

Synergistic Long-Range Interaction of Co-Cu Dual-Atom Sites on Hollow CeO₂ Nanostructures for Bifunctional Oxygen Electrocatalysis

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The rational design of nonprecious bifunctional electrocatalysts for oxygen evolution/reduction reactions (OER/ORR) is critical yet challenging for sustainable energy systems. While long-range synergistic (LRS) effects, governed by spatial arrangements and electronic coupling of active sites, critically influence metal coordination environments and orbital overlap for optimized intermediate adsorption, their fundamental mechanisms remain elusive. Herein, Co-Cu dual-atom sites within CeO₂ hollow spheres (CoCu@CeO₂) via an effective electrostatic adsorption strategy are anchored. The catalyst demonstrates low OER overpotential (235 mV @10 mA cm⁻²) and superior ORR activity (0.878 V vs RHE for half-wave potential), surpassing most reported bifunctional systems. Mechanistic investigations reveal distinct reaction pathways: the OER predominantly occurs at Co sites, while Cu sites preferentially facilitate the ORR. Crucially, density functional theory calculations further demonstrate that LRS induces interfacial electron redistribution and modulates *d*-band centers, thereby optimizing the binding energies of key intermediates. This work proposes a novel mechanism for engineering dual-atom architectures through long-range electronic interactions, providing valuable insights into the advancement of advanced electrocatalysts for sustainable energy conversion systems.

still limited by the inherently sluggish kinetics of multielectron transfer. The development of advanced electrocatalysts capable of simultaneously lowering energy barriers for both OER and ORR is a critical pathway to maximize the overall power output efficiency of these devices.^[3,4] Hitherto, iridium/ruthenium- and platinum-group catalysts are still the commonly used OER and ORR catalysts.^[5,6] Nevertheless, their widespread deployment faces limitations arising from geological scarcity, prohibitive costs, and insufficient durability.^[7] Consequently, the development of catalysts with abundant terrestrial reserves and significant economic advantages as substitutes for precious metals has become a key research focus over the past few decades.

Single-atom catalysts (SACs) with well-defined coordination structures have garnered considerable research interest owing to their maximized metal atom utilization efficiency and distinctive electronic configurations.^[8] Nevertheless, the isolated monometallic active sites in SACs limit their capacity to catalyze complex

1. Introduction

As pivotal processes in sustainable energy conversion systems, electrochemical oxygen evolution and oxygen reduction reactions (OER/ORR) play a particularly significant role in metal–air battery technologies.^[1,2] However, their practical implementation is

multistep reaction pathways, particularly for coupled processes, such as OER/ORR, which require distinct active centers for different intermediates.^[9] This inherent limitation has driven the exploration of dual-atom catalysts (DACs), which provide superior catalytic versatility via bimetallic site cooperativity.^[10,11] Carbon materials, renowned for their high conductivity and extensive surface area, are widely considered normal supports for DACs in electrocatalytic applications.^[12–14] However, carbon-supported DACs are prone to carbon degradation or corrosion during electrocatalysis, particularly under high-current conditions.^[15] Metal oxide nanomaterials typically serve as important catalyst supports in heterogeneous catalysis, causing their controllable synthesis with different exposed crystal facets, abundant oxygen vacancies, and strong electronic interaction with metals.^[16–19] As a pivotal 4f oxide, CeO₂ is considered a commonly employed support for atomic metal active sites, especially for noble metal atoms, owing to its capability to anchor and stabilize single metal atoms by forming bonds with surface O/OH groups or through substitution at Ce sites.^[20,21]

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The simultaneous presence of two active metal centers in dual-atom catalysts leads to the occurrence of specific interactions between active sites. Such interactions, referred to as long-range synergistic (LRS), play an important role in determining the rate and selectivity of a reaction.^[22] The optimal combination of metal centers must be determined to achieve the targeted efficiency. The catalytic efficiency of DACs is largely associated with the LRS between the two metallic centers.^[23] The LRS effect in heterogeneous catalysis fundamentally arises from the electronic coupling between spatially separated active centers in DACs, where the catalytic performance is directly dictated by the strength and nature of these interatomic interactions.^[24] Central to LRS is the precise intermetallic distance, which governs both the spatial arrangement of active sites and their electronic transmission pathways. This geometric parameter not only profoundly influences the local coordination environment of metal centers but also determines the orbital overlap conditions critical for optimizing adsorption geometries and charge transfer kinetics. By strategically adjusting the atomic spacing, the spatial complementarity of reactant adsorption sites can be systematically engineered, and electron transport characteristics can be effectively modulated, thereby enabling precise control over catalytic behavior. Recent progress in oxide-supported DACs, especially CeO₂-based systems, has demonstrated significant catalytic improvements attributed to LRS effects.^[25] Nevertheless, the underlying fundamental mechanisms of these long-range electronic correlations remain poorly understood. Elucidating the intricate relationship among bimetallic center distance, electronic compatibility, and catalytic synergy represents not only a critical challenge but also a key design principle for the development of next-generation targeted catalysts.

In this study, we strategically engineered atomically dispersed cobalt-copper diatomic pairs anchored on CeO₂ hollow nanostructures to systematically investigate the interplay among coordination architecture, metal-support interactions, and their collective influence on OER/ORR. This approach exploits the principle of strong electrostatic adsorption, wherein charged metal precursors are selectively immobilized on oppositely charged oxide surfaces through precise pH control relative to the support's point of zero charge. The dual-metal centers were precisely integrated via a strongly controlled electrostatic adsorption strategy, ensuring optimal spatial distribution and electronic coupling between Co and Cu species. The resultant CoCu@CeO₂ DACs exhibited exceptional bifunctional performance, achieving a remarkably low OER overpotential of 235 mV at 10 mA cm⁻² and an outstanding ORR half-wave potential of 0.878 V in alkaline media, with a record-low OER/ORR potential gap ($\Delta E = 0.633$ V). When incorporated into a practical zinc-air battery (ZAB), CoCu@CeO₂ also exhibits good activity and stability superior to commercial Pt/C, thereby highlighting its potential for advanced energy conversion technologies. The volcano plot revealed that the LRS effect between spatially separated Co and Cu centers can effectively modulate both the electronic structure and coordination environments. The comprehensive theoretical analysis demonstrated that the CoCu diatomic pair, with an interatomic distance of 4.341 Å, exhibits appropriate long-range synergy, thereby forming an optimized transition metal *d*-band center and enabling suitable adsorption/desorption energies for oxygen-

containing intermediates. This effectively enhances the kinetics of OER/ORR.

2. Results and Discussion

2.1. Fabrication and Characterization

As schematically depicted in **Figure 1a**, the CoCu@CeO₂ catalyst was synthesized by the strong electrostatic adsorption and thermal anchoring steps. Specifically, the CeO₂ hollow nanospheres with a high surface roughness were prepared by utilizing carbon spheres as sacrificial templates.^[26] Subsequently, by adjusting the solution pH value to 12.0, the surface of the CeO₂ hollow nanosphere was endowed with a negatively charged (Figure S1, Supporting Information), which provided a favorable environment for the adsorption of Co/Cu cations.^[27] Then, the CoCu-precursor atomic thin layer with a dense and uniform distribution at the CeO₂ surface was rapidly formed through the strong electrostatic attraction effect (CoCu precursor@CeO₂).^[28] Eventually, the coated Co/Cu atoms were embedded into the CeO₂ lattice through thermal reduction, forming the CeO₂-supported CoCu dual-atom catalyst (CoCu@CeO₂).^[29] The electronic metal-support interaction provided a guarantee for the formation of uniform, dense, and stable bimetallic active sites, endowing CoCu@CeO₂ with excellent electrocatalytic performance. Additionally, the stability of the proposed structures was preliminarily appraised by calculating the formation energies (E_f) of all possible atomic configurations. The calculation results show that Co and Cu single atoms have lower formation energies on the (220) crystal plane of CeO₂. Therefore, dual atoms tend to be embedded in the (220) crystal plane of CeO₂ (Figures S2 and S3, Supporting Information). For dual atom catalysts where metal atoms were not directly bonded, the distance between two heteronuclear atoms has a pivotal impact on the selectivity and activity.^[30] Figure 1b shows all considered atomic configurations. For the CoCu dual atoms catalyst, three possible configurations based on the variation of distance between cobalt and copper atoms were represented as D1-CoCu@CeO₂, D2-CoCu@CeO₂, and D3-CoCu@CeO₂. From D1 to D3, it represents an increase in the distance between Co and Cu atoms. If the atomic distance continues to increase (similar to uniformly dispersed and completely isolated single atoms), the electronic interactions between cobalt and copper will weaken, leading to a decrease in their promoting effect on electrocatalytic reactions.^[31] All the possible structures were found to be thermodynamically stable and experimentally feasible, as revealed by their respective negative E_f values (Figure 1c).

Scanning electron microscopy (SEM) images demonstrated that the formed CoCu@CeO₂ exhibits a spherical structure, which perfectly retained the original morphology and size of the carbon templates (Figures 2a and S4, Supporting Information). The CoCu@CeO₂ nanospheres presented a rough surface and an average sphere diameter of ≈ 200 nm (inset Figure 2a). The Co@CeO₂, Cu@CeO₂, and CeO₂ samples had an analogous morphology to CoCu@CeO₂ (Figure 2b and Figures S5–S7, Supporting Information), which presented a hollow spherical structure with a diameter of ≈ 200 nm. The hollow architecture of the catalyst provided abundant active sites, shortened mass/charge transport distances, and enlarged catalyst-electrolyte interface contact

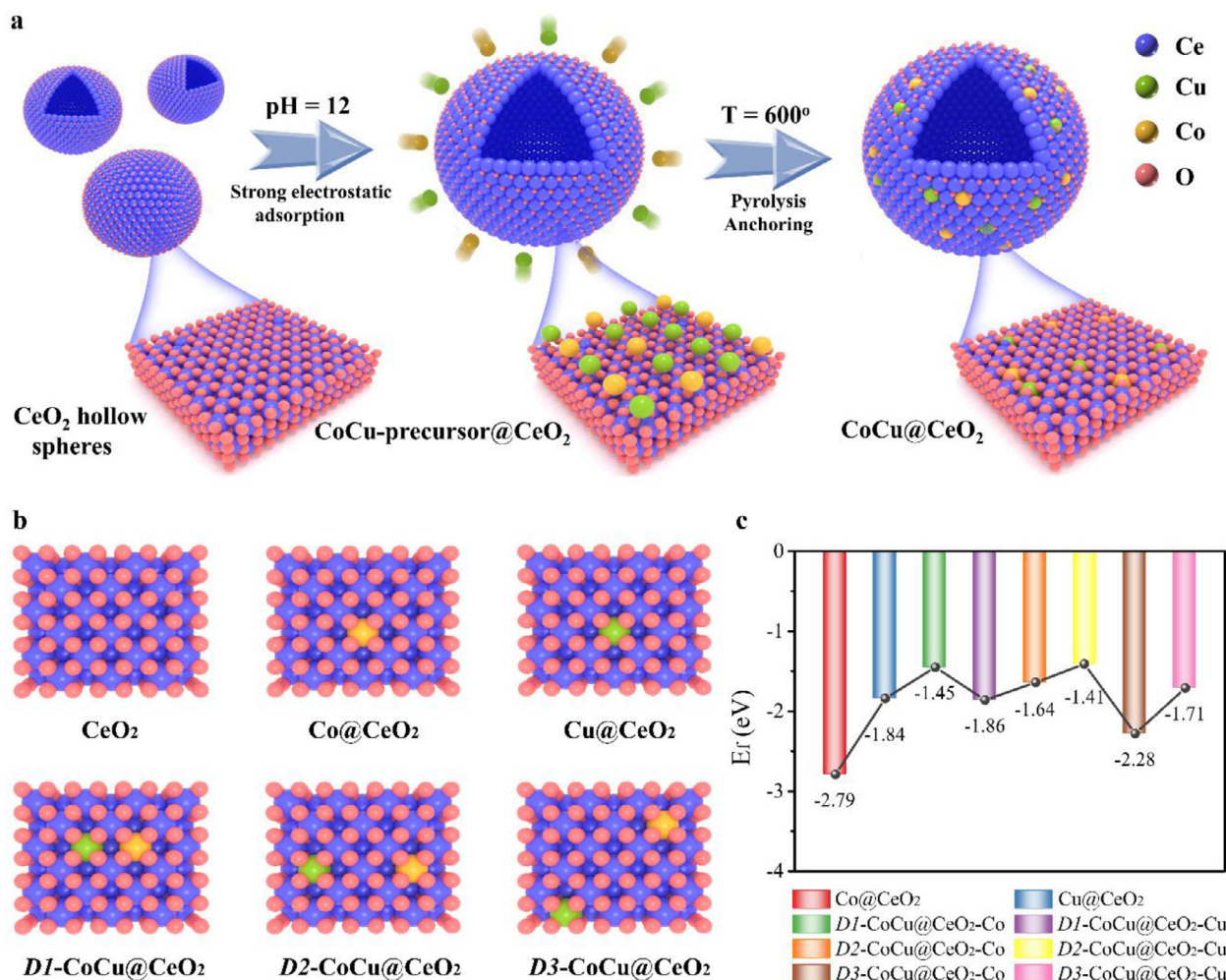


Figure 1. a) The illustration of the synthetic strategy for CoCu@CeO_2 . b) The constructed DFT models of proposed catalysts in the (220) crystal plane of CeO_2 (top view). c) The formation energy (E_f) of the corresponding catalysts in (b).

area. The nanosized shell thickness enabled the materials with good permeation, reduced diffusion resistance, and improved accessibility. Further, the high magnification TEM image (HRTEM) of the CoCu@CeO_2 in Figure 2c appeared obvious lattice fringes with the d -spacing of 0.191 and 0.312 nm, which were assigned to the (220) and (111) planes of CeO_2 , respectively. Moreover, no conspicuous metal nanoparticles were found on CeO_2 , implying that the metals might be at the atomic level. From the dark-field TEM images of CoCu@CeO_2 in Figure 2d, the thickness of the hollow sphere was about 31 nm. Energy-dispersive X-ray spectroscopy (EDS) mapping images of the CoCu@CeO_2 (Figure 2e) corroborated the homogeneous distribution of Co, Cu, Ce, and O elements spread over the surface of the catalyst. The atomic-scale chemical imaging via electron energy loss spectroscopy (EELS) mapping was further adopted to validate the existence of Co and Cu species on ceria with dual atoms rather than clusters (Figure S8, Supporting Information). Due to the lower atomic numbers of cobalt and copper compared to cerium, the smaller and darker dots under dark field conditions represented cobalt or copper single atoms (marked by circles in Figure 2f). In addition, three distribution configurations of CoCu dual-atoms

(marked with rectangles) were observed in the CoCu@CeO_2 catalyst, which was certified by linear intensity profile analysis as well as the corresponding TEM and simulated linear intensity profile (Figures 2g–i). The distances between Co and Cu atoms in the $D1\text{-CoCu@CeO}_2$, $D2\text{-CoCu@CeO}_2$, and $D3\text{-CoCu@CeO}_2$ structures were 4.341, 7.554, and 8.615 Å, respectively. Meanwhile, the experimental values of the distance between Co and Cu atoms matched well with the calculated ones. The morphology characterizations delineated that CoCu dual atoms were uniformly embedded in the CeO_2 (220) lattice, indicating the successful synthesis of the hollow CoCu@CeO_2 catalyst.

The X-ray diffraction (XRD) pattern (Figure S9a, Supporting Information) showed that the phases of CoCu@CeO_2 , Co@CeO_2 , and Cu@CeO_2 were consistent with pure CeO_2 (PDF #34-0394). Additionally, there are no other discernible sharp peaks that appear in the XRD results of the CoCu@CeO_2 , indicating that there are no other crystalline Co and Cu-based nanoparticles or oxides formed.^[32] Furthermore, in the Raman peaks of CoCu@CeO_2 and the comparative samples, the fluorite F_{2g} symmetry mode (464 cm^{-1}) and defect-induced mode (596 cm^{-1}) were found, which corresponded to the characteristic

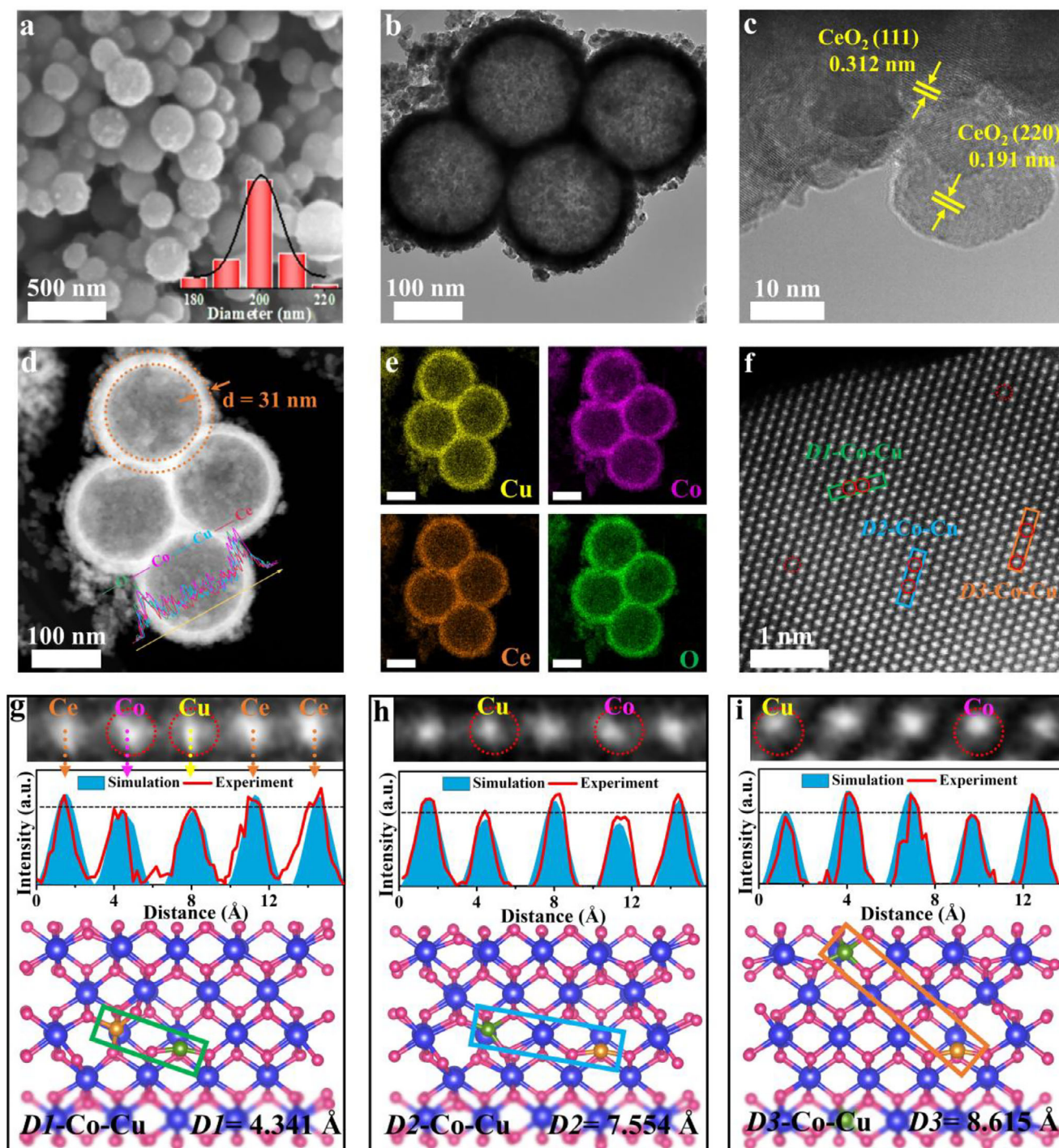


Figure 2. Morphology characterization of CoCu@CeO₂. a) SEM images. Inset of (a): diameter distribution of CoCu@CeO₂ nanospheres. b–d) TEM, HRTEM, and HAADF-STEM images of CoCu@CeO₂. Inset (d): The EDS line scanning of hollow CoCu@CeO₂ nanospheres. e) Corresponding element mapping of CoCu@CeO₂. Scale bar: 100 nm. f) AC HAADF-STEM image of CoCu@CeO₂. Single atoms are marked with circles. Double atoms with different atomic distances are marked with rectangles. g–i) The top parts are the CoCu diatoms with different atomic distances within the rectangles of Figure 2f (the relatively smaller and darker spots are Co/Cu). The experimental and simulated intensity profiles of D1-CoCu@CeO₂, D2-CoCu@CeO₂, and D3-CoCu@CeO₂ (in the middle part). The bottom parts are the corresponding DFT calculation models and the distances between the Co and Cu dual atoms. Blue, orange, green, and pink balls represent Ce, Co, Cu, and O atoms, respectively.

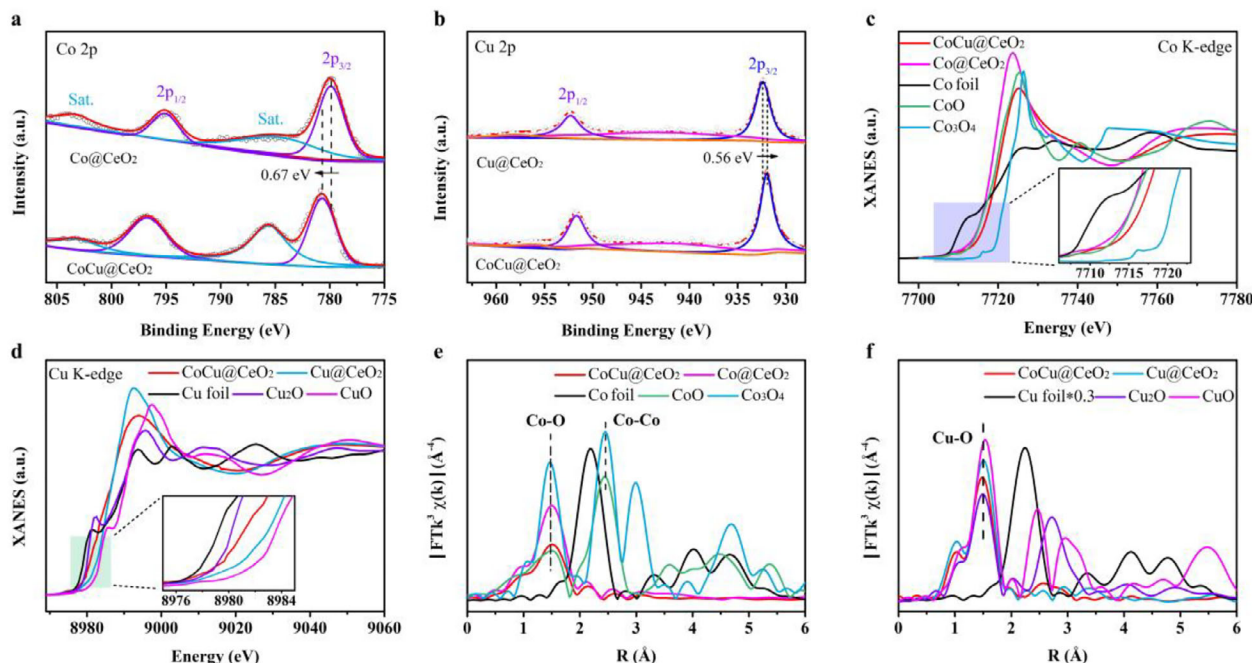


Figure 3. Characterization of the CoCu@CeO₂ catalyst. XPS spectra for a) Co 2p and b) Cu 2p. c) Co K-edge XANES spectra (inset shows the magnified corresponding near-edge region) and e) Co K-edge Fourier transform of the EXAFS spectra of CoCu@CeO₂, Co@CeO₂, Co foil, CoO, and Co₃O₄. d) Cu K-edge XANES spectra (inset shows the magnified corresponding near-edge region) and f) Cu K-edge Fourier transform of the EXAFS spectra of CoCu@CeO₂, Cu@CeO₂, Cu foil, Cu₂O, and CuO.

peaks of CeO₂ (Figure S9b, Supporting Information).^[33] The electron paramagnetic resonance spectroscopy of the unpaired electrons could be detected at $g = 2.003$, and the signal intensity was proportional to the number of oxygen vacancies (Figure S9c, Supporting Information).^[34] The slightly increased oxygen vacancies on CoCu@CeO₂ could be ascribed to stronger metal-support interactions than those of Co@CeO₂ and Cu@CeO₂.^[35] The specific surface area and the distribution of the pore size were measured by the N₂ adsorption/desorption isotherm (Figure S10 and Table S1, Supporting Information). The CoCu@CeO₂ had a similar Brunauer-Emmett-Teller (BET) surface area and pore size distribution to Co@CeO₂ and Cu@CeO₂, which was slightly smaller than that of CeO₂. Meanwhile, the pore volume also exhibited the same trend of change. Indeed, the lower BET surface area and decreased pore volume of CoCu@CeO₂ were due to the addition of metal atoms.^[36] Temperature-programmed reduction profiles were performed to characterize the reducibility of the catalyst. Compared to the electrostatically adsorbed monometallic Co and Cu atoms, the peaks of coadsorbed CoCu diatomic shifted to higher temperatures (Figure S11, Supporting Information), declaring a stronger synergistic interaction between the CoCu dual-atoms and the CeO₂ support.^[37]

Additionally, an X-ray photoelectron spectroscopy (XPS) survey spectrum was performed to detect the surface chemical states of the elements on CoCu@CeO₂ (Figure S12, Supporting Information). For the CoCu@CeO₂ catalyst, the Co 2p_{3/2} and Co 2p_{1/2} peaks are at 780.8 and 796.7 eV, which are situated between Co³⁺ 2p_{3/2} and Co²⁺ 2p_{3/2} (780.2 and 781.8 eV) and Co³⁺ 2p_{1/2} and Co²⁺ 2p_{1/2} (795.6 and 797.5 eV), suggesting the ionic Co^{δ+} ($0 < \delta < 3$) nature of cobalt in CoCu@CeO₂ (Figures 3a and S13a,

Supporting Information).^[38] Similarly, the Cu 2p XPS spectra of CoCu@CeO₂ (Figure 3b and Figure S13b, Supporting Information) show the binding energy value of 932.4 and 952.4 eV (between 932.2 and 933.6 eV (Cu⁺ 2p_{3/2}) and Cu²⁺ 2p_{3/2}) and 952.0 and 955.2 eV (Cu⁺ 2p_{1/2} and Cu²⁺ 2p_{1/2})), implying the low valance state of Cu^{δ+} ($1 < \delta < 2$).^[39] Compared with Co@CeO₂ and Cu@CeO₂, the peak positions of Co 2p (positive shift about 0.67 eV) and Cu 2p (negative shift about 0.56 eV) in CoCu@CeO₂ had changed, providing supportive evidence for surface charge rearrangement and electronic interactions in the catalyst.^[40,41] Notably, the positions of the Ce 3d peaks gradually moving toward low binding energy follow the sequence of Co@CeO₂, Cu@CeO₂, and CoCu@CeO₂, which was evident as a stronger interaction between dual atoms and support (Figure S14, Supporting Information).^[42] The high-resolution peaks for O 1s are shown in Figure S15 (Supporting Information). XPS results substantiated the existence of electron transfer and strong interaction between the metal species and the support interface.^[43] Besides, inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis further confirmed Co and Cu content of about 1.0 and 1.8 wt% in CoCu@CeO₂, basically matching with the XPS result.

To investigate the chemical state and coordination environment of Co and Cu atoms in the CoCu@CeO₂, the X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure measurements (EXAFS) were implemented.^[44] The XANES spectrum (Figure 3c) of the Co K-edge indicated that the absorption edge of Co atoms in CoCu@CeO₂ was between those of CoO and Co₃O₄, suggesting that the Co atoms predominantly exist between +2 and +3 valence states.^[45] The

correlation between the Co oxidation state and the energy position of the XANES spectrum, determined as the first maximum of the first derivative spectrum of CoCu@CeO₂ and different Co reference compounds (Figure S16a,b, Supporting Information).^[46] The linear fitting of the Co K-edge energy in XANES spectra revealed an average Co oxidation state of +2.25 in CoCu@CeO₂, higher than that in CoO (+2.00), suggesting that microenvironmental changes influence charge distribution. Notably, the observed increase in Co oxidation state (from +1.86 in Co@CeO₂ to +2.25 in CoCu@CeO₂) demonstrated that the coupling of Cu atom effectively modulated the electronic environment of the Co centers, highlighting a synergistic interaction between single-atomic Cu and Co sites.^[47] In addition, from the EXAFS spectra in Figure 3e, an apparent peak at 1.50 Å could be observed for both CoCu@CeO₂, Co@CeO₂, and Co₃O₄, which was typically assigned to the Co—O bond, elucidating the definite Co—O coordination environment in CoCu@CeO₂.^[48] However, no predominant peaks ascribed to Co—Co bonds from the CoO and Co₃O₄ are observed. This implies that the Co species are not in the form of small CoO_x clusters. The lack of Co—Co scattering at ≈2.5 Å is probably due to the sole existence of Co single atoms (Figure S17a, Supporting Information). Similarly, the Cu K-edge XANES adsorption edge position of CoCu@CeO₂ (Figure 3d) suggested the average valence of Cu between Cu₂O (Cu⁺) and CuO (Cu²⁺).^[49] By comparing the XANES spectra and the first derivative of Cu K-edge energy, the average valence state of Cu atoms in CoCu@CeO₂ could be assigned as 1.16 (Figure S16c,d, Supporting Information). Compared to Cu@CeO₂, the negative shift of the XANES edge presented the reduction valence state of Cu in CuCo@CeO₂ (from +1.66 in Cu@CeO₂ to +1.16 in CoCu@CeO₂). The XANES results were consistent with those of XPS data, indicating an electron transfer from Co to Cu. As displayed in Figure 3f, the Cu K-edge FT-EXAFS spectrum of CoCu@CeO₂ possessed a predominant peak at 1.50 Å, which belonged to Cu—O coordination.^[50] No high-shell Cu—Cu bond (in CuO and Cu₂O) coordination at 2.51 and 2.75 Å was observed, demonstrating the atomic Cu on the CeO₂ matrix (Figure S17b, Supporting Information). Further, the quantitative EXAFS fitting is studied to authenticate the local coordination configuration of Co and Cu in Co foil, Cu foil, Co@CeO₂, Cu@CeO₂, and CoCu@CeO₂ (Figures S18–S20, Supporting Information). The fitting results revealed that the coordination configurations of Co@CeO₂, Cu@CeO₂, and CoCu@CeO₂ are the Co—O and Cu—O moieties, respectively. The fitting results show that Co and Cu only have a unitary coordination configuration (no metal–metal coordination). The fitting values of structural parameters are listed in Tables S2 and S3 (Supporting Information). Therefore, the lack of prominent metallic peaks corresponding to Co—Co and Cu—Cu coordination in CoCu@CeO₂ indicates that the Co and Cu species are present in an atomically dispersed form.^[51]

2.2. Electrocatalysis for OER

The OER performance of CoCu@CeO₂ was evaluated in 1.0 M KOH on a standard three-electrode system. In Figure 4a, the CoCu@CeO₂ attained a current density of 10 mA cm^{−2} at a low overpotential of 235 mV, outperforming RuO₂ (255 mV),

Co@CeO₂ (305 mV), Cu@CeO₂ (335 mV), and CeO₂ (470 mV), respectively. For the Tafel slope derived from the LSV curves (Figure 4b), the lower value of CoCu@CeO₂ manifested that it had more favorable reaction kinetics.^[52] Comparing the overpotentials (η) at different current densities of these samples, results showed that the CoCu@CeO₂ possessed the potential for industrialization and commercialization (Figure 4c). A well-fitted electrochemical impedance spectroscopy (EIS) curve in Figure 4d further revealed that CoCu@CeO₂ had the smallest charge transfer resistance (R_{ct}) and the most favorable OER kinetics.^[53] The double-layer capacity (C_{dl}), obtained from the cyclic voltammetry tests in the non-Faraday region (Figure S21, Supporting Information), was a measure of the electrochemically active surface area (ECSA). The calculation results in Figure 4e gave a C_{dl} value of 14.9 mF cm^{−2} for CoCu@CeO₂ and smaller values of 4.5, 4.2, and 2.8 mF cm^{−2} for Co@CeO₂, Cu@CeO₂, and CeO₂, respectively. The corresponding ECSAs for different catalysts are shown in Table S4 (Supporting Information). By comparison, the CoCu@CeO₂ had the largest ECSA, proclaiming that it provided more active sites during the reaction.^[54] Furthermore, the relative double-layer capacity-normalized LSV curves displayed the optimal overpotential of CoCu@CeO₂, indicating its better intrinsic OER activity (Figure S22, Supporting Information).^[55] Additionally, CoCu@CeO₂ exhibited a TOF value of 10.21 s^{−1} per Co/Cu atoms at 300 mV in 1.0 M KOH (Figure 4f), about 10 times larger than that of Co@CeO₂ (1.03 s^{−1} per Co atom) and 24 times larger than that of Cu@CeO₂ (0.43 s^{−1} per Cu atom), respectively. Moreover, chronopotentiometry and cyclic voltammetry tests were evaluated to characterize the stability of catalysts (Figure 4g). After a 200 h stability test in 1.0 M KOH, the potential decay rate was about 5%. Meanwhile, after 5000 cycles of accelerated testing, the CoCu@CeO₂ revealed no obvious change, which suggested that the CoCu@CeO₂ had good OER stability. As shown in Tables S5 and S6 (Supporting Information), the metal contents of Co and Cu in the CoCu@CeO₂ catalyst after the durability test are comparable to their fresh values, which indicates only a minor amount of metal dissolved into the electrolyte. According to the ICP results of Co and Cu contents before and after CV activation, the corresponding TOF values were calculated and compared. The activity of the catalyst and the number of active sites is maintained well before and after OER (Figure S23, Supporting Information). The Faradaic efficiency of CoCu@CeO₂ for oxygen evolution was quantified at 99% during integrated water electrolysis, employing a volumetric gas quantification setup that monitored gas products from the anode compartment (Figure 4h). Notably, the radar chart in Figure 4i manifested that compared to other nonprecious metal DACs, CoCu@CeO₂ had a significant advantage in comprehensive performance.

2.3. Electrocatalysis for ORR

Electrochemical evaluation of ORR activities for CoCu@CeO₂ and control groups was conducted using a rotating ring-disk electrode (RRDE) system in O₂-saturated 0.1 M KOH electrolyte, with the working electrode maintained at 1600 rpm rotational speed under a standard three-electrode configuration. The CV curves of CoCu@CeO₂ and analogues were exhibited in

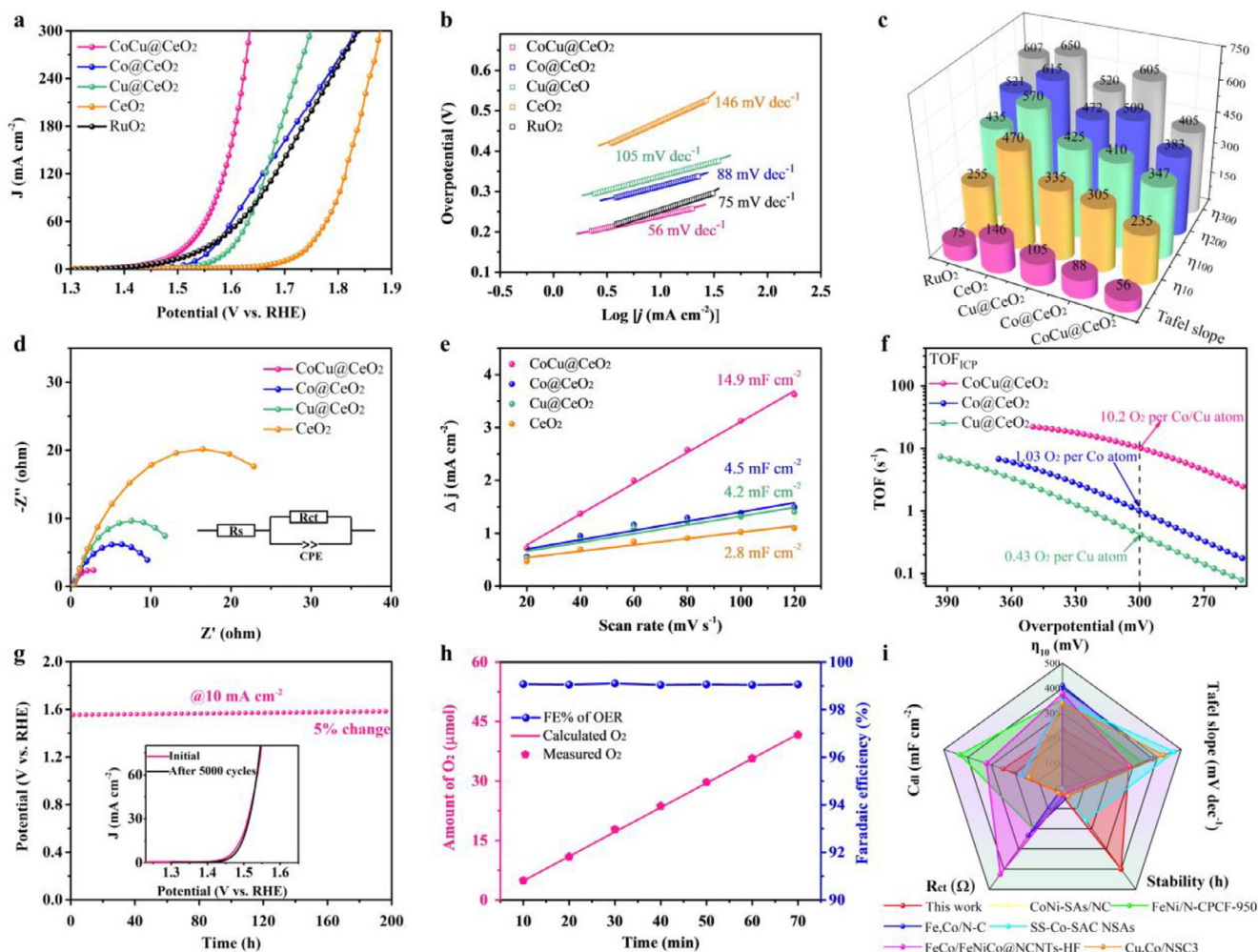


Figure 4. OER performance in 1.0 M KOH. a) LSV curves. b) Tafel slopes, and c) contrasting the overpotential and the Tafel slope for the prepared catalysts. d) EIS plots. Inset (d): the equivalent circuit. e) C_{dl} plots of CoCu@CeO₂, Co@CeO₂, Cu@CeO₂, and CeO₂ derived from CV curves. f) TOF values of the prepared catalysts were calculated based on the loaded CoCu, Co, and Cu atoms at different overpotentials. g) Chronopotentiometric measurement of CoCu@CeO₂ for 200 h at 10 mA cm⁻² (inset: LSV curves after 5000 CV cycles). h) Measured O₂ production and theoretical quantities for CoCu@CeO₂ with the corresponding Faraday efficiency. i) Comparison of the comprehensive properties of CoCu@CeO₂ to other reported catalysts. The detailed information is given in Table S7 (Supporting Information).

O₂- and N₂-saturated 0.1 M KOH in Figure S24 (Supporting Information). As shown in Figures 5a and S25 (Supporting Information), the superior ORR performance of CoCu@CeO₂ was demonstrated by its notable onset potential (E_{onset}) reaching 1.07 V, a value approaching the benchmark Pt/C catalyst (1.09 V). The LSV curves disclose that CoCu@CeO₂ embraces the most positive half-wave potential ($E_{1/2}$) of 0.878 V among these samples, which is 22 mV larger than Pt/C (0.856 V). Specifically, $E_{1/2}$ of Cu@CeO₂, Co@CeO₂, and CeO₂ were 0.853, 0.821, and 0.724 V, respectively. The lowest Tafel slope of CoCu@CeO₂ (79 mV dec⁻¹) among those of Cu@CeO₂ (95 mV dec⁻¹), Co@CeO₂ (105 mV dec⁻¹), CeO₂ (130 mV dec⁻¹), and Pt/C (122 mV dec⁻¹) also supported the superior ORR kinetics of CoCu@CeO₂ (Figure 5b). Moreover, CoCu@CeO₂ illustrated a remarkable kinetic current density (j_k) of 11.65 mA cm⁻² at 0.85 V versus RHE, about 1.3 and 2.3 times higher than that of Cu@CeO₂ (9.14 mA cm⁻²) and Co@CeO₂ (5.18 mA cm⁻²), re-

spectively (Figure 5c). As displayed in Figure 5d and Figure S26 (Supporting Information), the C_{dl} during ORR process was determined to be 16.1 mF cm⁻², significantly larger than that of the Cu@CeO₂ (9.1 mF cm⁻²), Co@CeO₂ (5.5 mF cm⁻²), and CeO₂ (1.2 mF cm⁻²), confirming the more exposed active sites on CoCu@CeO₂.^[30] The corresponding ECSAs for different catalysts are shown in Table S8 (Supporting Information). Results indicate that the CoCu@CeO₂ achieves the highest specific surface area and electrochemically active area.

Koutecky–Levich (K–L) plots derived from LSV curves at various rotating speeds ranging from 400 to 2500 rpm (Figures 5e and Figure S27, Supporting Information) provided potential-related quantification of electron transfer numbers (n), offering mechanism insights into the ORR process. The linearity of K–L plots (inset Figure 5e) demonstrated first-order kinetics concerning dissolved O₂ concentration. Quantitative analysis via the Koutecky–Levich equation yielded an electron transfer number

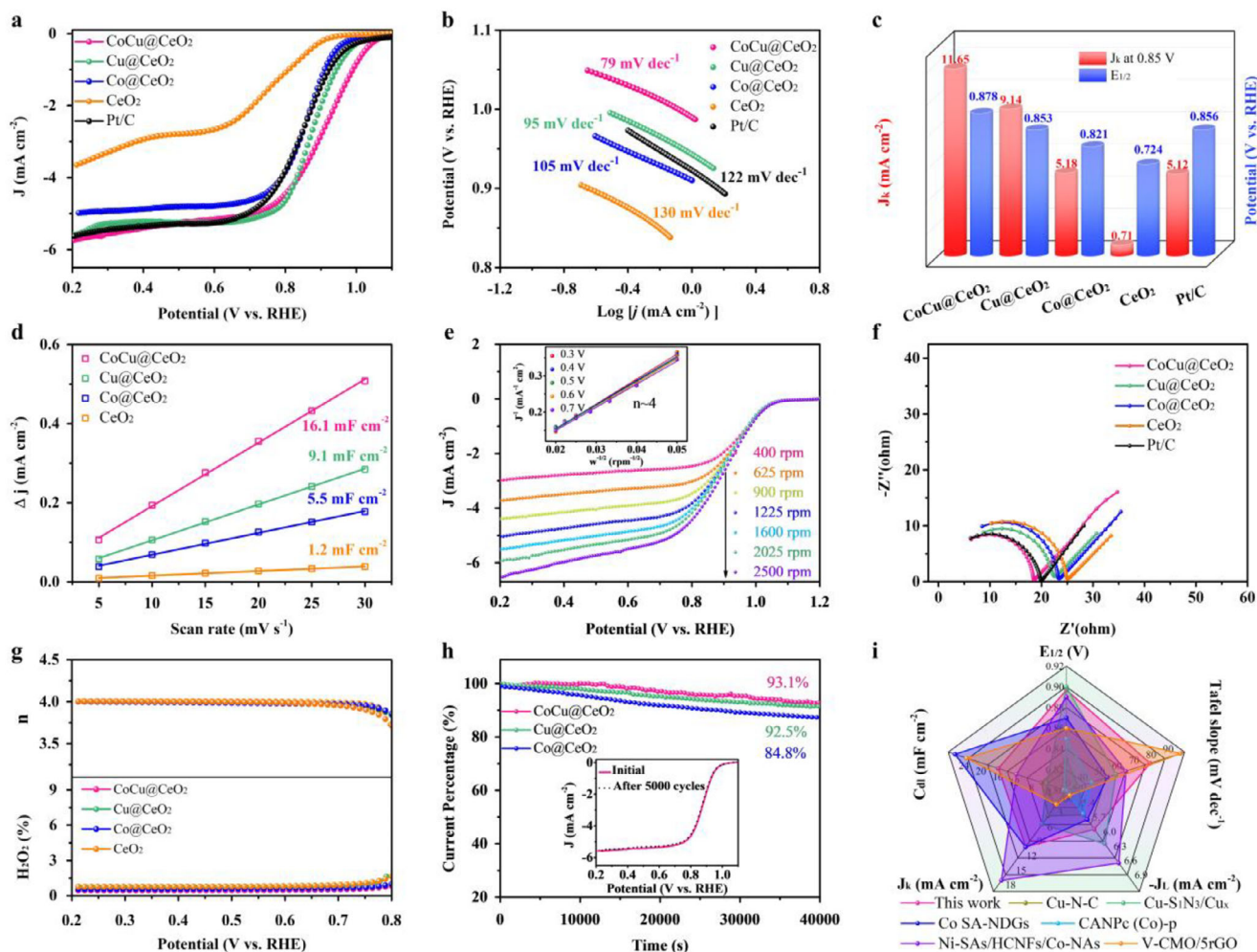


Figure 5. ORR performance in 0.1 M KOH. a) LSV curves and b) Tafel plots of the as-prepared catalysts. c) Kinetic current density (J_k) at 0.85 V and half-wave potentials of CoCu@CeO₂, Cu@CeO₂, Co@CeO₂, CeO₂, and Pt/C catalysts. d) Calculated C_{dl} values of different samples. e) LSV curves of CoCu@CeO₂ at various rotation rates. Inset (e): The K–L plots. f) EIS curves. g) n (Electron transfer number, top) and H₂O₂ yield (bottom) for CoCu@CeO₂. h) Stability test of CoCu@CeO₂. Inset (h): LSV curves before and after 5000 cycles CV test. i) Comparison of performance-determining factors between CoCu@CeO₂ and other reported catalysts. The detailed information is given in Table S10 (Supporting Information).

of ≈ 4 , confirming a dominant $4e^-$ pathway in the ORR process. Furthermore, EIS curves in Figure 5f and Table S9 (Supporting Information) corroborated that the charge transfer resistance of CoCu@CeO₂ was smaller than that of Cu@CeO₂, Co@CeO₂, and CeO₂, suggesting its fastest charge transfer rate at the interface. The RRDE test analysis conclusively validated the predominance of the $4e^-$ ORR on CoCu@CeO₂ (Figure 5g), with detected peroxide yields below 3% and corroborating the suppressed $2e^-$ byproduct test formation and enhanced direct $4e^-$ transfer. The results suggested the encouraging catalytic ORR performance of CoCu@CeO₂ with high selectivity toward direct four-electron transfer. In addition, the catalyst exhibited negligible activity loss ($< 5\%$) over 40 000 s of chronoamperometric testing at a constant potential, demonstrating exceptional operational stability under prolonged electrochemical conditions (Figure 5h). After 5000 cycles of accelerated durability test, the half-wave potential of the LSV curve for CoCu@CeO₂ showed a small negative shift of only 8 mV (inset Figure 5h), revealing its excellent stabil-

ity. Notably, the CoCu@CeO₂ demonstrated ORR activity rivaling state-of-the-art catalysts (Figure 5i), as evidenced by comparative benchmarking against commercial Pt/C and other noble-metal systems in Table S10 (Supporting Information), positioning it as a viable noble-metal-free alternative for sustainable energy applications. The SEM, TEM, XRD, and XPS characterization of the CoCu@CeO₂ after the durability test was displayed in Figures S28 and S29 (Supporting Information), attesting that the catalyst had excellent structural stability.

2.4. Zinc–Air Battery Catalyzed by CoCu@CeO₂

The outstanding bifunctional oxygen electrocatalytic performance could be appraised by the potential gap (ΔE) between the $E_{1/2}$ (for the ORR) and the overpotential η_{10} (for the OER). We tested the potential difference in 0.1 M KOH, and the results showed that CoCu@CeO₂ possessed a smaller ΔE of 0.633 V

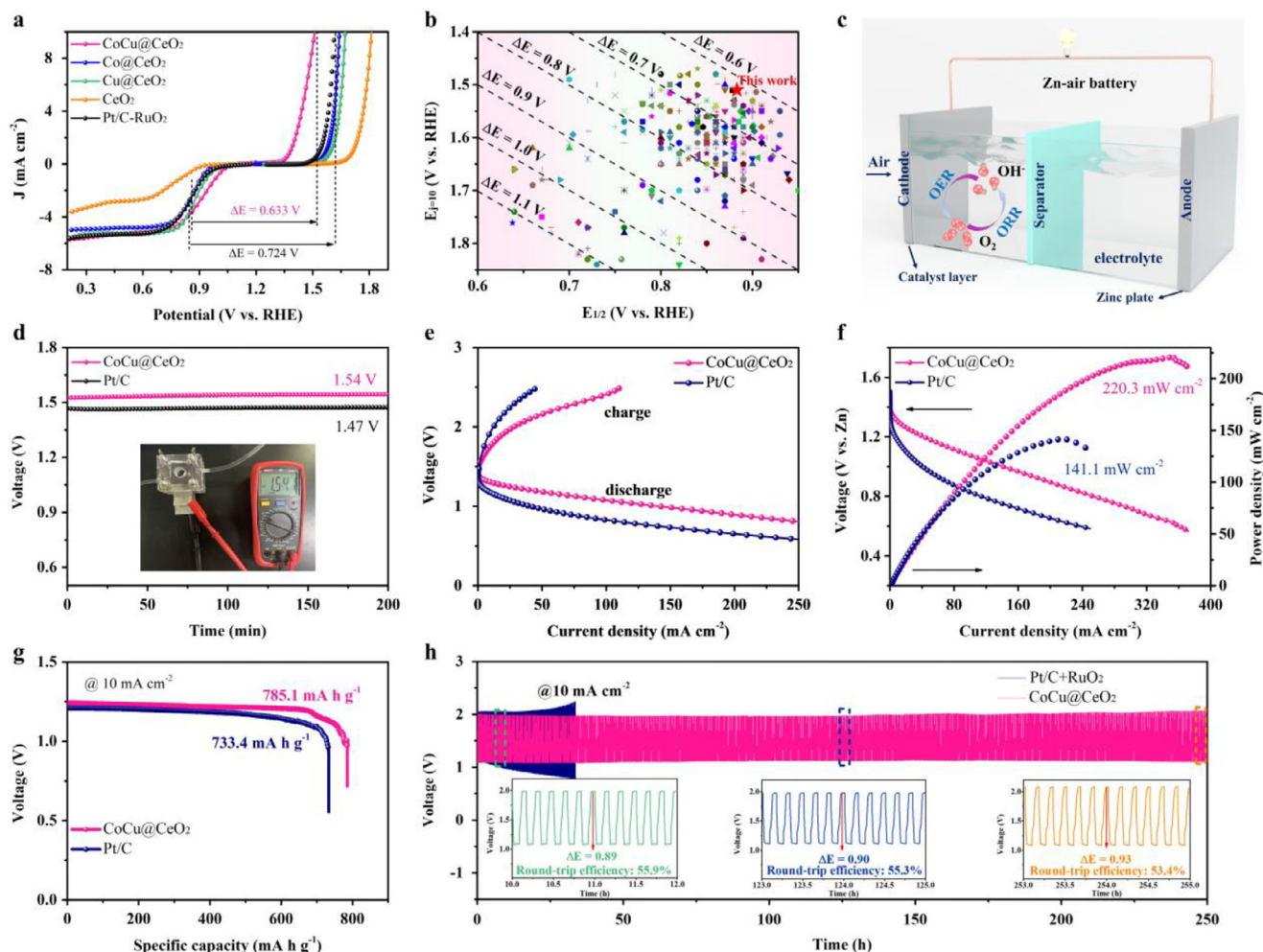


Figure 6. Zinc–air battery performance. a) Bifunctional catalytic curves for different catalysts. b) The diagram for bifunctional performance comparison among CoCu@CeO₂ and other reported bifunctional electrocatalysts is in Table S11, Supporting Information. c) Schematic illustration of a Zn–air battery. d) Open circuit plot. Inset (d): Photo of the open circuit voltage for the assembled ZAB. e) Charge/discharge polarization. f) Discharge polarization and power density curves of CoCu@CeO₂ and Pt/C. g) Galvanostatic discharge curves at 10 mA cm⁻². h) Charge/discharge cycling stability of CoCu@CeO₂ and Pt/C at a current density of 10 mA cm⁻². Inset (h): Charge/discharge cycle RHE curves and round-trip efficiency of different cycles.

(Figure 6a), outperforming commercial Pt/C + RuO₂ (0.724 V). Especially, when compared with other recently reported bifunctional oxygen electrocatalysts, CoCu@CeO₂ had significant superiority, confirming its potential application in rechargeable zinc–air batteries (Figure 6b and Table S11, Supporting Information). A primary ZAB was engineered with CoCu@CeO₂-coated carbon cloth as the bifunctional air electrode, providing direct experimental validation of this catalyst's viability in practical energy conversion systems (Figure 6c and Figure S30, Supporting Information). The CoCu@CeO₂-based ZAB (Figure 6d) demonstrated a high open-circuit voltage (OCV) of 1.54 V, outperforming the benchmark Pt/C + RuO₂ system (1.47 V) by 70 mV. Charging/discharging polarization curves of catalysts were recorded, and a narrow voltage gap was observed for CoCu@CeO₂, indicating excellent rechargeability (Figure 6e). In Figure 6f, the CoCu@CeO₂-based battery achieved a peak power density of 220.3 mW cm⁻², surpassing the Pt/C + RuO₂ benchmark system (141.1 mW cm⁻²) by 56.1%, establishing excellent energy

output capabilities in nonprecious metal catalysts. In Figure 6g, under galvanostatic discharge at 10 mA cm⁻², the CoCu@CeO₂ cathode exhibited a specific capacity of 785.1 mA h g⁻¹, reaching 89.2% of the theoretical zinc capacity (880 mA h g⁻¹), indicative of highly efficient active material utilization. The cycling stability of zinc–air batteries was assessed via constant-current cycling (10 mA cm⁻²) with 10-min discharge/charge intervals per cycle. The CoCu@CeO₂ elucidated negligible voltage decay in 250 h, revealing superior long-term durability than the Pt/C + RuO₂-based battery (Figure 6h). Note that the charge–discharge voltage gap was measured 0.89 V during the first 10-h cycle, accompanied by a 55.9% round-trip efficiency. The voltage gap was maintained at 98.9% and 95.5% at 125 and 250 h, respectively. Especially, the round-trip efficiency remained above 50% even after the 250 h (inset Figure 6h). To further clarify the superiority of the CoCu@CeO₂ catalyst, the zinc–air performance was compared with those of the reported catalysts. As presented in Table S12 (Supporting Information), CoCu@CeO₂ is among the

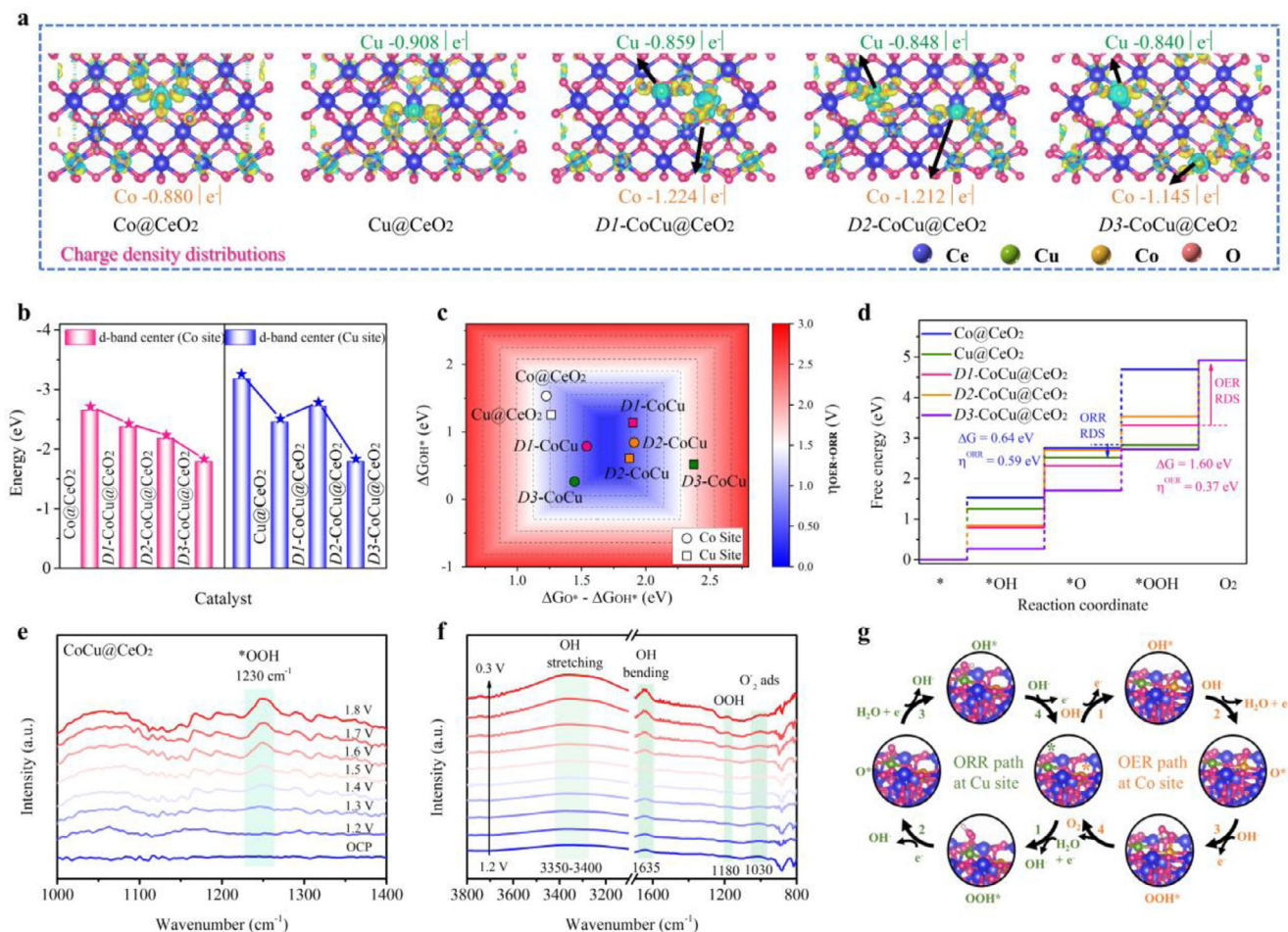


Figure 7. Theoretical calculation. a) Charge density distributions ($0.005 \text{ e}/\text{\AA}^3$) and Bader charge at the Co and Cu sites, b) the d -band center at the Co and Cu sites for Co@CeO_2 , Cu@CeO_2 , D1-CoCu@CeO_2 , D2-CoCu@CeO_2 , and D3-CoCu@CeO_2 . c) Calculated total theoretical overpotential (η^{total}) volcano plot with $\Delta G_{\text{O}^*} - \Delta G_{\text{OH}^*}$ and ΔG_{OH^*} as descriptors. d) Theoretical overpotential of the catalyst for OER (at Co site) and ORR (at Cu site) for Co@CeO_2 , Cu@CeO_2 , D1-CoCu@CeO_2 , D2-CoCu@CeO_2 , and D3-CoCu@CeO_2 . e) In situ FT-IR spectra of CoCu@CeO_2 for e) OER and f) ORR. g) OER path at Co site and ORR path at Cu site for D1-CoCu@CeO_2 . Blue, cerium; orange, cobalt; green, copper; red, oxygen.

best in terms of zinc–air performance. Collectively, these findings demonstrate the exceptional potential of CoCu@CeO_2 as an advanced electrocatalyst for zinc–air battery applications.

2.5. Density Functional Theory (DFT) Mechanism Exploration

Theoretical calculations for the reaction active sites and mechanisms are conducted to explore the synergy between the CeO_2 confined Co and Cu diatoms in tuning the OER/ORR activities. Due to the isolated and uniform active sites of Co and Cu atoms (without Co–Cu bonds), the influence of the distance between Co and Cu atoms on catalytic activity cannot be ignored.^[56] Integrated with experimental results, three possible theoretical models with different atomic distances are constructed to probe the long-range synergistic effects between the two metallic centers and the reactivity of CoCu@CeO_2 (Figure S31, Supporting Information). The charge density difference and Bader charges analysis were used to further dig out the accurate charge distribution of the constructed models. Different degrees of elec-

tron localization are derived from the strong metal support interaction and the bimetallic synergistic effect.^[57] As explicitly shown in Figure 7a, compared with Co@CeO_2 and Cu@CeO_2 , Co and Cu in CoCu@CeO_2 lose electrons and gain electrons, respectively, consistent with XPS and XANES results. For D1-CoCu@CeO_2 , Co loses the most electrons (0.344 e) and Cu gains the least electrons (0.049 e), indicating that Co and Cu in D1-CoCu@CeO_2 have the strongest electronic interaction than those of D2-CoCu@CeO_2 and D3-CoCu@CeO_2 .^[58] Meanwhile, neighboring Ce atoms on the interface acquire electrons. Based on the density of states data, the Crystal Orbital Hamiltonian population between Co and Cu in the three samples was further calculated. As the distance between Co and Cu increases, the intensity of the electronic states in the plot gradually weakens, indicating a reduction in the electronic interaction between Co and Cu (Figure S32, Supporting Information).

The analysis of the d -band center (ϵ_d) of Co and Cu atoms at the surface is displayed in Figure 7b and Figure S33, Supporting Information. The calculation data imply that the Cu atom in D1-CoCu@CeO_2 possesses moderate ϵ_d values around the Fermi

energy level, indicating the Cu atoms have neither strong nor weak adsorption capacity for reaction intermediates. For the Co atom, the *d*-band center in *D1*-CoCu@CeO₂ (−2.37 eV) is negatively shifted toward the Fermi energy level than those of *D2*-CoCu@CeO₂ (−2.18 eV) and *D3*-CoCu@CeO₂ (−1.79 eV). As the *d*-band center shifts toward lower energy levels, it allows effective tuning of the adsorption strength between the Co site and adsorbed species.^[59]

The total density of states analysis in Figures S34 and S35 (Supporting Information) illustrates that the *D1*-CoCu@CeO₂ has a greater density of states near the Fermi level, expanding its improved conductivity.^[60] Then, the total theoretical overpotential (η^{total}) volcano is plotted according to the function of $\Delta G_{\text{O}^*} - \Delta G_{\text{OH}^*}$ and ΔG_{OH^*} (Figure 7c). The blue central region is located at the top of the volcano, with the lowest total theoretical overpotential, and hence, the highest ORR and OER performance.^[61] Compared to other catalysts, the catalytic activity of *D1*-CoCu@CeO₂ is more prominent because its position is more concentrated in the central region. The free energy diagrams of OER and ORR on various dual-atom models to explore the reaction mechanism are shown in Figure 7d and Figure S36 (Supporting Information). A preliminary evaluation is conducted by calculating Gibbs reaction free energy (ΔG) for the OER/ORR of single atom Co@CeO₂ and Cu@CeO₂. The results show that the OER tends to occur at the Co site, while ORR has an advantage at the Cu site. Subsequently, the ΔG values are calculated on *D1*-CoCu@CeO₂, *D2*-CoCu@CeO₂, and *D3*-CoCu@CeO₂ catalysts with three different atomic spacings between Co and Cu atoms. For OER, the Co site on *D1*-CoCu@CeO₂ has the most advantage with a lower ΔG (1.60 eV) of the rate determination steps (RDS: *OOH → O₂) than the other two models. For ORR, the reaction tends to occur at the Cu site, with the lowest ΔG (0.64 eV) of the RDS (*OOH → *O). The corresponding adsorption models of different catalysts for reaction intermediates during OER/ORR are displayed in Figures S37–S41 (Supporting Information). Compared to *D2*-CoCu@CeO₂ and *D3*-CoCu@CeO₂, *D1*-CoCu@CeO₂ has the lowest theoretical overpotentials (Figure S42, Supporting Information), indicating stronger interactions and better bifunctional OER/ORR activity between the Co and Cu atoms with a distance of 4.341 Å.

In addition, the influence of the mechanism pathway on the adsorption of reaction intermediates is measured by in situ Fourier transform infrared (FT-IR) spectroscopy. The in situ FT-IR spectra of CoCu@CeO₂ for OER (in 1.0 M KOH) and ORR (in O₂-saturated 0.1 M KOH solution) are shown in Figure 7e,f. During OER, an infrared absorbed peak of *OOH (at ≈1230 cm^{−1}) appeared under anodic potentials and gradually enhanced when the voltage applied changed from 1.2 to 1.8 V.^[62] The increase of *OOH intermediates corroborated the traditional four-step adsorbate evolution mechanism reaction pathway of the CoCu@CeO₂ catalyst.^[63] In addition, under ORR operating conditions, there are four absorption peaks. The broad peaks at 3350–3400, 1635, 1180, and 1030 cm^{−1} are ascribed to stretching vibration of O–H bonds, bending vibration of H–O–H, *OOH absorption peaks, and *O₂[−] absorption peaks, respectively.^[64] As the applied voltage decreases, the intensity of the peak at 1180 cm^{−1} increases gradually, suggesting that the coupling of *OOH species is a dynamic process. The absence of peroxo-like oxygen (*O–O*) at ≈1090 cm^{−1} confirms that CoCu@CeO₂ cata-

lysts follow the 4e[−] associative ORR pathway.^[65] Figure 7g shows the OER and ORR pathways performed at the Co and Cu sites, respectively. The synergistic effect of Co and Cu dual atoms endows CoCu@CeO₂ with excellent intrinsic activity and synergistically catalyzes the oxygen electrocatalysis reactions.

3. Conclusion

In conclusion, we successfully synthesized a diatomic CoCu@CeO₂ catalyst featuring uniformly isolated Co and Cu dual-atom sites via the strong electrostatic adsorption method. The CoCu@CeO₂ catalyst enabled superior catalytic performance for OER (η_{10} = 235 mV), ORR ($E_{1/2}$ = 0.878 V), and a small potential gap (ΔE = 0.633 V), thereby outperforming most reported nonprecious metal diatomic catalysts. In addition, CoCu@CeO₂ exhibits good applicability as the anode in assembled zinc–air batteries (peak power density of 220.3 mW cm^{−2}), indicating its promising application prospects. Kinetic studies revealed minimal activation energy barriers and distinct reaction pathway preferences, with OER processes predominantly localized at Co sites while ORR preferentially occurs on Cu centers. Systematic DFT simulations further demonstrated that the LRS coupling between bimetallic centers induces significant electronic structure modifications, including optimized *d*-band center positions and reduced energy barriers compared to single-atom counterparts. The synergistic interplay between geometrically optimized active sites (4.341 Å interatomic spacing) and enhanced metal–support charge transfer simultaneously facilitates oxygen intermediate adsorption/desorption kinetics. This atomic-level engineering of heteronuclear diatomic systems not only offers deep insights into long-range electronic correlations in oxide-supported catalysts but also establishes a novel framework for atomic-level catalyst design in advanced energy conversion technologies.

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 in the Supporting Information of this article.

Keywords

CoCu@CeO₂, long-range synergistic, oxygen evolution reaction, oxygen reduction reaction, zinc–air battery

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