

CeO_{2-δ} as Electron Donor in Co_{0.07}Ce_{0.93}O_{2-δ} Solid Solution Boosts Alkaline Water Splitting

Gege Su, Yichao Hou, Jie Yin,* Jiayi Yang, Zhenglong Li, Xin Du,* Xin Zhang, Pinxian Xi,* and Chun-Hua Yan

Optimizing the electronic structure with increasing intrinsic stability is a usual method to enhance the catalysts' performance. Herein, a series of cerium dioxide (CeO_{2-δ}) based solid solution materials is synthesized via substituting Ce atoms with transition metal (Co, Cu, Ni, etc.), in which Co_{0.07}Ce_{0.93}O_{2-δ} shows optimized band structure because of electron transition in the reaction, namely Co³⁺ (3d⁶4s⁰) + Ce³⁺ (4f¹5d⁰6s⁰) → Co²⁺ (3d⁷4s⁰) + Ce⁴⁺ (4f⁰5d⁰6s⁰), with more stable electronic configuration. The in situ Raman spectra show a stable F2g peak at ≈452 cm⁻¹ of Co_{0.07}Ce_{0.93}O_{2-δ}, while the F2g peak in CeO_{2-δ} almost disappeared during HER progress, demonstrating the charge distribution of *H adsorbed on Co_{0.07}Ce_{0.93}O_{2-δ} is more stable than *H adsorbed on CeO_{2-δ}. Density functional theory calculations reveal that Co_{0.07}Ce_{0.93}O_{2-δ} solid solution increases protonation capacity and favors for formation of *H in alkaline media. General guidelines are formulated for optimizing adsorption capacity and the volcano plot demonstrates the excellent catalytic performance of Co_{0.07}Ce_{0.93}O_{2-δ} solid solution. The alkaline anion exchange membrane water electrolysis based on Co_{0.07}Ce_{0.93}O_{2-δ}/NiFe LDH realizes a current density of 1000 mA cm⁻² at ≈1.86 V in alkaline seawater at 80 °C and exhibits long-term stability for 450 h.

innovative solution to energy security challenges.^[1,2] In this field, catalyst design is key to improving catalytic efficiency and reducing costs. Alkaline anion exchange membrane water electrolysis (AEMWE), based on inexpensive and readily available materials, has been widely adopted as a promising hydrogen production method.^[3–8] Additionally, alkaline seawater electrolysis, an emerging hydrogen production technology, not only utilizes abundant seawater resources but also enhances energy efficiency while lowering costs. Transition metal-based electrocatalysts, such as layered hydroxides,^[9] spinel oxides,^[10] and sulfides,^[11] typically enhance OER performance more than Ir, Ru, and their corresponding oxides.^[12,13] However, many of them, like Raney nickel,^[14] show limited hydrogen production performance in alkaline media due to their restricted protonation ability in alkaline water,^[15,16] which constrains AEMWE's operation at higher current densities.^[17,18] This limitation affects their application in anion exchange membrane water electrolysis. Therefore, exploring alternative catalysts with stronger protonation capabilities is crucial for improving the overall performance and efficiency of AEMWE.

Interface engineering,^[19] atomic exposure,^[20] and doping strategies^[21] have demonstrated that HER activity can be op-

1. Introduction

Hydrogen energy is one of the most promising carriers in the future sustainable energy system, and electrocatalytic water splitting for hydrogen production is widely regarded as an

G. Su, Y. Hou, J. Yin, J. Yang, Z. Li, P. Xi, C.-H. Yan
State Key Laboratory of Applied Organic Chemistry
Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province
Frontiers Science Center for Rare Isotopes
College of Chemistry and Chemical Engineering
Lanzhou University
Lanzhou 730000, P. R. China
E-mail: yinjl@lzu.edu.cn; xipx@lzu.edu.cn

X. Du
College of Chemistry
Zhengzhou University
Zhengzhou 450001, China
E-mail: dux@zzu.edu.cn

X. Zhang
School of Nuclear Science and Technology
Lanzhou University
Lanzhou 730000, China

C.-H. Yan
Beijing National Laboratory for Molecular Sciences
State Key Laboratory of Rare Earth Materials Chemistry and Applications
PKU-HKU Joint Laboratory in Rare Earth Materials and Bioinorganic Chemistry
College of Chemistry and Molecular Engineering
Peking University
Beijing 100871, China

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/advs.202411845>

© 2024 The Author(s). Advanced Science published by Wiley-VCH GmbH. This is an open access article under the terms of the [Creative Commons Attribution](#) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/advs.202411845

timized through adjustments to electronic structures. Among these, ion doping is one of the effective strategies for enhancing HER performance. Generally, doping with exogenous atoms can alter the unit cell parameters and adjust valence electrons and local coordination, thereby effectively improving the adsorption behavior of reaction intermediates and further optimizing electrocatalytic performance.^[22–24] Cerium dioxide (CeO_2), as a cheap material with a strong Ce–O bond, exhibits superior stability under an oxygen-rich atmosphere and the fast redox reaction between Ce^{3+} and Ce^{4+} provides extra electron flow for electrochemical reactions,^[25–27] but high bandgap of CeO_2 (3.12 eV) limited the intrinsic performance in different electrochemical reactions. Doping transition metals into cerium dioxide can further enhance its catalytic performance. The introduction of exogenous atoms can alter unit cell parameters, adjust valence electrons, and modify local coordination, optimizing the adsorption behavior of reaction intermediates, which is particularly important for the hydrogen evolution reaction (HER). Current research has mostly focused on improving HER performance through noble metal doping, with limited attention on doping with transition metal elements. Although non-noble metals typically exhibit weaker catalytic performance, their high abundance and low cost still present significant potential for effective catalysis in hydrogen evolution reactions. Therefore, in-depth studies on the effects of transition metal doping in cerium dioxide could open new avenues and directions for enhancing HER performance. By combining the properties of cerium dioxide with doping strategies involving transition metals, we aim to design more efficient and cost-effective catalysts, laying the foundation for a sustainable hydrogen energy future.

Herein, a strategy of optimizing CeO_2 electronic structure was fabricated via transition metal atoms (M: Co, Ni, Zn, Cu, Cr) substituted Ce atoms in $\text{CeO}_{2-\delta}$ structure and formed $\text{M}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution materials. Among them, $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ with optimized electronic structure shows a slightly decreased bandgap of 3.08 eV and the highest HER performance. Then, a volcano relationship can be found between bandgap and HER activity, in which $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ at the top of the volcano means Co is the ideal dopant for $\text{CeO}_{2-\delta}$ to optimize intrinsic structure and increase the HER activity. The in situ Raman and attenuated total infrared absorption spectroscopy (ATR-IR) also indicates $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ surface with optimized electronic structure is favorable for intermediate adsorption. More importantly, the HER mechanism changed from Volmer–Heyrovsky of $\text{CeO}_{2-\delta}$ to Volmer–Tafel of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$. The density functional theory (DFT) calculations also indicate the optimized $^*\text{H}$ adsorption ($^*\text{H}_{\text{ad}}$) and promote proton coupling to form hydrogen gas. Interestingly, a volcano curve can be built based on the relationship between Bader charge and ΔG_{H^*} of those solid solution materials, in which $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ located at the top of the volcano and closer to $\eta = 0$ V exhibiting the most excellent HER activity. More importantly, The AEMWE based on $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ /NiFe LDH can get the current density of 1000 mA cm^{-2} at 2.05 and 1.86 V in alkaline seawater at 25 and 80 °C, respectively.

2. Results and Discussion

The rare earth (RE) elements with unique valence $4f^{0-14}5d^{0-1}6s^2$ electronic configurations show flexible 4f orbital due to the

shielding effect of 5s/5p or 6s electrons, suggesting an easy coupling with other orbitals.^[28–30] Ce shows an amazing redox shuttle of $\text{Ce}^{3+} (4f^1) - \text{Ce}^{4+} (4f^0)$ ion redox shuttle because of the unique valence state shift from Ce^{3+} to Ce^{4+} with the formation of a more stable $4f^0$ configuration. Therefore, $\text{CeO}_{2-\delta}$ with reversible charge transfer between Ce^{4+} and Ce^{3+} makes it an ideal model to understand the d–f electronic interaction in $\text{M}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$. In detail, the $\text{O}_h - [\text{CeO}_6]$ unit next to the $[\text{MO}_6]$ unit with a_{1g} , t_{1u} , e_g , t_{2g} symmetric orbitals and corresponding antibonding states of a_{1g}^* , t_{1u}^* , e_g^* , and t_{2g}^* , splits the seven degenerate 4f orbitals of the Ce atom into t_{1u} , t_{2u} , and a_{2u} symmetry. Thus, build the orbital coupling and form the $3d_M - 2p_O - 4f_{\text{Ce}}$ in $\text{M}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ with the t_{1u} and t_{2u} symmetric orbitals contribute to the RE–O bonding and the e_g and t_{2g} symmetric orbitals correlating with M–O bonding (Figure 1a). Then, we synthesized a series $\text{CeO}_{2-\delta}$ based solid solution with transition metal ion (Cr, Zn, Co, Cu, Ni) substituted Ce position via hydrothermal method.^[31] Despite introducing hetero-metal ions, the powder X-ray diffraction patterns of as-synthesized $\text{M}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ (Figure S1, Supporting Information) display a single crystalline phase attributed to the fluorite structure of $\text{CeO}_{2-\delta}$ (space group #43-1002, $\text{Fm } \bar{3} m$). Additionally, the Raman spectra of those prepared materials (Figure S2, Supporting Information) also show the main peaks of $\text{CeO}_{2-\delta}$. Therefore, they could form a substituted $\text{M}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ solid solution because the volume of ions (Cr^{3+} : 69 pm, Zn^{2+} : 74 pm, Co^{2+} : 63 pm, Cu^{2+} : 72 pm, Ni^{2+} : 62 pm) bigger than the interstitial space of CeO_2 cell. The inductively coupled plasma optical emission spectroscopy was used to test the content of those metal ions and obtain the chemical formula of those materials (Table S1, Supporting Information). Compared to pure $\text{CeO}_{2-\delta}$, the metal-substituted solid solution exhibited a corresponding blue shift or red shift in the absorption edge wavelength in UV–vis spectra (Figure 1b).

The band structure diagrams (Figure 1c) were obtained through UV–vis diffuse reflectance spectroscopy and Mott–Schottky plots (Figure S3, Table S2, Supporting Information).^[32] Additionally, we analyzed the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of original $\text{CeO}_{2-\delta}$ and other solid solution materials through DFT. For the pristine $\text{CeO}_{2-\delta}$, no obvious molecular orbitals are formed on its surface, but σ/π mixing bond formation are formed at the bottom. When Cu, Cr, Co, Ni, and Zn ions replace Ce atoms, the HOMO of $\text{CeO}_{2-\delta}$ forms σ/π mixing molecular orbitals (insert in Figure 1c).^[33] As we all know, the overlap degree of π bond is smaller than that of σ bond, so the bond energy of π bond is smaller than that of σ bond, its stability is lower than that of σ bond, the bond electrons are more active, so it is an active participant in chemical reactions. The HER performance of those materials was evaluated by using the linear scan voltammogram (LSV) in 1.0 M KOH (Figure 1d).^[34] Among them, $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ shows the best HER activity with a η of 75.18 mV at $j = 10 \text{ mA cm}^{-2}$ which is much lower than that of $\text{CeO}_{2-\delta}$ (419.68 mV), $\text{Cr}_{0.04}\text{Ce}_{0.96}\text{O}_{2-\delta}$ (266.89 mV), $\text{Cu}_{0.18}\text{Ce}_{0.82}\text{O}_{2-\delta}$ (233 mV), $\text{Zn}_{0.12}\text{Ce}_{0.88}\text{O}_{2-\delta}$ (221.1 mV), $\text{Ni}_{0.06}\text{Ce}_{0.94}\text{O}_{2-\delta}$ (210.46 mV). More importantly, $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ also shows excellent HER stability for 300 h under different current densities (10, 50, and 100 mA cm^{-2}) (Figure 1e). Finally, a volcano image can be found based on the HER activity and bandgap of those materials, in which $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ solid solution at the top of the volcano.

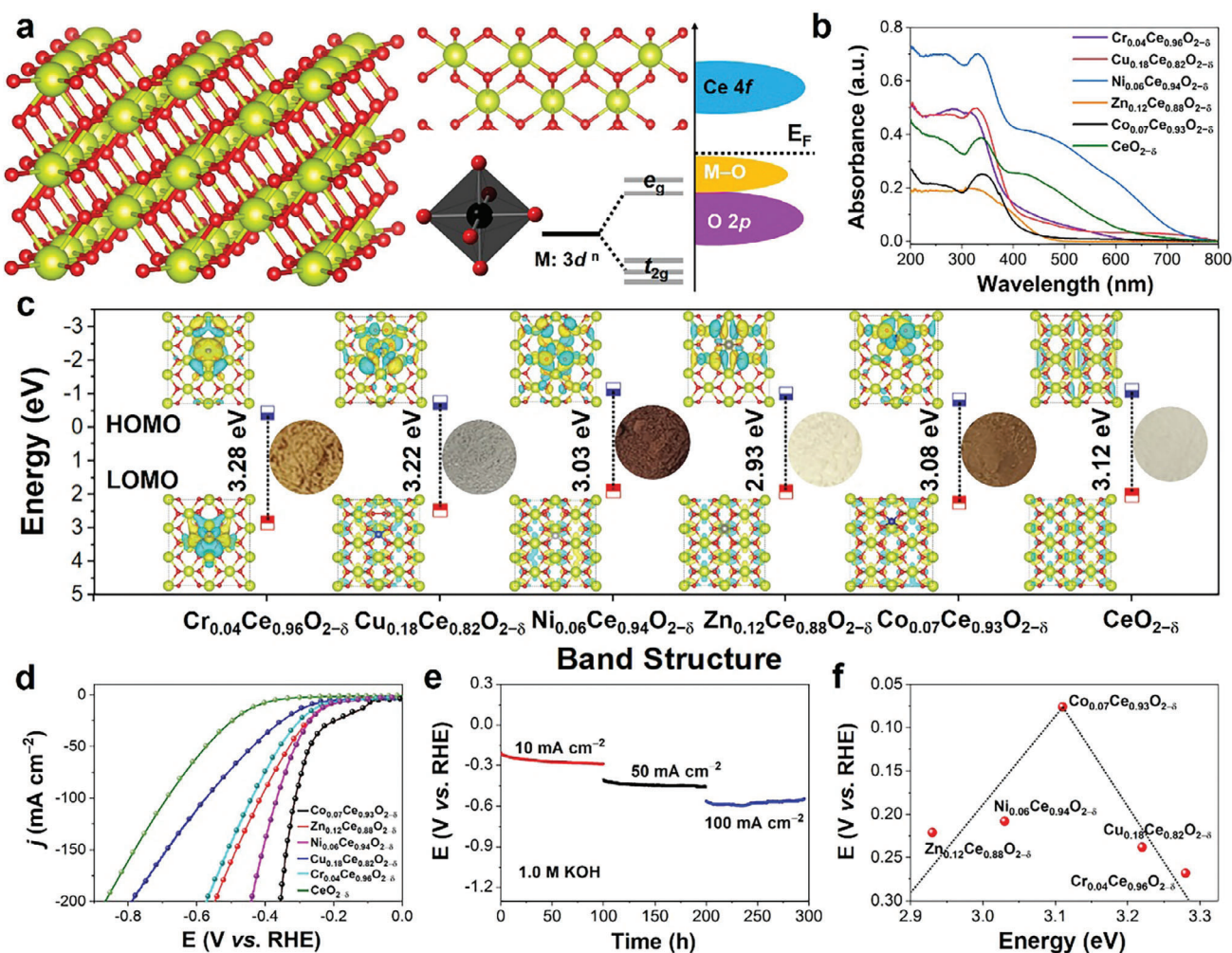


Figure 1. a) Schematic diagrams of the electron orbitals for $\text{CeO}_{2-\delta}$ and $\text{M}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$, illustrating the changes in the orbital configurations. b) UV-vis diffuse reflectance spectra of those materials. c) Band structure diagram and bandgap for those materials with different colors. The insert the calculated HOMO and LUMO of those materials through DFT. d) LSV curves of $\text{CeO}_{2-\delta}$ and $\text{M}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ for HER. e) Long-term stability of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ in 1.0 M KOH. f) A volcano plot formed by the combination of η and band structure.

To explain the excellent HER performance of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$, the high angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) was used to study the atomic structure of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ solid solution. Both $\text{CeO}_{2-\delta}$ (Figure S4, Supporting Information) and $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ (Figure 2a) show the nanosphere morphology in HAADF-STEM images, demonstrating that Co-substituting Ce atoms in $\text{CeO}_{2-\delta}$ structure maintain the nanosphere morphology. The average particle size of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ solid solution was ≈ 166 nm confirmed by distribution statistics (Figure S5, Supporting Information). The Energy dispersive X-ray spectroscopy elemental mapping results (Figure 2a; Figure S6, Supporting Information) indicate the uniform distribution of Co, Ce, O and Ce, O in the areas of multi-particles, single particle, and particle surface (as micrometer scale to sub-nanometer scale). The high-resolution scanning transmission electron microscopy (HR-STEM) images reveal the hierarchical structure of nanospheres. $\text{CeO}_{2-\delta}$ nanospheres are stacked by the sheets with stepped atomic edges (Figure S7, Supporting Information), which will exist abundant edge

active sites for catalytic reactions. Furthermore, the substructure of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ also maintains nanosheets atmosphere (Figure 2b) with corresponding fast Fourier transform (FFT) face of $(11\bar{1})$, $(1\bar{1}1)$, (002) and the nanosheets prefers orientation of the $\{110\}$ crystal plane family for $\text{CeO}_{2-\delta}$ in a different area (Figure 2b $_1$ -b $_3$).

To further investigate the existence form of Co atoms in $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$, the aberration-corrected scanning transmission electron microscopy (AC-STEM) was used (Figure 2c). Usually, the image intensity of HAADF-STEM is approximately proportional to the sample thickness and the atomic number as $Z^{1.8}$, which is widely used to confirm the metal atoms in different systems. Therefore, both 3D intensity (Figure 2d) and line intensity distributions (Figure 2e) show the contrast difference between the pure Ce column and the Ce + Co column demonstrating Co atoms substituted the Ce position and formed $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ solid solution. Based on high-resolution atomic images, the geometrical phase analysis (GPA) was further used to study the strain change after the formation of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ solid so-

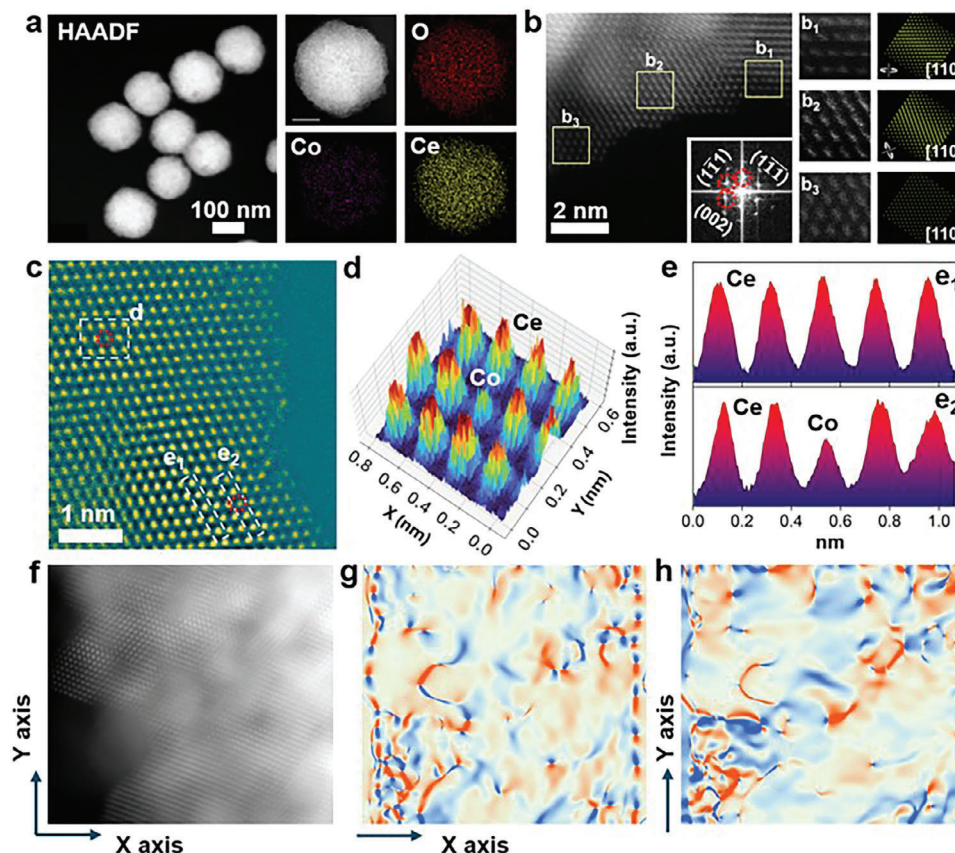


Figure 2. a) STEM, b) HR-STEM, and c) AC-STEM of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$. The difference between the pure Ce column and the Ce + Co column along the d) 3D intensity and e) line intensity distributions in (c). f) The strain field distribution in g) X and h) Y directions, with the strain degree from -3% to 3% .

lution. As shown in (Figure 2f–h), the strain field distribution in the X and Y directions is given with the strain degree from -3% to 3% , indicating the Co substituting Ce atoms and forming $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ structure will not bring strain effect in the material.

The electronic interaction between Co and $\text{CeO}_{2-\delta}$ spectra.^[35,36] Compared to $\text{CeO}_{2-\delta}$, a noticeable enhancement in white line intensity of Ce L₃-edge XANES spectra is observed for $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ and $\text{Co}_3\text{O}_4/\text{CeO}_{2-\delta}$ (Figure 3a), implying the strong coupling between two different species. Meanwhile, the shoulder peak at 5724.5 eV in Ce L₃-edge XANES spectra attributed to Ce^{3+} decreased after the introduced Co species,^[37] further demonstrating the CeO_2 and Co species probably serve as the electron donor and electron receptor in $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ structure, respectively. This conclusion can also be revealed by the Co K-edge XANES spectra (Figure 3b), in which $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ shows more negative edge shift compared with that of $\text{CeO}_{2-\delta}$ and $\text{Co}_3\text{O}_4/\text{CeO}_{2-\delta}$, indicating the decrease of the Co oxidation state of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ because of the electron transfer from CeO_2 to Co species. Additionally, the standard electrode potentials (E°) of $\text{Ce}^{4+}/\text{Ce}^{3+}$ and $\text{Co}^{3+}/\text{Co}^{2+}$ are 1.72 and 1.82 V, respectively, meaning the reaction between Ce^{3+} and Co^{3+} with an electron-transition ($\text{Ce}^{3+} + \text{Co}^{3+} \rightarrow \text{Ce}^{4+} + \text{Co}^{2+}$). The formation of the $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ structure is further confirmed by Ce L₃-edge and Co K-edge extended X-ray absorption fine

structure (EXAFS) spectra. As shown in the Ce L₃-edge EXAFS spectra (Figure 3c), $\text{CeO}_{2-\delta}$ exhibits two main peaks at ≈ 2.01 Å for Ce–O and ≈ 3.65 Å for Ce–O–Ce bond. An obvious negative shift can be found in Ce L₃-edge R space of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ and $\text{Co}_3\text{O}_4/\text{CeO}_{2-\delta}$ with ≈ 1.95 Å for Ce–O, ≈ 3.60 Å ($\text{Co}_3\text{O}_4/\text{CeO}_{2-\delta}$) and ≈ 3.62 Å ($\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$) for Ce–O–Ce bond. Additionally, $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ and $\text{Co}_3\text{O}_4/\text{CeO}_{2-\delta}$ show a clear peak centered at ≈ 1.35 Å because of the interaction of Co and Ce between O. The Ce–O–Co bonding interaction can also be revealed by the Co K-edge EXAFS spectra (Figure 3d). Compared to the Co_3O_4 spinel structure, a stronger peak at ≈ 2.58 Å for the Co–O–Ce structure appeared in $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$, while the $\text{Co}_3\text{O}_4/\text{CeO}_{2-\delta}$ heterostructure just shows slightly positive shift for three main peaks. More importantly, combined with the least-squares EXAFS curve-fitting analysis (Figure S8, Table S6, Supporting Information), it can be concluded that Co substituted Ce atoms and formed $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ solid solution structure. The wavelet transform (WT) analysis also identifies the existence of both Ce–O, Ce–O–Ce, Co–O, and Co–O–Ce bonds (Figure 3e) in $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$. These above characterizations prove that Co atoms doped into the CeO_2 lattice can be stabilized and form Co–O₄ sites in the Co–O–Ce structure. Further, the existence of Co–O–Ce bonding enhanced the first coordination shell of Ce–O, which also contributes to the stability of the $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ in electrochemical reactions.

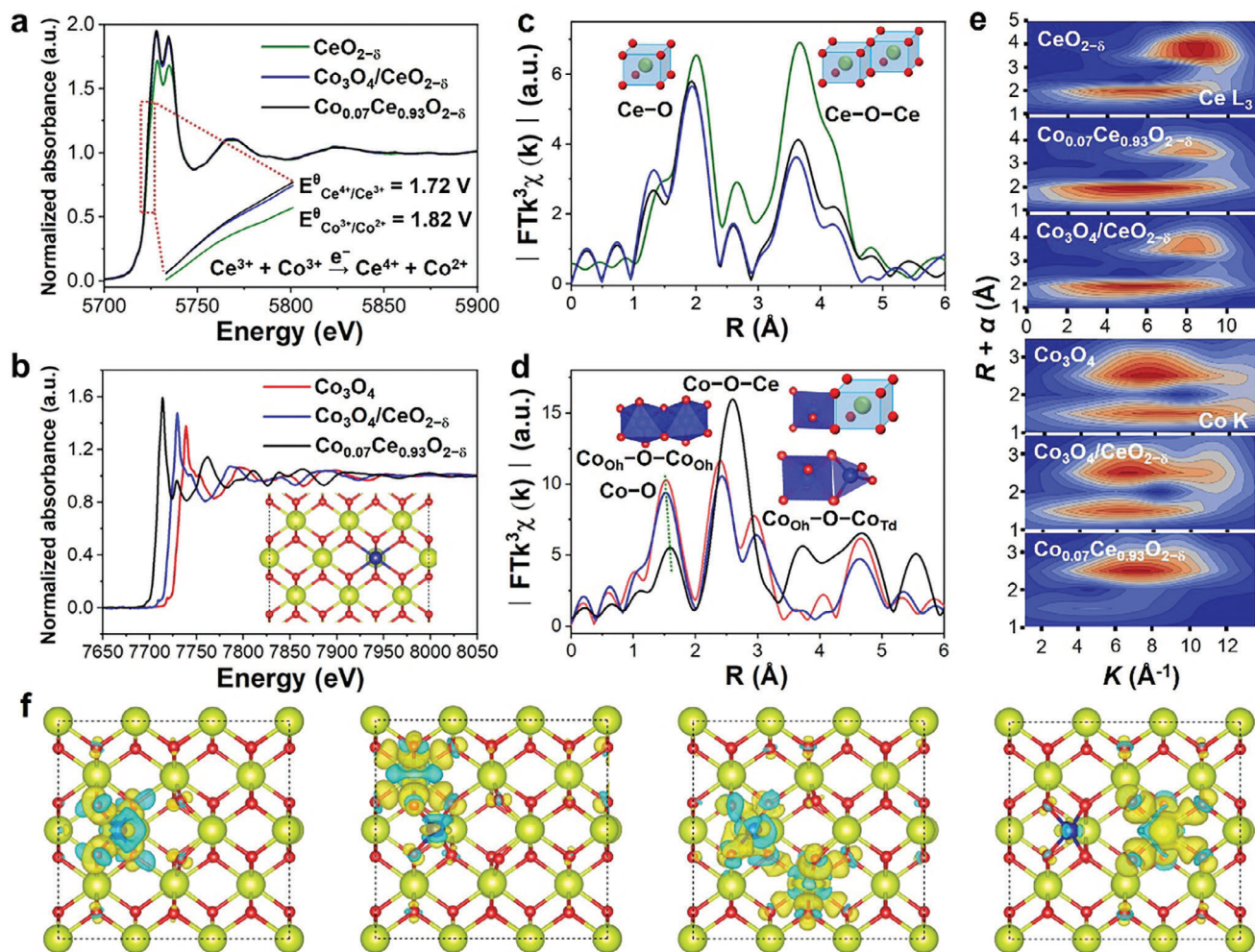


Figure 3. The normalized a) Ce L₃-edge, and b) Co K-edge EXAFS spectra for CeO_{2-δ}, Co₃O₄, Co_{0.07}Ce_{0.93}O_{2-δ}, and Co₃O₄/CeO_{2-δ}. c) Ce L₃-edge and d) Co K-edge FT-EXAFS in R space for CeO_{2-δ}, Co₃O₄, Co_{0.07}Ce_{0.93}O_{2-δ}, and Co₃O₄/CeO_{2-δ}. The fitting results for e) WT analysis of Ce L₃-edge and Co K-edge. f) The corresponding charge density differences of Co_{0.07}Ce_{0.93}O_{2-δ}.

Furthermore, X-ray photoelectron spectroscopy (XPS) was utilized to investigate the surface chemical states and interface charge transfer of the materials.^[38] XPS spectra revealed that the predominant peaks of CeO_{2-δ} corresponded to Ce⁴⁺ 3d_{5/2}, Ce⁴⁺ 3d_{3/2}, Ce³⁺ 3d_{5/2}, and Ce³⁺ 3d_{3/2}, with respective binding energy of 919.80, 902.50, 902.10, and 884.20 eV (Figure S9, Tables S3–S5 Supporting Information). Comparatively, the Co_{0.07}Ce_{0.93}O_{2-δ} solid solution and Co₃O₄/CeO_{2-δ} heterostructure exhibited slight shifts in the binding energies of Ce³⁺ 3d_{5/2} and 3d_{3/2} peaks toward higher values, whereas the binding energies of Ce⁴⁺ 3d_{5/2} and 3d_{3/2} peaks displayed a slight shift toward lower values. The Ce³⁺/Ce⁴⁺ peak area ratio decreased from 0.84 to 0.70 and 0.82, indicating partial oxidation of Ce³⁺ to Ce⁴⁺ in the presence of Co and the occurrence of charge transfer at the interface, consistent with the XANES data. Compared to CeO_{2-δ} and Co₃O₄, the O 1s XPS lattice oxygen peak of both Co_{0.07}Ce_{0.93}O_{2-δ} and Co₃O₄/CeO_{2-δ} exhibit positive and negative shifts confirming the electron transfer process between Co and Ce. Furthermore, the binding energy of Co 2p_{3/2} in Co_{0.07}Ce_{0.93}O_{2-δ} and Co₃O₄/CeO_{2-δ} shows a negative shift com-

pared to Co₃O₄, providing further evidence of electron transfer and electron coupling between Co and Ce. The charge density changes in Co_{0.07}Ce_{0.93}O_{2-δ} between the surface atoms and the atoms in the next layer (Co and Ce) of CeO_{2-δ} before and after Co substituting were further studied to evaluate the electron transition by DFT. The charge distribution of Ce atoms in pristine CeO_{2-δ} at the four positions is the same with the electrons of Ce and O transfer to the middle position (Figure S10, Supporting Information). However, the stronger bonding of Ce–O in the Co_{0.07}Ce_{0.93}O_{2-δ} solid solution can be found (Figure 3f). Then, we analyzed the differential charge of the two atoms of Co_{0.07}Ce_{0.93}O_{2-δ} and pristine CeO_{2-δ} (Figure S11, Supporting Information). The charge distribution around the two Ce atoms and O atoms on the surface of the original CeO_{2-δ} is uniform, and there is no charge offset phenomenon. However, when Co atoms replace Ce atoms, the charge distribution is uneven. The electrons around Ce and O atoms have a slight tendency to shift toward Co, which further illustrated that the Ce atoms could provide electrons to Co atoms in Co_{0.07}Ce_{0.93}O_{2-δ} solid solution.

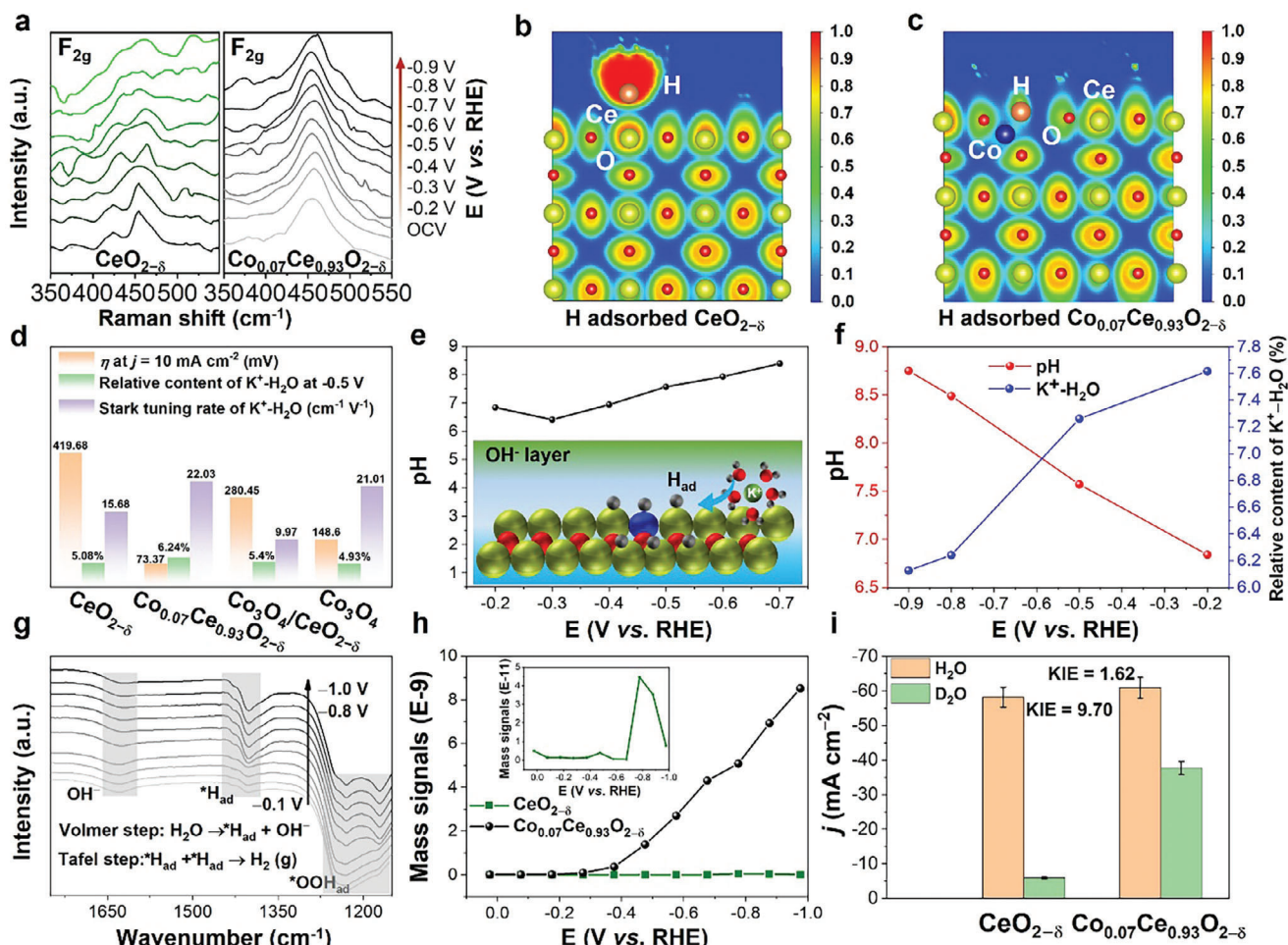


Figure 4. a) The in situ Raman spectra of CeO_{2-δ} and Co_{0.07}Ce_{0.93}O_{2-δ}. b,c) The ELF of H adsorption on CeO_{2-δ} and Co_{0.07}Ce_{0.93}O_{2-δ}. d) The influence of interfacial water on alkaline HER performance. e) Local pH of Co_{0.07}Ce_{0.93}O_{2-δ} in alkaline HER process. f) The Relationship between local pH and K⁺·H₂O. g) The in situ ATR-IR spectra of Co_{0.07}Ce_{0.93}O_{2-δ} for HER. h) The DEMS signals of CeO_{2-δ} and Co_{0.07}Ce_{0.93}O_{2-δ}. i) The KIE of CeO_{2-δ} and Co_{0.07}Ce_{0.93}O_{2-δ}.

Then, The HER performance of CeO_{2-δ}, Co_{0.07}Ce_{0.93}O_{2-δ} solid solution, Co₃O₄/CeO_{2-δ} heterostructure, and Co₃O₄ was further evaluated in alkaline media. As expected, Co_{0.07}Ce_{0.93}O_{2-δ} displays the best HER performance with the lowest overpotential (75.18 mV) than that of CeO_{2-δ} (419.68 mV), Co₃O₄/CeO_{2-δ} (280.45 mV), and Co₃O₄ (148.60 mV) at j = 10 mA cm⁻² (Figure S12, Supporting Information). Meanwhile, Co_{0.07}Ce_{0.93}O_{2-δ} annealing under 500 °C shows the best HER performance compared with the materials obtained at 300 and 700 °C (Figure S13, Supporting Information). By comparing the cyclic voltammetry, change-data-capture listing (C_{dl}), and electrochemical impedance spectroscopy of CeO_{2-δ} and Co_{0.07}Ce_{0.93}O_{2-δ}, it can be more intuitively observed that Co_{0.07}Ce_{0.93}O_{2-δ} has more excellent electrochemical properties (Figures S14–S16, Supporting Information). Therefore, Co_{0.07}Ce_{0.93}O_{2-δ} solid solution with 3d_{Co}–2p_O–4f_{Ce} orbital coupling optimized electronic structure shows excellent HER performance compared with other recently reported works (Table S7, Supporting Information).

Furthermore, the in situ spectra were used to confirm the catalysts' structure and adsorption intermedia in HER. First, the in

situ Raman spectra were used to study the structure of those catalysts in HER. As shown in Figure 4a, the characteristic vibrational peak of CeO_{2-δ} at ~452 cm⁻¹ for the F_{2g} peak decreased because the charge distribution in the Ce–O–Ce structure changed with enhanced *H_{ad} under increased HER potentials. Surprisingly, the F_{2g} peak for CeO₂ in Co_{0.07}Ce_{0.93}O_{2-δ} structure maintains under the same conditions demonstrating the Co substituting Ce atomic position in CeO_{2-δ} structure can further stabilize the charge structure under HER.^[39] Then, the DFT calculation also evidenced the H adsorption processes of CeO_{2-δ} and Co_{0.07}Ce_{0.93}O_{2-δ}. The results of electronic localization function (ELF) for pristine CeO_{2-δ} and Co_{0.07}Ce_{0.93}O_{2-δ} adsorption of H ions (Figure 4b,c). The maximum ELF value between Co and H is ~0.6, indicating a weak covalent-like nature of the Co–H bond,^[40] while the Ce–H bond has a larger maximum ELF value demonstrating a stronger adsorption capacity for H on the pristine CeO_{2-δ}, which is very unfavorable for the desorption of H. This in turn confirms that Co doping could effectively reduce the adsorption capacity of the overall material for H and could effectively improve the HER performance. Ad-

ditionally, in situ Raman spectra from 3000 to 3700 cm^{-1} of those catalysts (Figures S17, S18, Supporting Information) are assigned to the O–H stretching mode ($\nu_{\text{O-H}}$) of interfacial water with three distinct components of interfacial water, namely 4–HB·H₂O, 2–HB·H₂O, and K⁺·H₂O, respectively.^[41] The frequencies of adsorbate exhibit the vibrational Stark effect, and the steeper Stark tuning rate shows high sensitivity to the local environment of the electrode. In detail, Co_{0.07}Ce_{0.93}O_{2-δ} shows higher content of K⁺·H₂O and Stark tuning rate of (22.03 $\text{cm}^{-1} \text{V}^{-1}$) than those of CeO_{2-δ}, Co₃O₄, and Co₃O₄/CeO_{2-δ} (Figure 4d), demonstrating more free water on Co_{0.07}Ce_{0.93}O_{2-δ} interface. Therefore, the Co_{0.07}Ce_{0.93}O_{2-δ} solid solution structure optimized adsorbed K⁺·H₂O and reduced the OH⁻ ions coverage on the interfacial water layer, promoting HER processes because active sites can adsorb more proton from free water molecules, which is consistent with the Volmer step ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ad}} + \text{OH}^-$). The RRDE method was used to further study the relationship between interfacial free water and local pH on the Co_{0.07}Ce_{0.93}O_{2-δ} surface.^[42] Based on the negative correlation between local pH variation and Raman interface water (Figure 4e), namely the content of interface water decreases as the local pH increases, indicating that the presence of interface water is suppressed under high pH conditions. This negative correlation can be explained through the following mechanistic analysis. In a high pH environment, the concentration of hydroxide ions (OH⁻) is higher. These hydroxide ions react with hydrogen ions (H⁺) in the interface water, leading to the dissociation of water molecules and a decrease in free water content. Additionally, under high pH conditions, hydroxide ions may also react with other substances at the interface, forming hydrates or other compounds. These reactions may result in the transformation or depletion of interface water, thereby reducing the content of interface water. Therefore, based on the negative correlation between local pH variation and interface water, we can conclude that an increase in local pH under high pH conditions leads to a decrease in interface water (Figure 4f). This finding reveals the influence of local pH on the dynamic equilibrium of interface water, providing important clues for a deeper understanding of interfacial reactions and phenomena.

The in situ ATR-IR measurement further demonstrated the adsorption intermedia in HER.^[4] The in situ ATR-IR spectra of Co_{0.07}Ce_{0.93}O_{2-δ} show obvious *OOH adsorption (*OOH_{ad}) intermedia peaks with increased HER potentials (Figure 4g), which can be attributed to the first step, namely water dissociation (Volmer step: $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ad}} + \text{OH}^-$), for HER in alkaline media. The enhanced *H_{ad} peaks also confirmed the second step for HER, namely the Tafel step (*H_{ad} + *H_{ad} → H₂(g)), with a faster HER rate than that of CeO_{2-δ} under the same condition (Figure S19, Supporting Information). The in situ isotope-labeled differential electrochemical mass spectrometry (DEMS) tests were conducted in 1.0 M KOH–H₂O and KOH–D₂O solutions (Figures S20, S21, Supporting Information). It can be observed that CeO_{2-δ} and Co₃O₄/CeO_{2-δ} exhibit a decrease or leveling off of hydrogen with increased potentials due to the highly enhanced adsorption of *H on CeO_{2-δ} at high HER potentials (Figure S20, Supporting Information). Except for Co_{0.07}Ce_{0.93}O_{2-δ}, the other three materials produce similar amounts of HD and DD in KOH–D₂O solution, indicating the occurrence of both HD generation (H⁺/D⁺ exchange) and DD generation reactions in D₂O both co-existing (Figure S21, Supporting Information). This phenomenon sug-

gests Co_{0.07}Ce_{0.93}O_{2-δ} exhibits good HER activity in a wide potential window, and the rate of HER accelerates with higher overpotentials. The kinetic isotope effect (KIE) test was conducted (Figure 4i), and the KIE of CeO_{2-δ} is 9.70 exhibiting a significantly higher value than 1, indicating the Volmer step is the rate-determining step. Combined with DEMS, a substantial amount of HD gas was generated, suggesting the occurrence of H/D exchange and involvement of the Heyrovsky step during HER with the Volmer–Heyrovsky mechanism. However, the KIE of Co_{0.07}Ce_{0.93}O_{2-δ} is 1.62 exhibiting a value close to 1, indicating that the proton transfer step is not the rate-determining step. The substantial production of DD indicates that the Tafel step dominates the reaction and primarily follows the Volmer–Tafel mechanism.^[43] Therefore, Co substituting Ce in CeO_{2-δ} structure alters the HER mechanism of pure CeO_{2-δ}, which can be attributed to the enhanced proton coupling on Co_{0.07}Ce_{0.93}O_{2-δ} with the improved catalytic activity of HER. Additionally, the structure and morphology of Co_{0.07}Ce_{0.93}O_{2-δ} were maintained after long-term stability tests (Figure S22, Supporting Information).

The DFT methods were used to calculate the hydrogen adsorption Gibbs free energy (ΔG_{H^*}) and evaluate the HER activity by comparing the value of $|\Delta G_{\text{H}^*}|$ on different materials. The calculated ΔG_{H^*} on the CeO_{2-δ} is ≈ 2.55 eV (Figure 5a), which is higher than that of other solid solution catalysts. Notably, ΔG_{H^*} of Co_{0.07}Ce_{0.93}O_{2-δ} is only 0.36 eV, which is distinctly lower than Cr_{0.04}Ce_{0.96}O_{2-δ} (0.88 eV), Cu_{0.18}Ce_{0.82}O_{2-δ} (1.94 eV), Ni_{0.06}Ce_{0.94}O_{2-δ} (1.41 eV), and Zn_{0.12}Ce_{0.88}O_{2-δ} (2.47 eV), demonstrating transition metal substituting promotes H adsorption and desorption behaviors in HER. Interestingly, a volcano curve can be obtained based on the function between Bader net charge value (Figure S23, Supporting Information) and ΔG_{H^*} of pristine CeO_{2-δ} and M_xCe_{1-x}O_{2-δ} for HER (Figure 5b), the negative sign represents the loss of charge, in which Co_{0.07}Ce_{0.93}O_{2-δ} locates in the middle of the volcano curve and closest to the $\eta = 0$ V position, indicating that Co_{0.07}Ce_{0.93}O_{2-δ} has the most excellent HER catalytic performance. Then, the density of states (DOS, TDOS/PDOS) and Band of those materials were calculated with the Fermi level aligned at 0 eV. Compared to CeO_{2-δ}, Co_{0.07}Ce_{0.93}O_{2-δ} shows a decreased band gap, and an impurity energy level composed of Co–O is generated between the conduction band and the valence band (VB) (Figure 5c,d), which is beneficial to the transfer of electrons and significantly improve the HER properties.^[44] The intensity of band and DOS on the Co_{0.07}Ce_{0.93}O_{2-δ} near the VB increased compared to CeO_{2-δ}, suggesting conductivity increased after Co substituting Ce position. This phenomenon is also found in the DOS and band results of other solid solutions (Figure S24, Supporting Information) with increased conductivity. The ELF and 2D-charge density cross-section of those materials were further studied. The electron localization is reduced after Co, Cr, Cu, Ni, and Zn substituting Ce position in CeO_{2-δ} structure (Figure 5e,f; Figure S25, Supporting Information), indicating transition metal can effectively reduce the binding ability of atomic nuclei to electrons and enhance their mobility.^[45] This is very beneficial for the transfer of electrons in the catalytic process. We also found that the electron center shifted to the doping position, which further proved Ce can donate electrons to Co. The charge density of pristine CeO_{2-δ} is evenly distributed, while the charge density of Ce near Co in

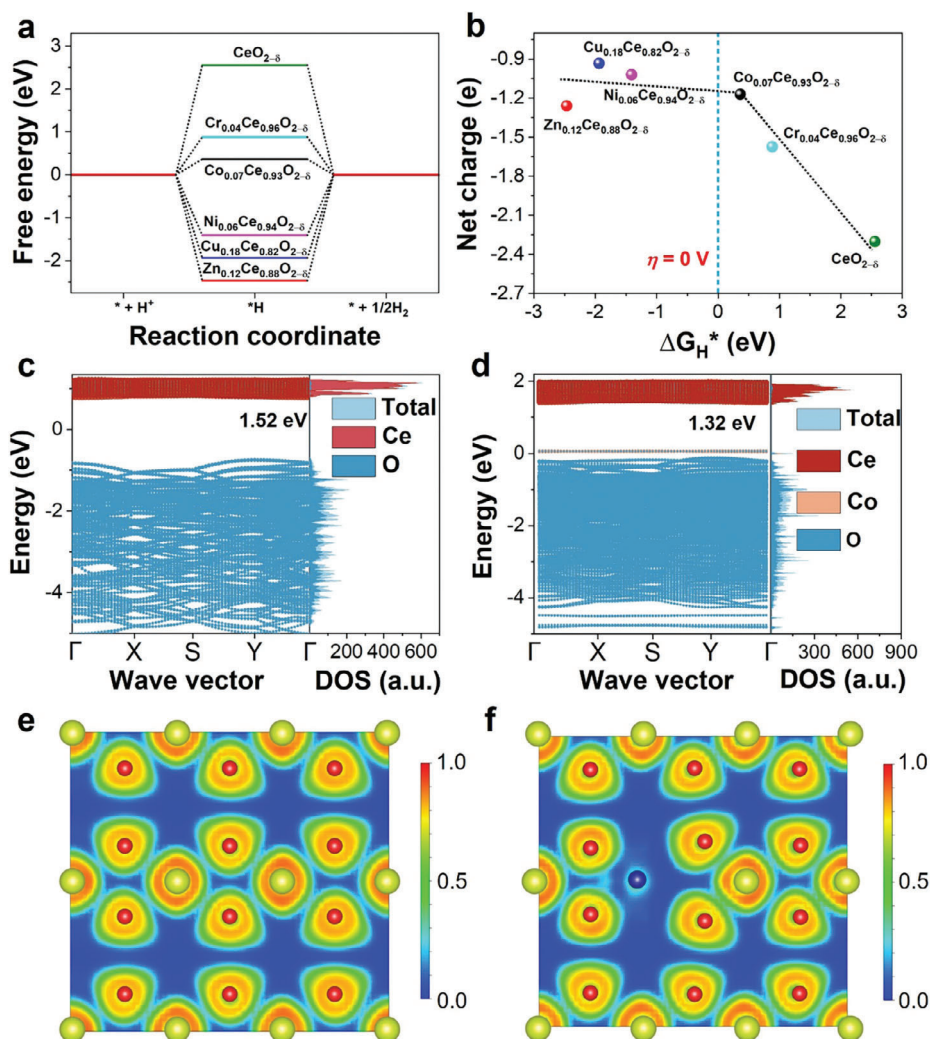


Figure 5. a) The calculated Gibbs free energy diagram (ΔG_{H^*}) for the hydrogen adsorption on the pristine $\text{CeO}_{2-\delta}$ and $\text{M}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$. b) The relationship between Bader net charge and ΔG_{H^*} of those materials. c,d) DOS and Band, and e,f) ELF of $\text{CeO}_{2-\delta}$ and $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$.

$\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ is significantly higher (Figure S26, Supporting Information), which further illustrates that the charge shift is consistent with the trend of ELF. Similarly, we also found that since the substituting atoms bind electrons less strongly than Ce atoms, the charge density around them is reduced.

We move on to the performance of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ for both actual and alkaline seawater splitting (Figures S27,S28, Supporting Information). The catalytic performance for HER was evaluated by using the LSV in alkaline seawater (1.0 M KOH). In an alkaline seawater system, compared with commercial Pt/C (20%), $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ shows lower η at higher current density (larger than 200 mA cm^{-2}), but $\text{CeO}_{2-\delta}$ shows negligible HER activity under the same condition (Figure 6a). The turnover frequencies (TOF), responding to the intrinsic activity per site, are calculated based on the hypothesis all Co—O—Ce active centers can access the reaction. The TOF of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ is 0.21 s^{-1} at η of 0.2 V (Figure 6b). Meanwhile, $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ also shows higher mass activity of 64.15 A mg^{-1} at 100 mV closer to that of Pt/C (20%) (Figure 6c). Additionally, $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ displays excellent HER

stability for 300 h under different current densities (10, 50, and 100 mA cm^{-2}) in alkaline seawater (Figure 6d), while Pt/C (20%) only reaches 25 h (Figure S29, Supporting Information), suggesting $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ has superior durability at high current densities in alkaline seawater splitting. The electrocatalytic performances of $\text{CeO}_{2-\delta}$, $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$, and Pt/C (20%) were further evaluated and compared using a radar chart analysis (Figure 6e) and other recently reported works (Table S8, Supporting Information), demonstrating $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ is a promising catalyst for alkaline seawater splitting. Moreover, the DEMS measures further indicate that H_2 is the only product without producing any other things in $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ catalyzed alkaline seawater HER (Figure 6f).

Finally, the AEMWE device was further developed based on $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ as cathode and nickel-iron-based layered double-metal hydroxide (NiFe LDH) as the anode (Figure 6g).^[46] Before testing, the membrane electrode assembly (MEA) was activated by alkaline seawater flow for 20 min to ensure adequate membrane hydration. At 25°C , the MEA constructed with

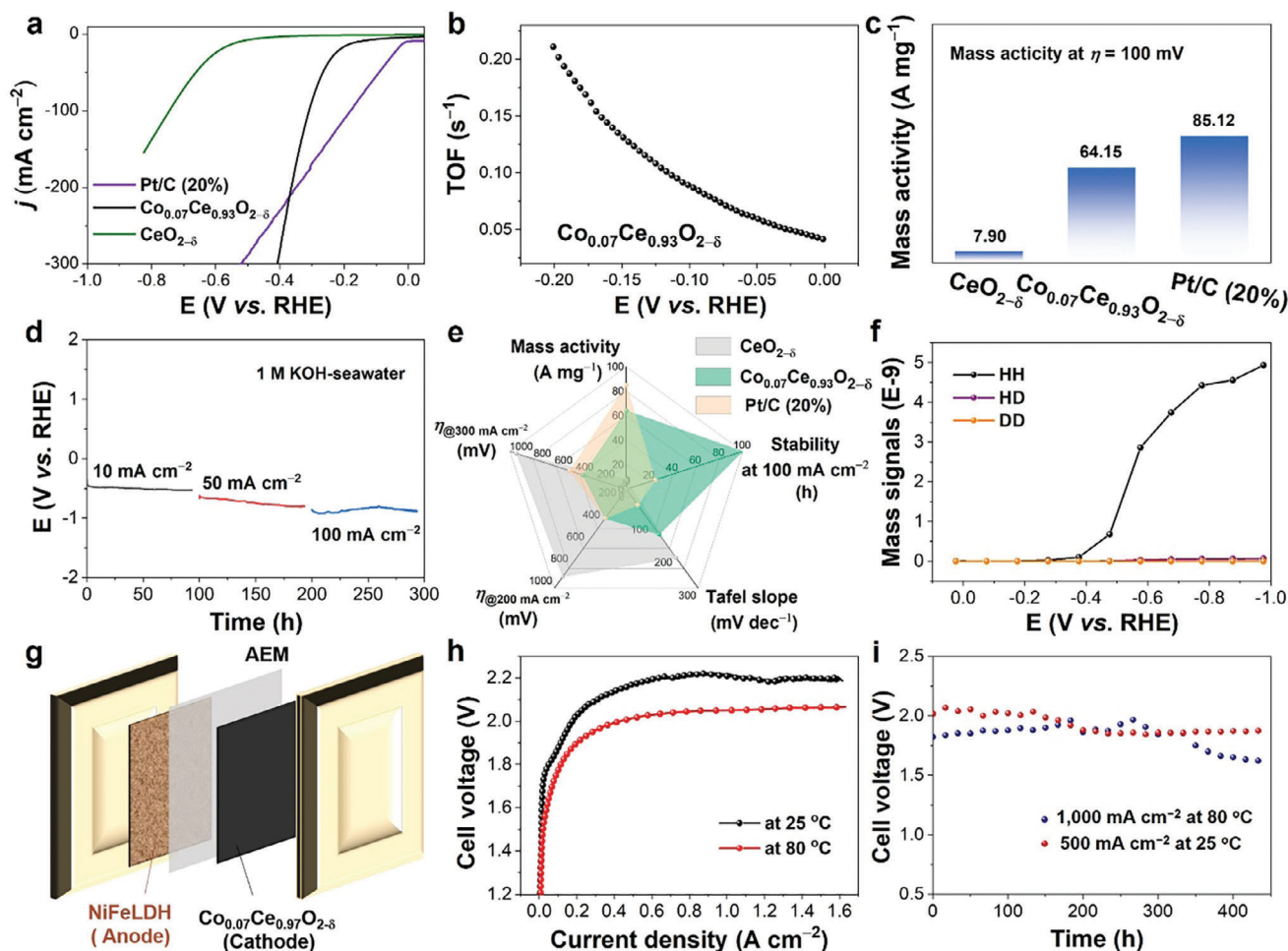


Figure 6. a) The LSV polarization curves of $\text{CeO}_{2-\delta}$, $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ and Pt/C (20%). b) TOF, and c) mass activity of those materials. d) The long-term stability of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ in 1.0 M alkaline seawater. e) The Radar chart of $\text{CeO}_{2-\delta}$, $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ and Pt/C (20%). f) The DEMS signals of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ in 1.0 M alkaline seawater. g) The diagram of the membrane electrode schematic. h) LSV, and i) stability of $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ and NiFeLDH fabricated device for seawater splitting in alkaline media.

the optimized $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ achieved the current density of 1000 mA cm⁻² at a cell voltage of 2.05 V. Impressively, when increasing the temperature to 80 °C, the cell voltage significantly decreased to 1.86 V to get the same current density (Figure 6h), demonstrating the excellent high-temperature activity of this catalyst. In addition, the $\text{Co}_{0.07}\text{Ce}_{0.93}\text{O}_{2-\delta}$ based alkaline seawater splitting device shows excellent long-term stability for 450 h at 500 and 1000 mA cm⁻² with a cell voltage of ≈ 1.89 and ≈ 1.75 V at 25 and 80 °C (Figure 6i), indicating its outstanding durability under the operating conditions evaluated.

Supporting Information

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

Acknowledgements

G.S. and Y.H. contributed equally to this work. This work was funded by the National Key R&D Program of China (2021YFA1501101), the National

Natural Science Foundation of China (NSFC) (Nos. 22471111, 22201115, 2221001, 21931001, and 22271124), the Special Fund Project of Guiding Scientific and Technological Innovation Development of Gansu Province (2019ZX-04), the Postdoctoral Fellowship Program of CPSF under Grant Number GZB20240283, and the 111 Project (B20027), Natural Science Foundation of Gansu Province (24JRR387), the Science and Technology Major Plan of Gansu Province (23ZDGA012), as well as by the Fundamental Research Funds for the Central Universities (Izujbky-2023-eyt03).

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 supplementary material of this article.

Keywords

alkaline water splitting, $\text{CeO}_{2-\delta}$, electronic structures, HER, solid solutions

Received: September 25, 2024
Revised: November 13, 2024
Published online: December 2, 2024

- [1] J. A. Turner, *Science* **2004**, 305, 972.
- [2] Y. Xu, V. Ramanathan, D. G. Victor, *Nature* **2018**, 564, 30.
- [3] Q. Hu, K. Gao, X. Wang, H. Zheng, J. Cao, L. Mi, Q. Huo, H. Yang, J. Liu, C. He, *Nat. Commun.* **2022**, 13, 3958.
- [4] K. Sun, X. Wu, Z. Zhuang, L. Liu, J. Fang, L. Zeng, J. Ma, S. Liu, J. Li, R. Dai, X. Tan, K. Yu, D. Liu, W.-C. Cheong, A. Huang, Y. Liu, Y. Pan, H. Xiao, C. Chen, *Nat. Commun.* **2022**, 13, 6260.
- [5] Z.-Y. Wu, F.-Y. Chen, B. Li, S.-W. Yu, Y. Z. Finrock, D. M. Meira, Q.-Q. Yan, P. Zhu, M.-X. Chen, T.-W. Song, Z. Yin, H.-W. Liang, S. Zhang, G. Wang, H. Wang, *Nat. Mater.* **2023**, 22, 100.
- [6] S. Li, B. Chen, Y. Wang, M.-Y. Ye, P. A. van Aken, C. Cheng, A. Thomas, *Nat. Mater.* **2021**, 20, 1240.
- [7] J. Suntivich, K. J. May, H. A. Gasteiger, J. B. Goodenough, Y. Shao-Horn, *Science* **2011**, 334, 1383.
- [8] F. Wang, P. Zou, Y. Zhang, W. Pan, Y. Li, L. Liang, C. Chen, H. Liu, S. Zheng, *Nat. Commun.* **2023**, 14, 6019.
- [9] Z. He, J. Zhang, Z. Gong, H. Lei, D. Zhou, N. Zhang, W. Mai, S. Zhao, Y. Chen, *Nat. Commun.* **2022**, 13, 2191.
- [10] Z.-F. Huang, J. Song, Y. Du, S. Xi, S. Dou, J. M. V. Nsanzimana, C. Wang, Z. J. Xu, X. Wang, *Nat. Energy* **2019**, 4, 329.
- [11] X.-L. Zhang, P.-P. Yang, Y.-R. Zheng, Y. Duan, S.-J. Hu, T. Ma, F.-Y. Gao, Z.-Z. Niu, Z.-Z. Wu, S. Qin, L.-P. Chi, X. Yu, R. Wu, C. Gu, C.-M. Wang, X.-S. Zheng, X. Zheng, J.-F. Zhu, M.-R. Gao, *Angew. Chem., Int. Ed.* **2021**, 60, 6553.
- [12] J. Diao, Y. Qiu, S. Liu, W. Wang, K. Chen, H. Li, W. Yuan, Y. Qu, X. Guo, *Adv. Mater.* **2020**, 32, 1905679.
- [13] S. Niu, W.-J. Jiang, Z. Wei, T. Tang, J. Ma, J.-S. Hu, L.-J. Wan, *J. Am. Chem. Soc.* **2019**, 141, 7005.
- [14] Z. Zhu, Y. Lin, P. Fang, M. Wang, M. Zhu, X. Zhang, J. Liu, J. Hu, X. Xu, *Adv. Mater.* **2024**, 36, 2307035.
- [15] R. Subbaraman, D. Tripkovic, D. Strmcnik, K.-C. Chang, M. Uchimura, A. P. Paulikas, V. Stamenkovic, N. M. Markovic, *Science* **2011**, 334, 1256.
- [16] C. Wan, Z. Zhang, J. Dong, M. Xu, H. Pu, D. Baumann, Z. Lin, S. Wang, J. Huang, A. H. Shah, X. Pan, T. Hu, A. N. Alexandrova, Y. Huang, X. Duan, *Nat. Mater.* **2023**, 22, 1022.
- [17] L. Zeng, Y. Chen, M. Sun, Q. Huang, K. Sun, J. Ma, J. Li, H. Tan, M. Li, Y. Pan, Y. Liu, M. Luo, B. Huang, S. Guo, *J. Am. Chem. Soc.* **2023**, 145, 17577.
- [18] M. Li, Z. Zhao, Z. Xia, M. Luo, Q. Zhang, Y. Qin, L. Tao, K. Yin, Y. Chao, L. Gu, W. Yang, Y. Yu, G. Lu, S. Guo, *Angew. Chem., Int. Ed.* **2021**, 60, 8243.
- [19] H. Rong, S. Ji, J. Zhang, D. Wang, Y. Li, *Nat. Commun.* **2020**, 11, 5884.
- [20] Y. Gao, Y. Xue, H. Wu, S. Chen, X. Zheng, C. Xing, Y. Li, *J. Am. Chem. Soc.* **2024**, 146, 10573.
- [21] H. Lei, Q. Wan, S. Tan, Z. Wang, W. Mai, *Adv. Mater.* **2023**, 35, 2208209.
- [22] K. Qi, X. Cui, L. Gu, S. Yu, X. Fan, M. Luo, S. Xu, *Nat. Commun.* **2019**, 10, 5231.
- [23] Y. Yao, Y. Zhu, C. Pan, C. Wang, S. Hu, W. Xiao, X. Chi, Y. Fang, J. Yang, H. Deng, S. Xiao, J. Li, Z. Luo, Y. Guo, *J. Am. Chem. Soc.* **2021**, 143, 8720.
- [24] Y. Luo, Z. Zhang, F. Yang, J. Li, Z. Liu, W. Ren, S. Zhang, B. Liu, *Energy Environ. Sci.* **2021**, 14, 4610.
- [25] R. Schmitt, A. Nenning, O. Kraynis, R. Korobko, A. I. Frenkel, I. Lubomirsky, S. M. Haile, J. L. M. Rupp, *Chem. Soc. Rev.* **2020**, 49, 554.
- [26] X. Wang, C. Sun, F. He, E. Liu, C. He, C. Shi, J. Li, J. Sha, S. H. Ji, L. Ma, N. Zhao, *ACS Appl. Mater. Interfaces* **2019**, 11, 32460.
- [27] T. Montini, M. Melchionna, M. Monai, P. Fornasiero, *Chem. Rev.* **2016**, 116, 5987.
- [28] B. Zheng, J. Fan, B. Chen, X. Qin, J. Wang, F. Wang, R. Deng, X. Liu, *Chem. Rev.* **2022**, 122, 5519.
- [29] J. Xia, H. Zhao, B. Huang, L. Xu, M. Luo, J. Wang, F. Luo, Y. Du, C.-H. Yan, *Adv. Funct. Mater.* **2020**, 30, 1908367.
- [30] L. Wang, H. Zhou, J. Hu, B. Huang, M. Sun, B. Dong, G. Zheng, Y. Huang, Y. Chen, L. Li, Z. Xu, N. Li, Z. Liu, Q. Chen, L.-D. Sun, C.-H. Yan, *Science* **2019**, 363, 265.
- [31] M. Wang, N. Shang, W. Gao, X. Cheng, S. Gao, C. Wang, *Fuel* **2023**, 354, 129433.
- [32] P. Barnes, Y. Zuo, K. Dixon, D. Hou, S. Lee, Z. Ma, J. G. Connell, H. Zhou, C. Deng, K. Smith, E. Gabriel, Y. Liu, O. O. Maryon, P. H. Davis, H. Zhu, Y. Du, J. Qi, Z. Zhu, C. Chen, Z. Zhu, Y. Zhou, P. J. Simmonds, A. E. Briggs, D. Schwartz, S. P. Ong, H. Xiong, *Nat. Mater.* **2022**, 21, 795.
- [33] S. Ning, M. Li, X. Wang, D. Zhang, B. Zhang, C. Wang, D. Sun, Y. Tang, H. Li, K. Sun, G. Fu, *Angew. Chem., Int. Ed.* **2023**, 62, e202314565.
- [34] J. Yin, Q. Fan, Y. Li, F. Cheng, P. Zhou, P. Xi, S. Sun, *J. Am. Chem. Soc.* **2016**, 138, 14546.
- [35] P. Nachimuthu, W.-C. Shih, R.-S. Liu, L.-Y. Jang, J.-M. Chen, *J. Solid State Chem.* **2000**, 149, 408.
- [36] W.-Z. Yu, W.-W. Wang, S.-Q. Li, X.-P. Fu, X. Wang, K. Wu, R. Si, C. Ma, C.-J. Jia, C.-H. Yan, *J. Am. Chem. Soc.* **2019**, 141, 17548.
- [37] J. S. Elias, M. Risch, L. Giordano, A. N. Mansour, Y. Shao-Horn, *J. Am. Chem. Soc.* **2014**, 136, 17193.
- [38] G. Zhao, G. Hai, P. Zhou, Z. Liu, Y. Zhang, B. Peng, W. Xia, X. Huang, G. Wang, *Adv. Funct. Mater.* **2023**, 33, 2213170.
- [39] T.-X. Huang, X. Cong, S.-S. Wu, J.-B. Wu, Y.-F. Bao, M.-F. Cao, L. Wu, M.-L. Lin, X. Wang, P.-H. Tan, B. Ren, *Nat. Catal.* **2024**, 7, 646.
- [40] B. Wang, Q. Lu, Y. Ge, K. Zhang, W. Xie, W.-M. Liu, Y. Liu, *Phys. Rev. B* **2017**, 96, 134116.
- [41] X. Chen, X.-T. Wang, J.-B. Le, S.-M. Li, X. Wang, Y.-J. Zhang, P. Radjenovic, Y. Zhao, Y.-H. Wang, X.-M. Lin, J.-C. Dong, J.-F. Li, *Nat. Commun.* **2023**, 14, 5289.
- [42] Y. Yokoyama, K. Miyazaki, Y. Miyahara, T. Fukutsuka, T. Abe, *ChemElectroChem* **2019**, 6, 4750.
- [43] J. Huang, H. Sheng, R. D. Ross, J. Han, X. Wang, B. Song, S. Jin, *Nat. Commun.* **2021**, 12, 3036.
- [44] D. L. R. Smith, S. M. Prevot, D. R. Fagan, S. Trudel, P. C. Berlinguette, *J. Am. Chem. Soc.* **2013**, 135, 11580.
- [45] W. Chen, X. Zhu, W. Wei, H. Chen, T. Dong, R. Wang, M. Liu, K. Ostrikov, P. Peng, S.-Q. Zang, *Small* **2023**, 19, 2304294.
- [46] L. Zeng, Z. Zhao, Q. Huang, C. Zhou, W. Chen, K. Wang, M. Li, F. Lin, H. Luo, Y. Gu, L. Li, S. Zhang, F. Lv, G. Lu, M. Luo, S. Guo, *J. Am. Chem. Soc.* **2023**, 145, 21432.