{Ba}_3\text{Co}(\text{Co}_{0.25}\text{Ru}_{0.75})_2\text{O}_9$ (BCCRO). This material demonstrates exceptional bifunctional activity for alkaline OWS. In a symmetric electrolyzer in 1.0 M KOH, BCCRO achieves low cell voltages of only 1.50, 1.62, and 1.93 V to reach current densities of 0.01, 0.1, and 1 A cm^{-2} , respectively, while maintaining stable operation for 1000 h at 1 A cm^{-2} . In situ X-ray absorption spectroscopy (XAS) confirms the structural evolution of BCCRO during both OER and HER, with distinct changes in the oxidation states of Co and Ru. During OER, Co undergoes oxidation from +3 to +4, and Ru undergoes oxidation from +5 to +6. In contrast, during HER, both Co and Ru are reduced, leading to the formation of metallic Co and Ru species. Density functional theory (DFT) calculations reveal a Co–Ru synergy that underpins the bifunctional activity: in OER, a high-valent $\text{Co}^{4+}/\text{Ru}^{6+}$ framework creates a vacancy-open surface that enhances the Ba^{2+} spectator-cation effect to electrostatically stabilize O^* at Ru^* sites, thereby favoring the metal–site adsorbate evolution (MAE) pathway; in HER, it is the metallic CoRu nanoparticles that facilitate efficient hydrogen evolution. This work establishes BCCRO as a robust bifunctional catalyst that combines cost efficiency, structural simplicity, and excellent performance for both OER and HER.

2 | Results and Discussion

2.1 | Structural Characterization

The BCCRO catalyst possesses a 6H triple perovskite structure [36]. In this structure, CoO_6 octahedra connect with Co/Ru-O_6 octahedra via corner-sharing, while the Co/Ru-O_6 octahedra themselves are interconnected through face-sharing (Figure 1a). Within these face-shared octahedra, Co and Ru atoms are randomly distributed. Such a face-sharing network enhances structural robustness, consistent with the reported stability trend of corner- < edge- < face-sharing polyhedra [37]. Transmission electron microscopy (TEM) characterization revealed BCCRO nanoparticles with a size distribution of 30–60 nm (Figure S1). Rietveld refinement of the powder X-ray diffraction (XRD) pattern (Figure 1b) confirms a hexagonal phase (space group $P6_3/mmc$), with lattice parameters $a = b = 5.7081$ Å and $c = 13.9936$ Å (Table S1) and excellent agreement factors ($R_{wp} = 2.90\%$, $R_p = 2.11\%$). High-resolution TEM (HRTEM) images (Figure 1c,d) reveal lattice spacings of 0.286 nm and 0.495 nm, corresponding to the (110) and (100) planes, respectively. Inverse fast Fourier transform (IFFT) patterns derived from HRTEM

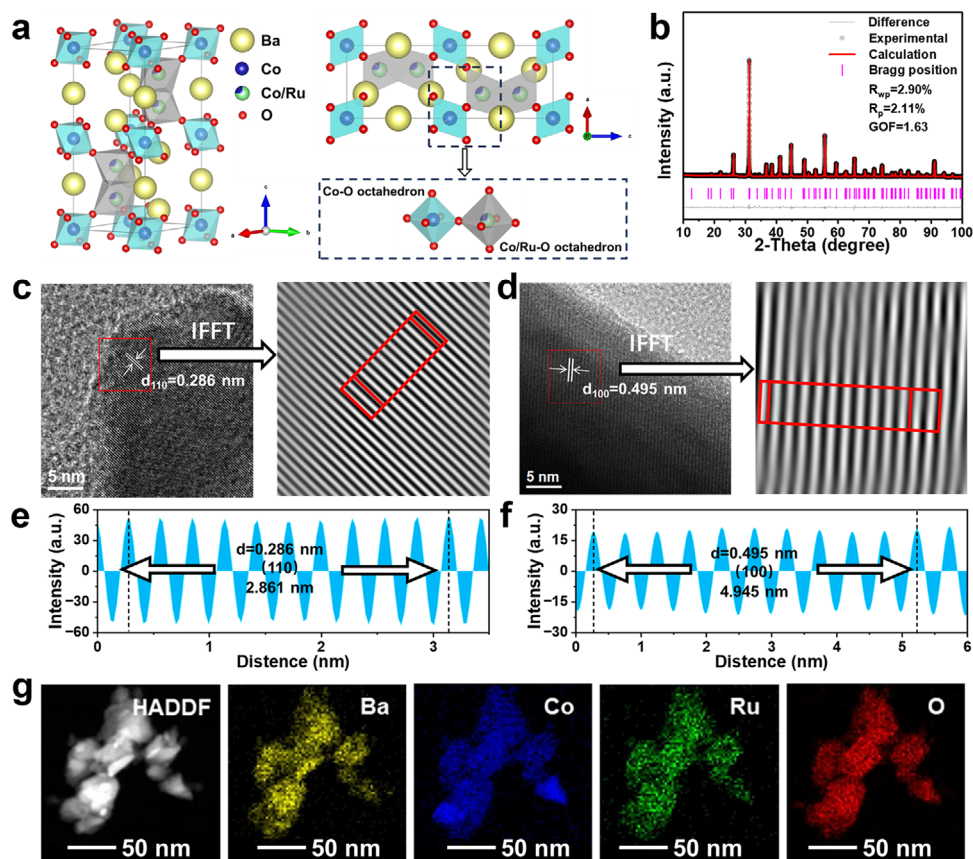


FIGURE 1 | Structural characterization. (a) Crystal structure illustration with corner-sharing CoO_6 and Co/Ru-O_6 octahedra. (b) XRD pattern of BCCRO pristine. (c, d) HRTEM images showing the (110) and (100) crystallographic planes, respectively. (e, f) Crystal lattice measurement diagram from (c) and (d). (g) EDX elemental mapping of BCCRO.

images (Figure 1e,f) further confirm the single-phase nature and crystallographic orientation. Selected-area electron diffraction (SAED) analysis along the $\bar{1}00$ zone axis (Figure S2) indicates high crystallinity. Inductively coupled plasma-mass spectrometry (ICP-MS) gives a Ba:Co:Ru molar ratio close to 2:1:1 (Table S2), while energy-dispersive X-ray spectroscopy (EDX) elemental mapping (Figure 1g) demonstrates the homogeneous distribution of Ba, Co, Ru, and O at the nanoscale. All these results verify the successful synthesis of phase-pure triple perovskite BCCRO. For comparison, a control sample $\text{Ba}_2\text{ScRuO}_6$ was synthesized. Its phase-purity, confirmed by XRD (Figure S3), enables an explicit assessment of the specific contribution of B-site Co to the OWS performance.

2.2 | Electrochemical Performance

The bifunctional electrocatalytic performance of BCCRO was evaluated in a standard three-electrode system using O_2 - and N_2 -saturated 1.0 M KOH for the OER and HER, respectively. Linear sweep voltammetry (LSV) scans were performed at a scan rate of 5 mV s^{-1} . All potentials were 95% iR-corrected and referenced to the reversible hydrogen electrode (RHE). For the OER, BCCRO exhibited superior activity, requiring an overpotential of only 178 mV to achieve 10 mA cm^{-2} (Figure 2a). The reported overpotentials were derived from the reverse (cathodic) LSV scan after sufficient activation to eliminate any contribution from oxidation

of the catalyst cations or substrates. This significantly outperforms the reference catalysts RuO_2 (340 mV), LaCoO_3 (406 mV), and the control sample $\text{Ba}_2\text{ScRuO}_6$ (Figure 2a). Notably, BCCRO maintained excellent performance at industrially relevant high current densities, requiring potentials of only 1.45 and 1.54 V versus RHE to reach 100 and 1000 mA cm^{-2} , respectively (Figure S4a). These values are substantially lower than those needed for commercial RuO_2 and LaCoO_3 . Tafel analysis derived from geometric area-normalized LSV curves (Figure 2b) revealed a favorable kinetic slope of $34.12 \text{ mV dec}^{-1}$ for BCCRO, compared to $77.34 \text{ mV dec}^{-1}$ for RuO_2 and $112.83 \text{ mV dec}^{-1}$ for LaCoO_3 . A direct comparison of the overpotential and Tafel slope for these catalysts is provided in Figure 2c.

For the HER, BCCRO demonstrated remarkable catalytic activity requiring an ultralow overpotential of 32 mV at 10 mA cm^{-2} (Figure 2d). This performance matches that of commercial 20% Pt/C and far surpasses the control sample $\text{Ba}_2\text{ScRuO}_6$ (76 mV). At industrial-scale current densities of 100 and 1000 mA cm^{-2} , BCCRO remained highly competitive, with overpotentials of only 105 and 314 mV, respectively (Figure S4b). These values are markedly lower than those of both the commercial 20% Pt/C and the $\text{Ba}_2\text{ScRuO}_6$ reference. Tafel analysis (Figure 2e) revealed a more favorable kinetic slope of $60.28 \text{ mV dec}^{-1}$ for BCCRO, compared to $90.37 \text{ mV dec}^{-1}$ for Pt/C and $130.40 \text{ mV dec}^{-1}$ for $\text{Ba}_2\text{ScRuO}_6$. The corresponding overpotential and Tafel slope comparison for the HER is summarized in Figure 2f. Notably,

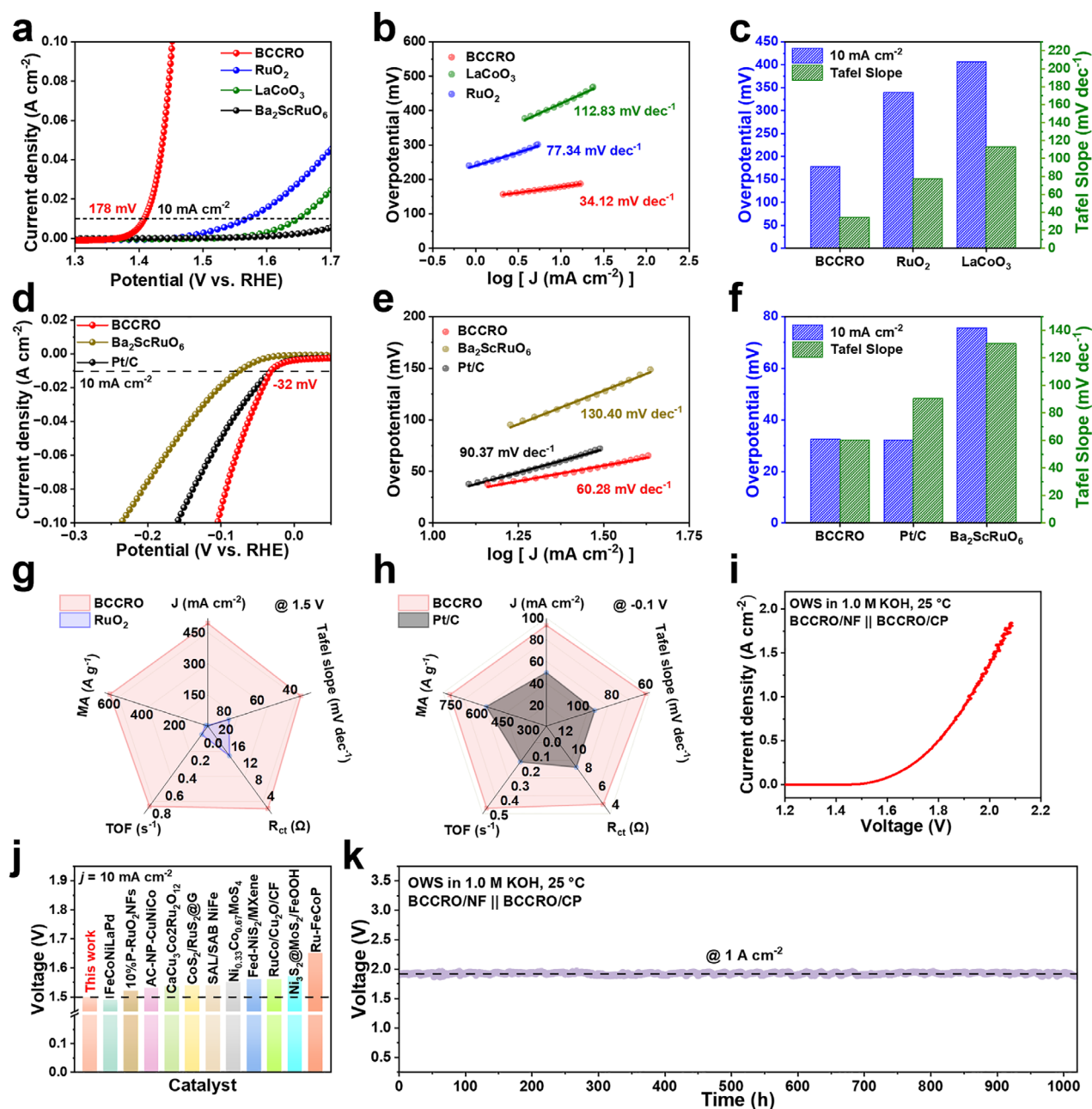


FIGURE 2 | Electrocatalytic performance. (a) OER LSV curves of BCCRO, RuO₂, LaCoO₃, and Ba₂ScRuO₆. (b) Tafel slope plots of BCCRO, RuO₂, and LaCoO₃ derived from the geometric area-normalized OER LSV curves. (c) Comparison between the overpotential at current density of 10 mA cm⁻² and the Tafel slope for BCCRO, RuO₂, and LaCoO₃. (d) HER LSV curves of BCCRO, Ba₂ScRuO₆, and Pt/C. (e) Tafel slope plots of BCCRO, Ba₂ScRuO₆, and Pt/C derived from the geometric area-normalized HER LSV curves. (f) Comparison between the overpotential at a current density of 10 mA cm⁻² and the Tafel slope for BCCRO, Ba₂ScRuO₆, and Pt/C. (g) The OER performance of BCCRO and commercial RuO₂. (h) The HER performance of BCCRO and commercial 20% Pt/C. (i) Polarization curves in a two-electrode system. (j) Comparison of cell voltages at a current density of 10 mA cm⁻² for BCCRO with previously reported high-activity OWS catalysts, all tested in 1.0 M KOH. (k) Long-term alkaline OWS stability of BCCRO was measured at the current density of 1 A cm⁻².

when Sc³⁺ replaces the B-site Co to form Ba₂ScRuO₆, both OER and HER activities decrease significantly. This clearly shows the key role of Co ions in achieving high-efficiency OWS.

To gain deeper insight into the performance of BCCRO, we investigated its charge transfer kinetics, electrochemically active surface area (ECSA), and intrinsic activity. According to electrochemical impedance spectroscopy (EIS) analysis (Figure S5) and the corresponding equivalent-circuit fitting parameters (Table

S3), BCCRO showed much lower charge transfer resistances (R_{ct}) than the reference catalysts, indicating faster charge transfer during both OER and HER. To avoid interference from gas diffusion, which becomes pronounced at high current densities, we performed EIS measurements at relatively low overpotentials to reliably determine the R_{ct} . ECSA was estimated from the electrochemical double-layer capacitance (C_{dl}), which was determined via cyclic voltammetry (CV) in a non-Faradaic potential region at various scan rates (Figures S6 and S7). After electrochemical

activation, BCCRO exhibited C_{dl} values of 9.21 and 16.46 mF cm⁻² for the OER and HER, respectively (Figures S6d and S7d). For the OER, this C_{dl} value is higher than those of RuO₂ (6.30 mF cm⁻²) and LaCoO₃ (3.85 mF cm⁻²). For the HER, it is slightly higher than that of 20% Pt/C (16.02 mF cm⁻²) and substantially greater than that of Ba₂ScRuO₆ (1.13 mF cm⁻²). These results indicate that BCCRO provides a larger number of accessible active sites for both reactions. To evaluate the intrinsic activity, the LSV curves were normalized by the corresponding ECSA. As shown in Figure S8, BCCRO exhibited higher ECSA-normalized current densities than commercial RuO₂ for OER and 20% Pt/C for HER, confirming its superior intrinsic activity in both reactions.

Its intrinsic activity was further quantified by calculating the turnover frequency (TOF). For OER at 1.50 V (vs. RHE), BCCRO achieved a TOF of 0.82 s⁻¹, which is about 170 times higher than that of commercial RuO₂ (0.005 s⁻¹) (Figure S9a). For HER at -0.1 V (vs. RHE), the TOF of BCCRO reached 0.51 s⁻¹, exceeding the value of commercial Pt/C (0.20 s⁻¹) by 2.6 times (Figure S9b). We also compared the mass activity (MA) of the catalysts at various potentials. As illustrated in Figure S10, BCCRO demonstrated the highest mass activity for both OER and HER. Specifically, at 1.55 V (vs. RHE) for OER, BCCRO showed a mass activity of 598.6 A g⁻¹, which is 37.4 times greater than that of commercial RuO₂ (16.0 A g⁻¹) (Figure S10a). For HER at -0.3 V (vs. RHE), the mass activity of BCCRO was 760.3 A g⁻¹, about 1.8 times higher than that of commercial Pt/C (424.1 A g⁻¹) (Figure S10b). As summarized in Figure 2g,h, these electrochemical analyses demonstrate the superior bifunctional performance of BCCRO over commercial benchmarks of RuO₂ and Pt/C. In addition, the performance of BCCRO was outstanding compared with other recently reported Co- or Ru-based perovskite oxides, as shown in Figure S11 and Tables S4 and S5.

Beyond high activity, long-term stability is critical for practical application. The stability of BCCRO was determined under 100 mA cm⁻² in a three-electrode system. Chronopotentiometric measurements (Figure S12) revealed negligible performance decay over 150 h of continuous operation, confirming its exceptional long-term stability. To assess its practical potential, a symmetric electrolyzer was assembled using BCCRO loaded on Ni foam (anode) and carbon paper (cathode) in 1.0 M KOH at 25°C. The electrolyzer delivered excellent OWS performance, requiring low cell voltages of only 1.50, 1.62, and 1.93 V to achieve current densities of 10, 100, and 1000 mA cm⁻², respectively (Figure 2i). As shown in Figure 2j and Table S6, BCCRO requires a lower cell voltage at 10 mA cm⁻² than many recently reported advanced OWS catalysts operating under the same alkaline conditions (1.0 M KOH). The long-term stability was evaluated under industrially relevant conditions. When maintained at a high current density of 1 A cm⁻² for 1000 h, the BCCRO||BCCRO system showed excellent stability with a voltage decay rate of only 29 μV h⁻¹ (Figure 2k). Given its exceptional durability, low operating voltages, and competitive performance, BCCRO represents a highly promising bifunctional catalyst for practical water splitting. To verify that the observed catalytic activity originates intrinsically from BCCRO, we evaluated the electrochemical performance of bare Ni foam (NF) and bare carbon paper (CP) under identical conditions. As shown in Figure S13, both bare supports exhibit negligible current densities within the operating potential window compared to the BCCRO-loaded electrodes.

These results confirm that the underlying supports function strictly as physical current collectors and do not contribute to the intrinsic catalytic activity.

The advantage of BCCRO is further highlighted by comparison with its single perovskite counterparts. While BaCoO₃-based materials show limited OER activity and poor stability [38], and BaRuO₃ exhibits only moderate HER performance [39], neither can achieve efficient OWS. In contrast, BCCRO demonstrates outstanding activity and stability for both OER and HER within a single phase, demonstrating the crucial synergistic interaction between Co and Ru sites.

2.3 | In Situ Spectroscopic Studies During OER

To elucidate the structural dynamics responsible for the high bifunctional activity of BCCRO, we conducted operando XAS studies. The X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions are exquisitely sensitive to oxidation states and local coordination environments, respectively, providing direct insight into the electronic and structural evolution of catalysts under working conditions [23, 35, 40–43].

The oxidation states in pristine BCCRO were first determined. The Co K-edge XANES spectrum in air exhibited an absorption edge energy closely matching that of the Sr₂Co³⁺IrO₆ reference, indicating a Co³⁺ state. Similarly, the Ru K-edge position aligned with the Sr₂GdRu⁵⁺O₆ standard, confirming a Ru⁵⁺ oxidation state (Figure 3a,b). Quantitative linear combination analysis (Figure 3c,d) indicated that upon immersion in electrolyte at open-circuit potential (OCP), the average oxidation states slightly changed to Co^{3.1+} and Ru^{4.95+}. Upon applying anodic potentials, the Co K-edge shifted progressively to higher energies (Figure 3a), showing a total shift of ~0.7 eV at 1.5 V relative to the OCP condition. This positive shift indicates the oxidation of Co³⁺ to Co⁴⁺. Quantitative analysis using reference compounds (Sr₂Co³⁺IrO₆ and BaCo⁴⁺O₃) estimated an average Co valence of +3.58 at 1.5 V (Figure 3c). Simultaneously, at 1.5 V, the Ru K-edge shifted up by 0.8 eV (Figure 3b), revealing an average Ru valence of +5.65 yielded by quantitative analysis (Figure 3d). It is worth noting that the formation of Ru⁶⁺ species has been rarely observed and reported under OER conditions [44]. XAS results demonstrate the concurrent formation of high-valent Co⁴⁺ and Ru⁶⁺ species during OER, which are identified as the real active sites in BCCRO. This is consistent with reports that high-valent Co and Ru centers are highly active for oxygen evolution [40]. These results capture the adaptive transformation of the BCCRO surface under OER conditions, as the catalyst undergoes a dynamic change to generate high-valent active sites in response to the applied potential. EXAFS provided further insight into the local coordination changes. The Fourier-transform EXAFS spectra for both Co and Ru exhibited a shift of the first-shell peak to higher R-space values with increasing potential (Figure 3e,f), indicating a contraction of the average metal-oxygen bond distance. Quantitative EXAFS fitting revealed that the Co–O bond distance shortened from 1.94 Å at OCP to 1.88 Å at 1.5 V, while the Ru–O bond decreased from 1.96 to 1.94 Å (Figure S14 and Table S7). This bond shortening enhances metal–oxygen covalency, which is known to facilitate OER kinetics [45].

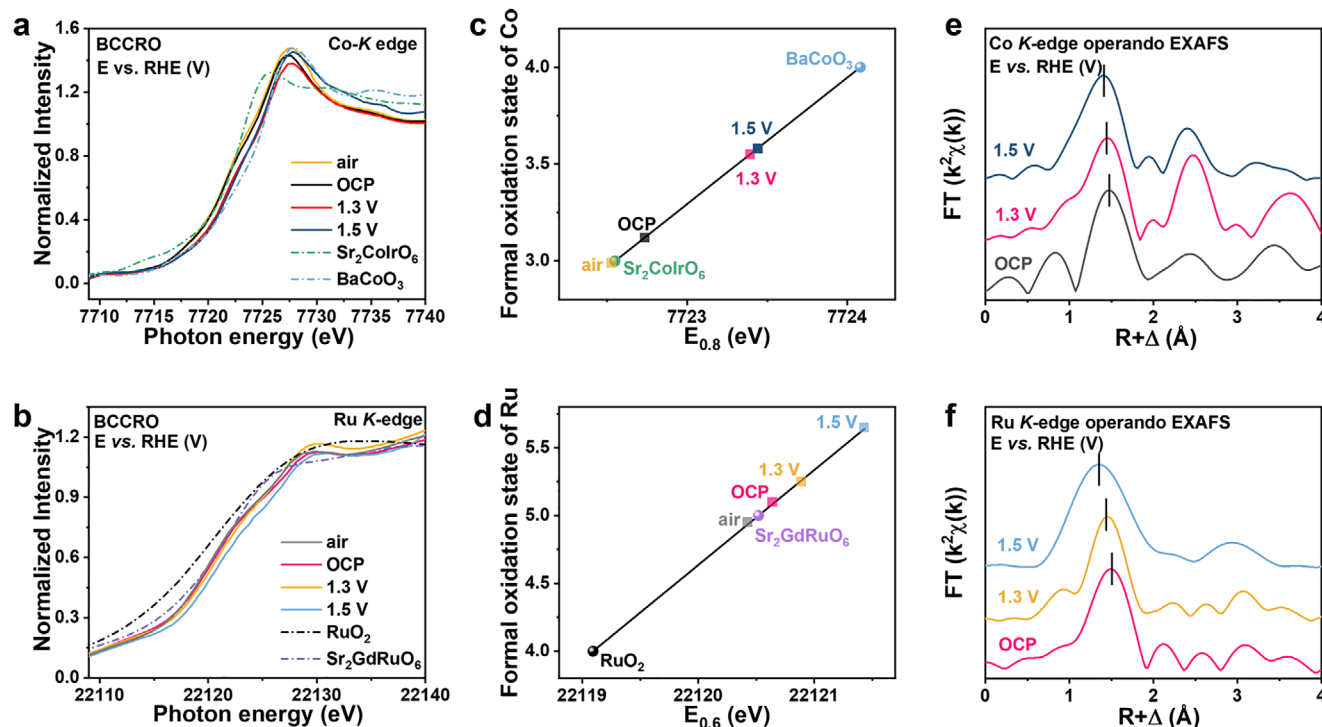


FIGURE 3 | In situ XAS spectra of BCCRO at different OER potentials. (a, b) Co K-edge and Ru K-edge XANES spectra of BCCRO at applied potentials; (c, d) oxidation states derived from a and b. (e, f) FT-EXAFS at the Co and Ru K-edge.

Subsequently, we employed in situ Raman spectroscopy to monitor surface transformations under operating conditions in 1.0 M KOH, as it is highly sensitive to crystal phases and chemical states [46]. As shown in Figure S15a, the spectrum of pristine BCCRO showed broad peaks at 454 and 660 cm⁻¹, characteristic of Co–O vibrations in the perovskite lattice. At an applied potential of 1.8 V, new peaks emerged at 468 and 588 cm⁻¹, which are characteristic of γ-CoOOH [46–49], indicating the in situ formation of high-valence Co species during OER. Distinct Ru-related features were not observed, likely due to their spectral overlap with the dominant Co–O vibrations. The surface reaction mechanism was further corroborated by in situ Fourier-transform infrared (FT-IR) spectroscopy (Figure S15b). An absorption band at 1243 cm⁻¹, attributed to the vibration of the adsorbed –OOH_{ad}* intermediate [50, 51], emerged at potentials ≥1.52 V, confirming the formation of this key OER intermediate.

The structural evolution of the catalyst under prolonged oxidative conditions was further probed by ex situ characterizations after 1000 h of continuous operation at 1 A cm⁻². Compared to the pristine sample, the XRD pattern of the post-OER catalyst (Figure S16) displays peak broadening and a reduced overall intensity, which indicates partial surface structural reconstruction.

HR-TEM revealed that the bulk crystallinity of the catalyst was largely preserved (Figure S17), displaying lattice fringes with slightly expanded d-spacings of 0.290 and 0.497 nm corresponding to the (110) and (100) planes of BCCRO, respectively. The corresponding SAED pattern retained all characteristic reflections of the 6H triple perovskite phase (Figure S18). Figure S19 shows the formation of an amorphous layer approximately 10 nm in thickness. This layer serves as the actual, highly active OER

region and physically accounts for the peak broadening observed in the XRD pattern. Furthermore, EDX elemental mapping confirmed that Ba, Co, and Ru remained uniformly distributed throughout the particles after OER (Figure S20).

Quantitative ICP-MS measurement precisely tracks the compositional changes during this structural reconstruction. Analysis of the post-OER electrode (Table S2) reveals extensive Ba leaching (decreasing from 50.36 at% in the pristine sample to 34.67 at%), while Co and Ru increase to 32.20 at% and 33.13 at%, respectively. Furthermore, absolute mass-loss analysis of the post-OER electrolyte (Table S8) confirms that while 48.53% of the initial Ba mass leaches out, the catalytically active transition metals exhibit exceptional solid-state retention, with mass losses of only 4.41% for Co and 1.64% for Ru. Collectively, these results definitively demonstrate that Ba leaching facilitates the surface amorphization and provides the charge compensation necessary to stabilize the high-valent Co⁴⁺ and Ru⁶⁺ states identified by operando XAS. The exceptional retention of these active Co/Ru metal sites underpins the catalyst's remarkable ability to maintain stable OER performance for 1000 h.

2.4 | In Situ Spectroscopic Studies During HER

Operando XAS uncovers a structural evolution pathway for BCCRO under HER conditions that is distinct from its behavior under OER. During cathodic polarization, the Co K-edge XANES spectra continuously shift to lower energies (Figure 4a). From OCP to –0.1 V, a total downshift of 2.23 eV is observed, accompanied by a gradual attenuation of the white-line intensity, both indicative of Co ion reduction. Correspondingly, in the EXAFS

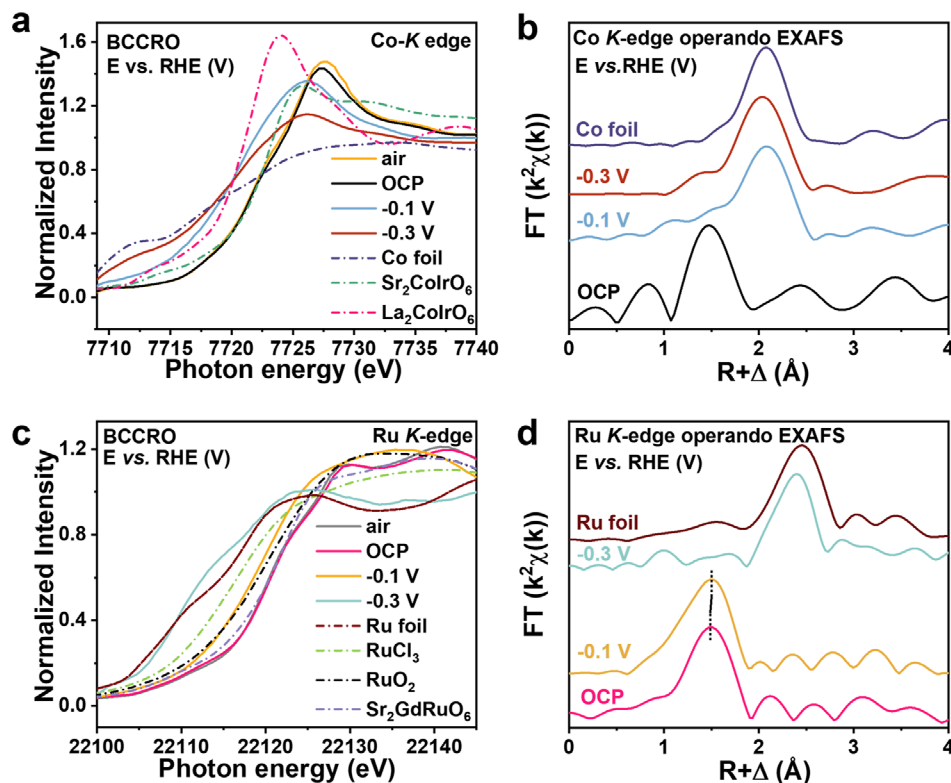


FIGURE 4 | In situ XAS spectra of BCCRO at different HER potentials. (a, c) Co K-edge and Ru K-edge XANES spectra of BCCRO at applied potentials; (b, d) FT-EXAFS at the Co and Ru K-edge.

spectra (Figure 4b), the Co–O coordination peak diminishes and vanishes at -0.1 V, while a new peak emerges near 2.0 Å. Quantitative fitting assigns this new feature to a metallic Co–Co bond (2.46 Å, Figure S21 and Table S7), confirming the complete reduction of Co ions to their metallic state.

In contrast to the rapid reduction of Co, the reduction of Ru proceeds more gradually. At -0.1 V, the Ru–K edge has shifted by 2.02 eV to lower energies (Figure 4c). EXAFS analysis at this potential reveals a lengthening of the Ru–O bond distance (Figure 4d), indicating a decrease in the Ru oxidation state. Quantitative fitting shows an increase in the Ru–O bond length from 1.96 to 1.97 Å (Figure S21 and Table S7). Upon further lowering the potential to -0.3 V, the absorption edge shifts more pronouncedly, with the spectrum becoming nearly identical to that of Ru foil (Figure 4c). The corresponding EXAFS spectrum reveals a new feature of Ru–Ru metallic bonding (Figure 4d) with a distance of 2.65 Å (Figure S21 and Table S7), demonstrating the formation of metallic Ru. This operando XAS study directly visualizes the adaptive transformation of BCCRO under cathodic conditions, where the catalyst dynamically reconstructs its surface into metallic CoRu nanoparticles in response to the reductive HER environment.

In situ Raman spectroscopy (Figure S22) captured the emergence of vibrational modes at 500 and 622 cm^{-1} at -0.055 V, characteristic of β -Co(OH)₂ [46, 52]. This suggests that Co³⁺ is first reduced to a β -Co(OH)₂ intermediate prior to its final metallization. The Raman peaks of β -Co(OH)₂ became weak at -0.09 V, and completely disappeared at -0.1 V, coinciding with the transformation into metallic Co species.

Moreover, HAADF-STEM images of BCCRO after 45 h HER (Figure S23) showed the formation of small nanoparticles. The corresponding elemental mapping indicated the leaching of Ba ions. Line-scan analysis across individual nanoparticles (Figure S24) confirms the distribution dominated by Co and Ru. To further elucidate the structural transformation, we performed bulk-sensitive ex situ characterizations on post-HER catalysts after 1000 h of continuous operation at 1 A cm^{-2} . XRD of the post-HER BCCRO (Figure S25) reveals only metallic diffraction peaks characteristic of a hexagonal close-packed (hcp) structure, confirming the complete transformation of the perovskite oxide into metallic phases. Concurrently, the SAED pattern of the post-HER catalyst (Figure S26a) exhibits diffraction rings that index perfectly to an hcp phase. TEM analysis indicates a significant reconstruction of the original perovskite into a multi-phase metallic structure (Figure S26b–d). HRTEM imaging identified lattice fringes with spacing of 0.208 , 0.215 , and 0.236 nm, corresponding to the (002) plane of CoRu alloy, the (100) plane of hexagonal Co metal, and the (100) plane of Ru metal, respectively. Elemental mapping exhibits a homogeneous distribution of Co and Ru within the resulting CoRu nanoparticles (Figure S27), giving a Co:Ru atomic ratio of $\sim 45.9:52.7$ and minimal Ba and O signals (Figures S27 and S28).

Quantitative ICP-MS analysis of the post-HER electrode after 1000 h (Table S2) shows that Ba is nearly completely leached (remaining only 0.69 at%), with Co and Ru accounting for 47.02 at% and 52.29 at%, respectively (Co:Ru $\approx 1:1.1$). Post-HER electrolyte analysis (Table S8) reveals Ba, Co, and Ru concentrations of 18.70 , 0.6403 , and 0.4450 ppm, corresponding to mass losses of 99.38% , 15.86% , and 6.43% , respectively. The near-complete loss of

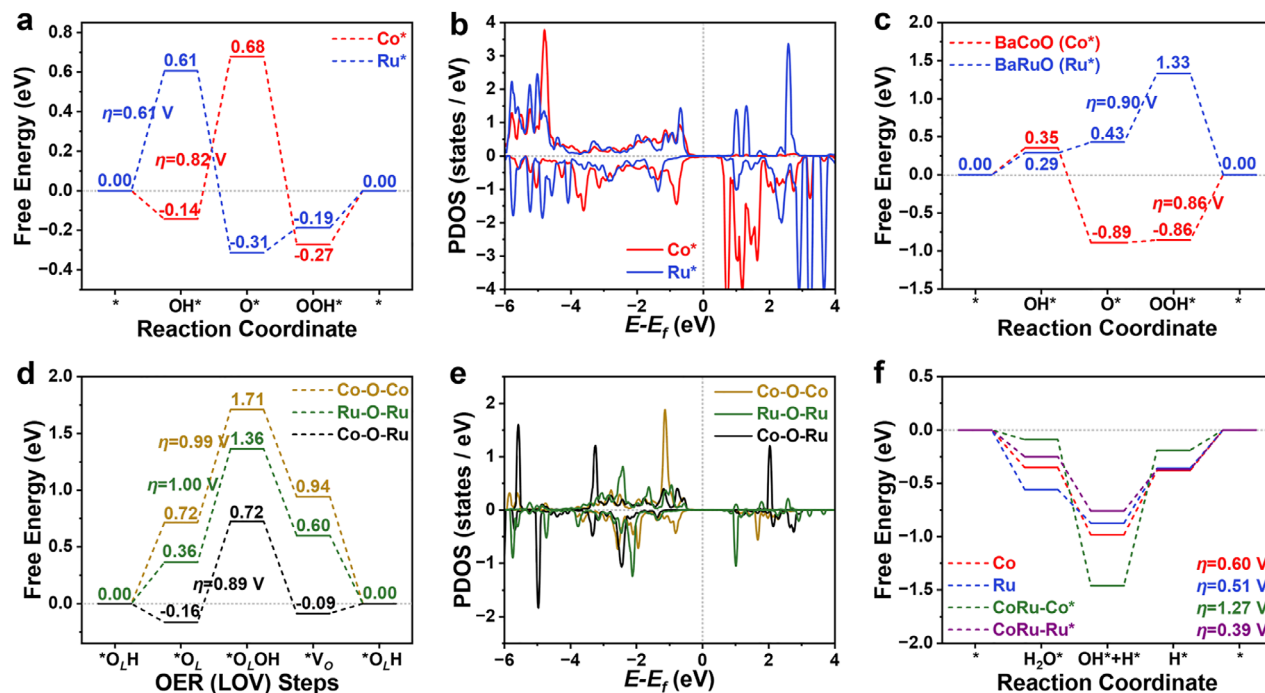


FIGURE 5 | DFT calculation results for BCCRO. (a) Calculated free energies of the OER intermediates in MAE. (b) pDOS of Co and Ru d states. (c) Calculated free energies of the OER intermediates on BaCo(3+)O and BaRu(5+)O. (d) Calculated free energies of the OER intermediates in LOV. (e) pDOS of O p_z states. (f) Calculated free energies of the HER intermediates.

Ba facilitates the reduction of Co^{3+} and Ru^{5+} , culminating in the formation of CoRu nanoparticles that serve as the active sites for HER.

2.5 | DFT Calculations to Elucidate Reaction Mechanisms

We further investigated the BCCRO-catalyzed OER and HER pathways using DFT calculations. The construction of the BCCRO slab is described in the Methods section. The most commonly reported OER mechanisms on metal oxides include the MAE [53–55], a canonical four-electron transfer pathway, and the lattice-oxygen-vacancy-site (LOV) [56, 57], which involves participation of lattice oxygen (Figure S29). For the MAE, both Co and Ru sites were evaluated as potential active centers. For the LOV, three distinct oxygen-bridging motifs were considered: Co–O–Co, Ru–O–Ru, and Co–O–Ru. The calculated energy profiles for each four-step reaction are shown in Figure 5a,d, and the corresponding intermediates are provided in Figure S30. All calculated potentials and overpotentials discussed here are referenced to the RHE scale. Therefore, within the computational hydrogen electrode (CHE)-based thermodynamic analysis, the reported limiting potentials/overpotentials do not explicitly depend on pH. Note that pH-dependent kinetic and interfacial effects are not considered in the present work.

For the MAE mechanism (Figure 5a), the theoretical overpotential is 0.61 V for the Ru active site (Ru^*), limited by the first step, and 0.82 V for the Co active site (Co^*), limited by the second step. This indicates that Ru^* is more active than Co^* within the MAE pathway. These calculations were performed using the oxidation states derived from operando XAS measurements under OER

conditions (approximately +3.58 for Co and +5.65 for Ru). The projected density of states (PDOS) for these sites is shown in Figure 5b. Ru^* exhibits a larger exchange (spin) splitting, whereas Co^* shows a smaller splitting; moreover, Co^* presents spin-down states near -0.9 eV, substantially closer to the Fermi level than those of Ru^* (≈ -1.5 eV). These features imply stronger adsorption on Co^* than on Ru^* (which stands for OH and OOH adsorption). In contrast, O adsorption is stronger on Ru^* , which we attribute to stabilization by a neighboring Ba^{2+} ion in the adsorption ensemble (Figure S30).

During surface relaxations, we observed geometries in which the oxygen in a Ba–O–Ru configuration sank slightly while the Ba shifted laterally toward the O^* bound on Ru, shortening the Ba... O^* separation without perturbing the primary Ru– O^* bond. We describe this as a spectator–cation effect: $\text{Ba}(2+)$, owing to its large ionic radius, provides through-space ionic stabilization of the negatively charged O^* , whereas Ru– O^* remains the chemically dominant interaction. Consistent with this interpretation, we did not find an analogous motif in our earlier $\text{Pb}_2\text{CoRuO}_7$ [40] or $\text{Ca}_2\text{CoRuO}_6$ [41] studies, where the smaller A-site cations disfavor such electrostatic stabilization.

To isolate the role of valence, we evaluated MAE pathways on BaCo(3+)O and BaRu(5+)O reference surfaces. As shown in Figure 5c, the calculated overpotentials are 0.86 and 0.90 V, respectively, both higher than on the Co(4+)/Ru(6+) surface. These comparisons establish that higher B-site oxidation states enhance OER performance in this family, yielding the activity order $\text{Ru}(6+) > \text{Co}(4+) > \text{Co}(3+) > \text{Ru}(5+)$. Notably, the Ba... O^* contact is absent on BaCo(3+)O and BaRu(5+)O but present on the Co(4+)/Ru(6+), suggesting that a high-valence electronic environment, together with vacancy-assisted lattice openness,

enables Ba to approach an O* already bound to Ru. This ensemble effect plays an important role in lowering the overpotential at Ru*.

For the LOV mechanism (Figure 5d), the three pathways exhibit similar trends: the overpotential is determined by the second step, and the intermediate with OH adsorbed on lattice oxygen has the highest free energy. Notably, Co–Ru synergy renders the black pathway in Figure 5d the most favorable, with the lowest intermediate free energies and an overpotential of 0.89 V.

In contrast to the strongest adsorption inferred from the reaction pathway, the total pDOS does not indicate that the Co–O–Ru motif binds most strongly; its oxygen p band center lies between those of Co–O–Co and Ru–O–Ru (Figure S31), suggesting only moderate adsorption. This implies that although the oxygen 2p-band position has rationalized OER activity in prior studies, it may be an unsuitable descriptor here. Because p_x and p_y primarily hybridize with metal d orbitals while adsorption interactions are dominated by p_z , we plotted a symmetry-resolved pDOS isolating p_z states. As shown in Figure 5e, Co–O–Ru displays p_z states closer to -0.7 eV, whereas Co–O–Co and Ru–O–Ru states are near -1.0 eV. We also observe that while the p_z states of Co–O–Co and Ru–O–Ru reside largely between -3 and -1 eV, those of Co–O–Ru are strongly split. A larger p–d splitting pushes the antibonding O–2p peak well above the Fermi level (i.e., the ~ 2 eV states), reducing the occupied O–2p weight near the Fermi energy and thereby strengthening adsorption. We attribute this to asymmetric p–d hybridization induced by hetero–bimetal synergy. Such synergy not only enlarges the bonding–antibonding splitting but also affords flexible charge compensation during adsorption—effects not captured by the total pDOS alone.

Overall, although Co–Ru synergy lowers the overpotential of the LOV pathway to 0.89 V, BCCRO's OER performance is dominated by the MAE pathway at Ru* (0.61 V). We attribute this to Ba...O* spectator–cation stabilization, enabled by Ba's large ionic radius and the vacancy-induced surface openness associated with high Co/Ru valence.

For HER, given the experimentally observed metallic Co and Ru, DFT calculations were performed on a CoRu bimetallic alloy using the typical alkaline mechanism. Both Co* and Ru* active sites were evaluated and compared against HER on pure metallic Co and Ru. As shown in Figure 5f, all pathways display the same trend, where all intermediates lie below zero free energy, indicating strong adsorption. The overpotential is determined by the third step, that is, OH* desorption. Relative to the pure metals, Co–Ru synergy markedly weakens OH adsorption, thereby reducing the overpotential to 0.39 V.

3 | Conclusion

In summary, we have developed a novel self-adaptive 6H triple perovskite oxide, BCCRO, as a highly efficient and robust single-phase bifunctional catalyst for OWS. It achieves low overpotentials of 32 mV for HER and 178 mV for OER at 10 mA cm^{-2} , while achieving practical cell voltages of 1.50 V at 10 mA cm^{-2} and 1.93 V at 1 A cm^{-2} , coupled with exceptional long-term stability demonstrated by steady operation for over

1000 h at the ampere-level current density (1 A cm^{-2}). In situ XAS studies directly capture its adaptive surface transformation under operational conditions: during OER, the oxidation of Co³⁺ and Ru⁵⁺ induces the formation of high-valent Co⁴⁺ and Ru⁶⁺ species while retaining the bulk perovskite structure; during HER, these ions undergo sequential reduction to form metallic CoRu nanoparticles. DFT calculations reveal that the synergistic interaction between Co⁴⁺ and Ru⁶⁺ drives efficient OER via a Ba²⁺ spectator–cation effect, while the metallic CoRu nanoparticles facilitate optimal hydrogen adsorption/desorption kinetics for HER. This work establishes a new design paradigm for single-phase oxide catalysts, demonstrating that targeted element-specific structural evolution under operational conditions can simultaneously deliver industrial-grade activity and durability, thereby overcoming the long-standing challenge of developing efficient, integrated catalysts for overall water splitting.

Author Contributions

Wenlong Sun: writing – original draft, investigation, validation, visualization, data curation, & methodology. **Chao Jing:** conceptualization, funding acquisition, investigation, writing – review & editing, methodology, project administration, formal analysis, supervision, & resources. **Shengjie Zhang:** writing – original draft, data curation, & validation. **Hao Zhang:** conceptualization, methodology, validation, & writing – review & editing. **Haoyu Zheng:** conceptualization & resources. **Changqing Jin:** conceptualization & resources. **Chengzhe Ni:** resources. **Jianfa Zhao:** conceptualization, investigation, writing – review & editing, methodology, validation, project administration, supervision, & resources. **Zhiwei Hu:** resources, supervision, data curation, formal analysis, project administration, visualization, validation, methodology, writing – review & editing, conceptualization, & investigation. **Linjuan Zhang:** conceptualization, investigation, funding acquisition, writing – review & editing, resources, supervision, data curation, project administration, formal analysis, & methodology.

Acknowledgments

This work was supported by the Strategic Priority Research Program of the Chinese Academy of Sciences (No. XDA0400000), the Fundamental Research Program of Industrial Foundation (SINAP–CYJJ–202502), the National Key Research and Development Program of China (No. 2024YFF0506300, 2022YFA1403800), the National Natural Science Foundation of China (W2441008, U24A20542, 12204515), the Photon Science Center for Carbon Neutrality, and the Talent Plan of Shanghai Branch, Chinese Academy of Sciences (CASSHB–QNP–2023–006), the Youth Innovation Promotion Association, Chinese Academy of Sciences (2023270). The authors acknowledge support from the Max Planck POSTECH/Hsinchu Center for Complex Phase Materials.

Conflicts of Interest

The authors declare no conflicts 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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Supporting Information

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