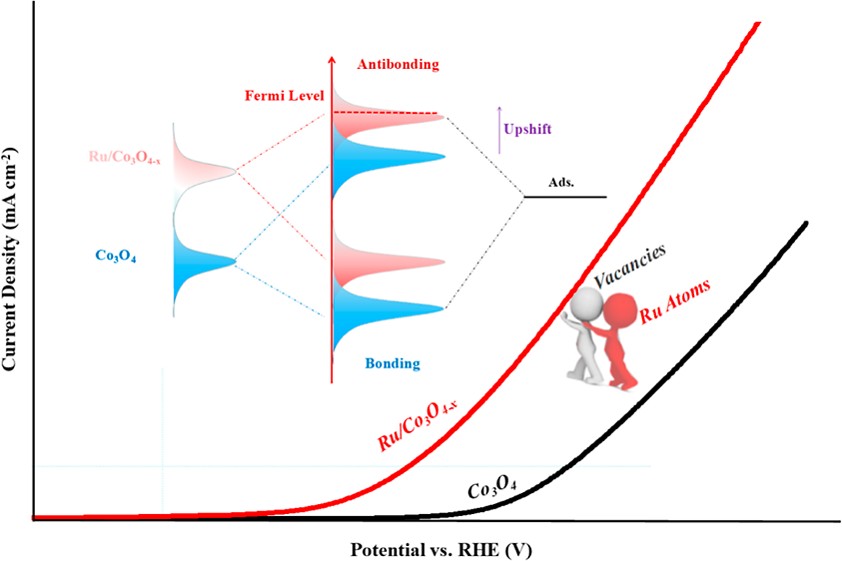


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**In Situ Immobilizing Atomically Dispersed Ru on Oxygen-Defective Co3O4 for Efficient Oxygen Evolution**

Research Article

[Cheng-Zong Yuan,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Cheng-Zong%2BYuan%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf)∇ [Shuo Wang,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Shuo%2BWang%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf)∇ [Kwan San Hui,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Kwan%2BSan%2BHui%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf)[\*](#_bookmark6) [Kaixi Wang,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Kaixi%2BWang%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf) [Junfeng Li,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Junfeng%2BLi%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf) [Haixing](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Haixing%2BGao%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf) [Gao,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Chenyang%2BZha%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf) [Chenyang Zha,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Chenyang%2BZha%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf) [Xiaomeng Zhang,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Xiaomeng%2BZhang%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf) [Duc Anh Dinh,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Duc%2BAnh%2BDinh%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf) [Xi-Lin Wu,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Xi-Lin%2BWu%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf) [Zikang Tang,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Zikang%2BTang%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf) [Jiawei Wan,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Jiawei%2BWan%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf)[\*](#_bookmark6) [Zongping Shao,](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Zongping%2BShao%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf)[\*](#_bookmark6) [and Kwun Nam Hui](https://pubs.acs.org/action/doSearch?field1=Contrib&text1=%22Kwun%2BNam%2BHui%22&field2=AllField&text2&publication&accessType=allContent&Earliest&ref=pdf)[\*](#_bookmark6)



ABSTRACT: The synergistic regulation of the electronic structures of transition-metal oxide-based catalysts via oxygen vacancy defects and single- atom doping is efficient to boost their oxygen evolution reaction (OER) performance, which remains challenging due to complex synthetic procedures. Herein, a facile defect-induced in situ single-atom deposition strategy is developed to anchor atomically dispersed Ru single-atom onto oxygen vacancy-rich cobalt oxides (Ru/Co3O4−*x*) based on the spontaneous redox reaction between Ru3+ ions and nonstoichiometric Co3O4−*x*. Accordingly, the as-prepared Ru/Co3O4−*x* electrocatalyst with the coex-

istence of oxygen vacancies and Ru atoms exhibits excellent performances

toward OER with a low overpotential of 280 mV at 10 mA cm−2, a small Tafel slope value of 86.9 mV dec−1, and good long-term stability in alkaline media. Furthermore, density functional theory calculations uncover that

oxygen vacancy and atomically dispersed Ru could synergistically tailor electron decentralization and d-band center of Co atoms, further optimizing the adsorption of oxygen-based intermediates (\*OH, \*O, and \*OOH) and reducing the reaction barriers of OER. This work proposes an available strategy for constructing electrocatalysts with abundant oxygen vacancies and atomically dispersed noble metal and presents a deep understanding of synergistic electronic engineering of transition-metal-based catalysts to boost oxygen evolution.

KEYWORDS: *defect-induced, in situ deposition strategy, oxygen vacancy defects, single-atom doping, electron decentralization, oxygen evolution reaction*

# INTRODUCTION

Sustainable energy conversion and storage technologies, such as electrocatalytic water electrolysis and rechargeable metal− air batteries, have been regarded as promising pathways for satisfying the global growing appetite for energy and ameliorating the rising environmental problems.[1](#_bookmark7)−[3](#_bookmark7) However, these energy-based technologies are severely constrained by the kinetically sluggish oxygen evolution reaction (OER) because of its complex four-electron-transfer steps.[4](#_bookmark7)−[6](#_bookmark7) Efficient and durable OER electrocatalysts are urgently required for accelerating reaction rate and reducing reaction barrier. Generally, noble metal-based materials (e.g., IrO2 and RuO2) can display superior OER activities; however, scarcity, high price, and instability restrict their practical applications.[7](#_bookmark7),[8](#_bookmark7) On this account, considerable efforts have been devoted to developing low-cost OER catalysts to replace noble metal- based materials, such as phosphides, chalcogenides, and hydro(oxy)oxides.[9](#_bookmark7)−[12](#_bookmark7) However, their activities and stabilities are still insufficient for practical applications. Therefore, the regulation of their electronic structures is a meaningful task to

boost the electrocatalytic performances and enhance the stabilities of transition-metal-based OER electrocatalysts.

Introducing atomically dispersed noble metals into tran- sition-metal-based nanomaterials has been one potential approach to regulate their electronic structures and boost the catalytic performance. For instance, atomically dispersed Pt atoms were anchored onto defective CoSe2−*x* with Pt−Co−Se moieties via the plasma-photochemical strategy, and an as- prepared CoSe2−*x*-Pt electrocatalyst with optimal electronic structures could exhibit superior OER performance.13 In addition, atomically dispersed Ru species on different PtCu alloys were fabricated by the acid etching and electrochemical leaching approaches, which can also display excellent OER

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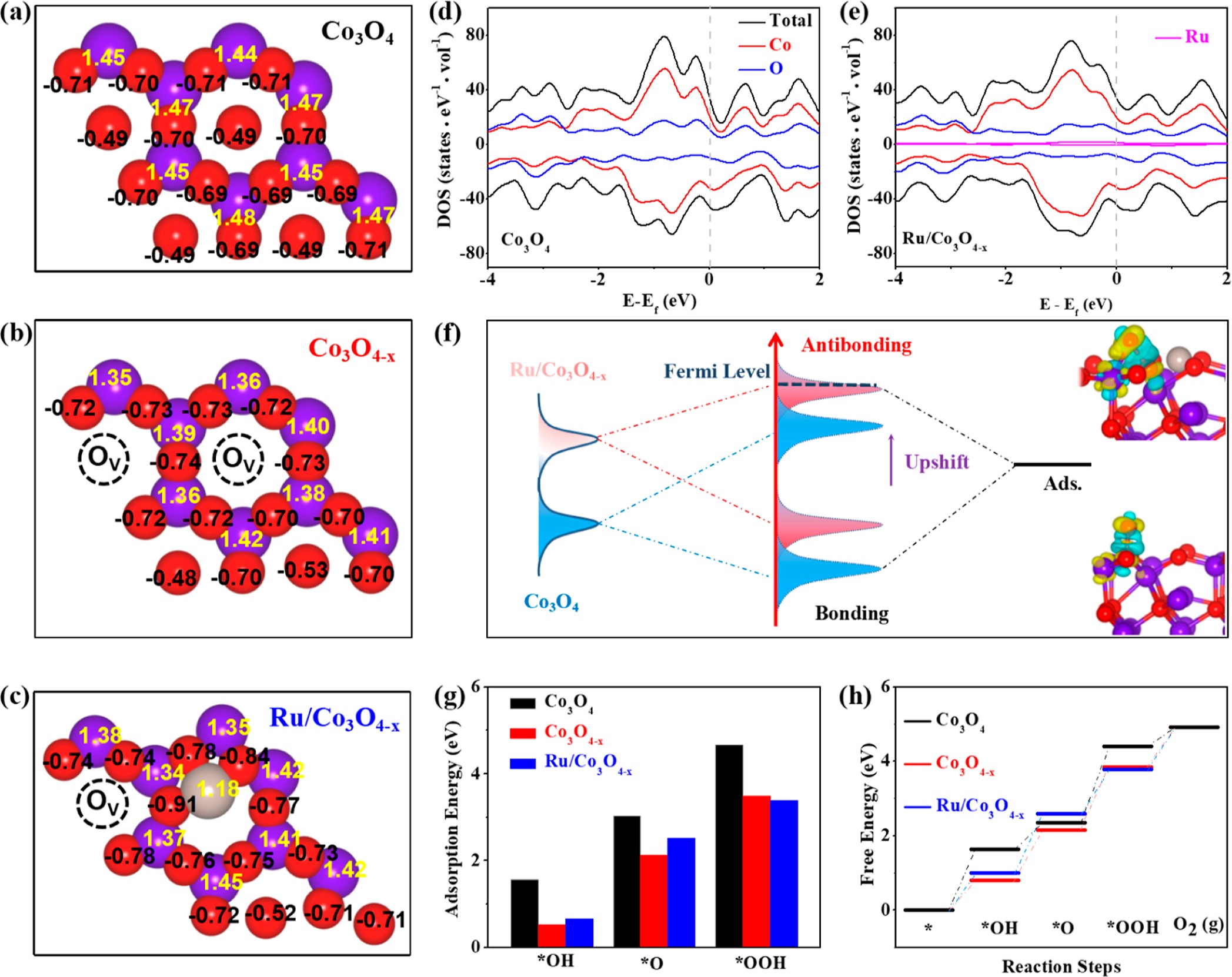


Figure 1. (a) Bader charge numbers of Co3O4, (b) Co3O4−*x*, and (c) Ru/Co3O4−*x*; (d) DOS of Co3O4 and (e) Ru/Co3O4−*x*; (f) d-band center of Co3O4 and Ru/Co3O4−*x*; and (g) calculated adsorption energies of \*OH, \*O, and \*OOH on Co3O4, Co3O4−*x* and Ru/Co3O4−*x*. (h) Free energy diagrams of OER over Co3O4, Co3O4−*x*, and Ru/Co3O4−*x*.

activities.14 Unfortunately, synthetic methods of introducing

boosting the OER properties. More importantly, oxygen

atomically dispersed metal sites into substrate materials are relatively difficult to execute because isolated metal atoms tend to migrate and aggregate during the synthetic process. Thus, developing a facile and efficient synthetic strategy to introduce atomically dispersed metal centers into transition-metal-based electrocatalysts is of great significance in tuning their electronic structures, further enhancing catalytic performances.

Moreover, the selective construction of vacancy defects is promising to regulate the electronic structures and boost the electrocatalytic activities of transition-metal-based cata- lysts.[15](#_bookmark7)−[17](#_bookmark7) For example, Xu et al. synthesized an efficient

vacancy defects in transition-metal oxides can result in low valence states of metal sites and high electron concentrations, which could react with the oxidative noble-metal ions at room temperature.[19](#_bookmark7)−[21](#_bookmark7) Inspired by this phenomenon, we propose that atomically dispersed metal atoms can be directly anchored onto defective transition-metal-based substrates through this in situ strategy even without the use of any reducing or stabilizing agents.

In this work, low-cost cobalt oxide (Co3O4) was selected to be an OER alternative electrocatalyst because of its intrinsic activity. One facile in situ strategy was developed to introduce

Co3O4 catalyst with abundant oxygen vacancy defects using the

atomically dispersed Ru into oxygen-defective Co3O4 (Ru/

plasma-engraving method, which could exhibit better OER performance than pristine Co3O4.16 Zheng et al. revealed that

Co3O4−*x*) via a spontaneous redox reaction between Ru3+ and nonstoichiometric Co3O4−*x* based on the weak reducing power

due to the existence of oxygen vacancies, new states were

of oxygen vacancy-rich cobalt oxide (Co3O4−*x*). Experimental

formed in the Co3O4 band gap, and electrons associated with Co−O bonds could be delocalized, thereby finally resulting in high conductivity and remarkable catalytic activities.18 According to the aforementioned findings, vacancy defects and single-atom doping could be highly effective in regulating electronic structures of the electrocatalysts synergistically and

characterization demonstrated that Ru/Co3O4−*x* coexists with oxygen vacancy defects, and atomically dispersed Ru atoms

were obtained successfully. Meanwhile, superior performance toward OER was achieved over the as-prepared Ru/Co3O4−*x* electrocatalyst with a low overpotential at 10 mA cm−2, a small Tafel slope value, as well as excellent long-term stability in the

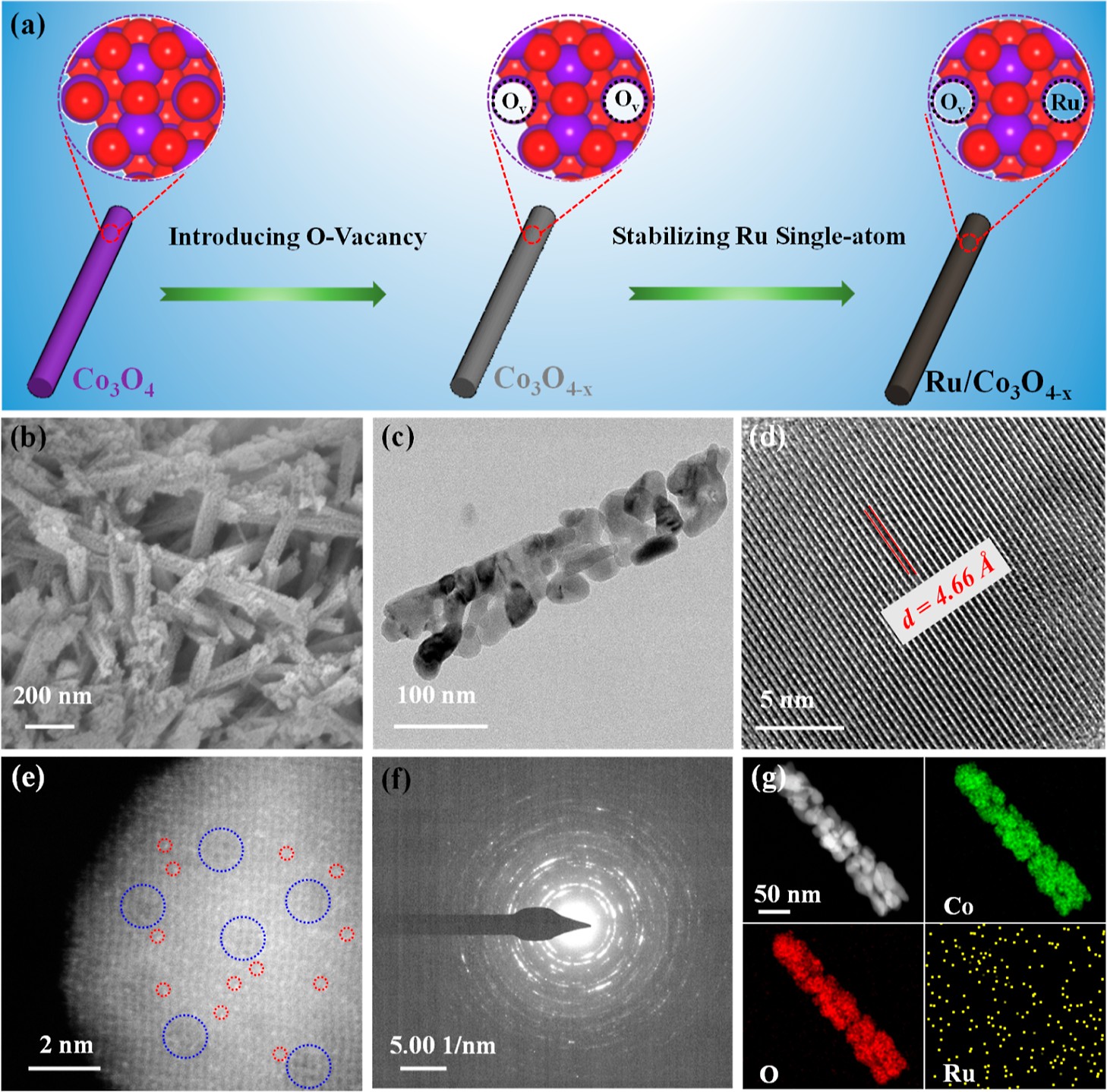


Figure 2. (a) Illustration of preparing Ru/Co3O4−*x* electrocatalyst via the defect-induced in situ synthesis strategy. Morphology characterization of as-prepared Ru/Co3O4−*x* sample: (b) SEM image, (c) TEM image, (d) HRTEM image, (e) HAADF−STEM image, (f) SAED pattern, and (g) STEM and corresponding elemental mapping images of the as-obtained Ru/Co3O4−*x* electrocatalyst.

1 M KOH electrolyte. Furthermore, the density functional however, electron redistribution is observed after introducing

theory (DFT) revealed oxygen vacancy and atomically oxygen vacancies and Ru atoms. [Figure 1](#_bookmark0)b shows that the

dispersed Ru could result in the electronic decentralization of Co3O4, tuned d-band center, optimized intermediate (\*OH,

\*O, and \*OOH) adsorption, and reduced reaction barriers of OER.

# RESULTS AND DISCUSSION

Spin-polarized DFT calculations were first carried out to theoretically verify the feasibility of anchoring atomically

oxygen vacancy makes electrons delocalized around the Co atoms and accumulate around the oxygen vacancy, and the extent of electron delocalization around the Co atoms is further enhanced after loading Ru atoms ([Figure 1](#_bookmark0)c). Accordingly, related effects were observed on their DOS due to the electron redistribution and the improved charge distribution asymmetry degrees ([Figure 1](#_bookmark0)d,e). Based on the calculated DOS, the d-band center value of the perfect Co3O4

dispersed Ru onto oxygen vacancy-rich Co3O4−*x* via this

is located at −1.62 eV. After introducing oxygen vacancies and

defect-induced in situ synthesis strategy. According to a previous study,13 the mimetic structures of Co3O4−*x* were constructed via removing two O atoms from a perfect Co3O4 model, and Ru/Co3O4−*x* was formed by loading one Ru atom

Ru atoms, the d-band center increased to −1.55 eV ([Figure](#_bookmark0) [1](#_bookmark0)f). The d-band center theory reveals that substrates with high electron density near the Fermi level are favorable for oxygen- based species adsorbate adsorption.[22](#_bookmark7),[23](#_bookmark7) Moreover, the Sabatier

to the oxygen vacancy. The corresponding simulative

principle indicates that an extremely strong interaction

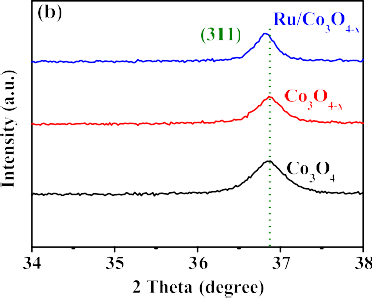
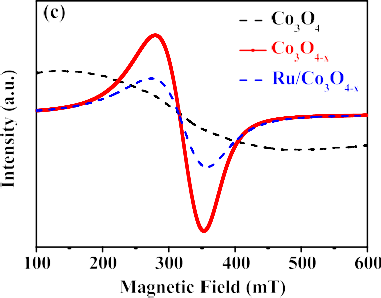
configurations of Co3O4, Co3O4−*x*, and Ru/Co3O4−*x* are

between active centers and oxygen-based species can be

shown in [Figure S1](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf). As expected, the formation energy of Ru/Co3O4−*x* is calculated to be −8.51 eV ([Figure S2](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf)), which is lesser than 0 eV, thereby confirming the relative stability of Ru/Co3O4−*x* and the feasibility of this defect-induced in situ synthetic strategy. To explore the roles of oxygen vacancies and Ru atoms in improving the OER activities of Co3O4, Bader charge and density of states (DOS) were also conducted. [Figure 1](#_bookmark0)a,b, and 1c displays Bader charge numbers of Co3O4, Co3O4−*x*, and Ru/Co3O4−*x*, respectively. The electron distribution in the perfect Co3O4 model is almost symmetric;

unbeneficial for the product desorption, whereas a weak interaction is unfavorable for the reactant activation. There- fore, the adsorption energies over Co3O4, Co3O4−*x*, and Ru/ Co3O4−*x* were also conducted. The adsorption configurations and related energies of oxygen-based species during OER are shown in [Figures S3](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf) and [1](#_bookmark0)g, respectively. The adsorption energies of \*OH over Co3O4 and Ru/Co3O4−*x* are 1.56 and

0.66 eV, respectively. Similarly, the adsorption energies of \*O and \*OOH over Co3O4 and Ru/Co3O4−*x* are also improved, indicating that the adsorption of intermedia over Co3O4 can be

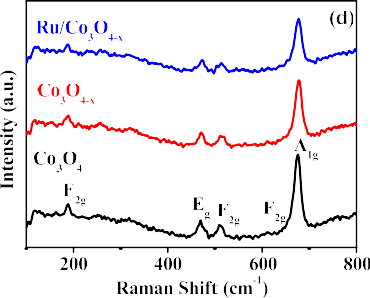
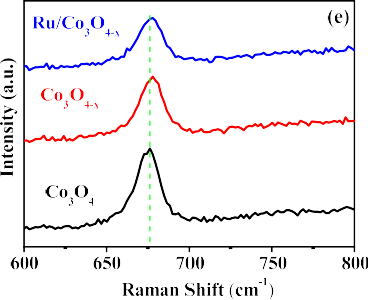
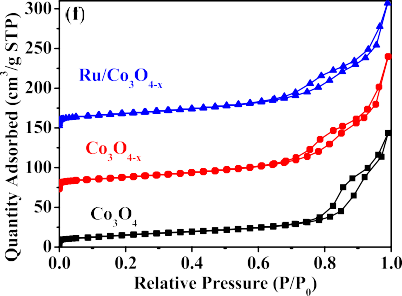
  

Figure 3. (a) XRD and (b) high-resolution XRD patterns of Co3O4, Co3O4−*x*, and Ru/Co3O4−*x*. (c) EPR spectra of Co3O4, Co3O4−*x*, and Ru/ Co3O4−*x*. (d) Raman and (e) high-resolution Raman spectra of Co3O4, Co3O4−*x*, and Ru/Co3O4−*x*. (f) Nitrogen adsorption−desorption isotherms of Co3O4, Co3O4−*x*, and Ru/Co3O4−*x* samples.

greatly optimized via the oxygen vacancies and Ru atoms,

after NaBH4 solution treatment and Ru atom loading. The

which can be further verified by the differences in charge density ([Figure S4](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf)). In addition, the potential determination steps and reaction barriers of OER over Co3O4, Co3O4−*x*, and Ru/Co3O4−*x* were investigated. [Figure S5](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf) exhibits the OER process with different intermedia in an alkaline electrolyte. Remarkably, the potential determination step ([Figure 1](#_bookmark0)h) over Co3O4 and Co3O4−*x* is \*O + H2O(l) → \*OOH + H+ + e−. Meanwhile, it changes into \*OH → \*O + H+ + e− on the surface of Ru/Co3O4−*x*, which is due to the fact that Ru atoms can also work as active sites. The OER reaction barrier over Co3O4 was calculated to be 0.82 eV, and it was reduced to 0.44 eV for Co3O4−*x* and further reduced to 0.38 eV for Ru/ Co3O4−*x*. The results confirm that oxygen vacancy defects and atomically dispersed Ru can synergistically regulate the electron redistribution of Co3O4, improve the adsorption of intermediates, and greatly lower the reaction barrier of OER. Based on the calculated results, we propose a facile defect- induced in situ synthetic strategy for the deposition of

HRTEM images of Co3O4 ([Figure S9](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf)), Co3O4−*x* ([Figure S10](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf)), and Ru/Co3O4−*x* ([Figure 2](#_bookmark1)d) exhibit clear crystal lattice fringes, declaring the exposed (111) crystal face and the retention of Co3O4 crystal structures. The inductively coupled plasma atomic emission spectroscopy (ICP-AES) confirms that the Ru amount of Ru/Co3O4−*x* sample is approximately 1.99 wt %. Even with high Ru loading, no aggregated species of Ru are detected in the HRTEM image of Ru/Co3O4−*x*. High-angle annular dark field−scanning transmission electron microscopy (HAADF−STEM) image of Ru/Co3O4−*x* ([Figure 2](#_bookmark1)e) evidently reveals the Ru atoms (circled bright dots) are individually dispersed onto the Co3O4−*x* substrate. The selected area electron diffraction (SAED) pattern of Ru/ Co3O4−*x* ([Figure 2](#_bookmark1)f) exhibits polycrystalline diffraction rings, revealing that it consisted of Co3O4 crystalline grains and Ru atoms. STEM and corresponding elemental mapping images proved that Ru atoms are uniformly dispersed in Ru/Co3O4−*x*, and no Ru nanoparticles or clusters were observed ([Figure 2](#_bookmark1)g).

atomically dispersed Ru on oxygen vacancy-rich Co3O4−*x*

The powder X-ray diffraction (XRD) was further performed

([Figure 2](#_bookmark1)a). The original Co3O4 nanorods ([Figure S6](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf)) were experimentally prepared by one hydrothermal approach followed by calcining. In order to introduce oxygen vacancies into Co3O4 nanorods, NaBH4 solution treatment was adopted.[18](#_bookmark7),[24](#_bookmark7) As shown in [Figure S7](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf), the optimized Co3O4−*x* treated by 0.05 M NaBH4 (denoted as Co3O4−*x*) exhibited the best OER activity among all the Co3O4−*x* samples treated with different NaBH4 concentrations. Thus, the optimized Co3O4−*x* was selected as the substrate to support Ru atoms. The well- designed Ru/Co3O4−*x* electrocatalyst was finally obtained via the reaction between Ru3+ and oxygen vacancies in aqueous solution, as illustrated [Figure 2](#_bookmark1)a. The SEM images of as- prepared Co3O4−*x* ([Figure S8](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf)) and Ru/Co3O4−*x* ([Figure 2](#_bookmark1)b) illustrate the morphology of nanorods, demonstrating that the synthetic process would not alter the morphology structures of pristine Co3O4. The TEM image of Ru/Co3O4−*x* in [Figure 2](#_bookmark1)c further proves the retention of Co3O4 nanorod morphology

for exploring the crystal structures of Co3O4, Co3O4−*x*, and Ru/Co3O4−*x*. All the diffraction patterns of Co3O4-based samples ([Figure 3](#_bookmark2)a) are in good agreement with the standard patterns of Co3O4 (PDF # 43-1003), and no new peak of Ru nanoparticles is detected in Ru/Co3O4−*x*. Notably, the (111) diffraction peak of Ru/Co3O4−*x* ([Figure 3](#_bookmark2)b) shifts to a lower angle compared with that of Co3O4, which is due to the increase in the interplanar space, suggesting the existence of Ru atom doping. The low-temperature electron paramagnetic resonance (EPR) spectra in [Figure 3](#_bookmark2)c show that all samples possess strong EPR signals at *g* = 2.001 because of oxygen vacancies.[25](#_bookmark7),[26](#_bookmark7) Notably, the signal of Co3O4−*x* is greatly increased compared with that of Co3O4, thereby conforming that oxygen vacancies are successfully introduced. Moreover, the signal of Ru/Co3O4−*x* is reduced, which signifies the reaction of oxygen vacancies and Ru3+. Raman spectra of pure Co3O4, Co3O4−*x*, and Ru/Co3O4−*x* display similar,



Figure 4. High-resolution XPS spectra of Co 2p in (a) Co3O4, (b) Co3O4−*x*, and (c) Ru/Co3O4−*x* and O 1s in (d) Co3O4, (e) Co3O4−*x*, and (f) Ru/Co3O4−*x*. (g) Ru K-edge XANES region, (h) corresponding *k*3-weighted *χ*(*k*) function of EXAFS, and (i) fitting curves for Ru/Co3O4−*x*.

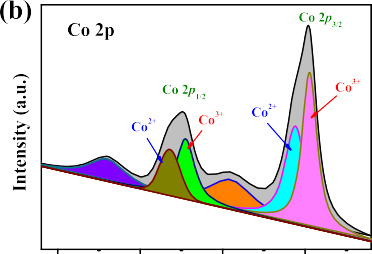
hence suggesting their identical same structure information. [Figure 3](#_bookmark2)d presents three obvious evident Raman peaks located at 467, 510, and 675 cm−1, corresponding to Eg, F2g, and A1g modes of crystalline Co3O4, respectively.[27](#_bookmark7)−[29](#_bookmark7) Strikingly, the peaks of Co3O4−*x* and Ru/Co3O4−*x* are slightly shifted and

than the ICP−MS result, suggesting that Ru atoms are dispersed on the surfaces of Co3O4−*x*. The high-resolution Co 2p XPS spectrum of Co3O4 ([Figure 4](#_bookmark3)a) displays two fitted peaks (at 781.2 and 796.4 eV) for Co2+ and two fitted peaks (at 779.4 and 794.5 eV) for Co3+, respectively.[32](#_bookmark8)−[34](#_bookmark8) Although

broadened ([Figure 3](#_bookmark2)e) due to the existence of oxygen

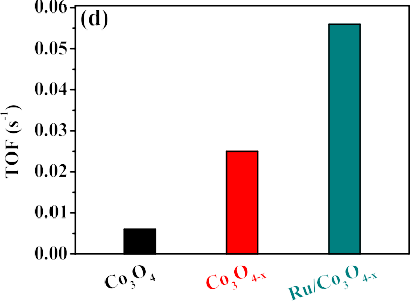
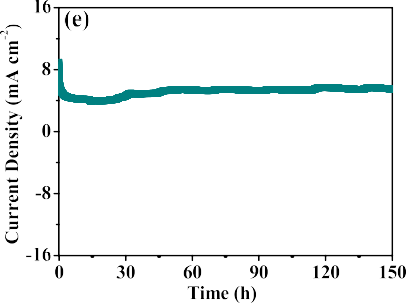
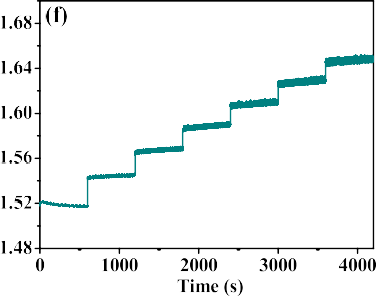
the Co 2p spectrum of Co3O4−*x* ([Figure 4](#_bookmark3)b) shows similar

vacancies and Ru doping.[30](#_bookmark7),[31](#_bookmark8) From Brunauer−Emmett−Teller (BET) analysis ([Figure 3](#_bookmark2)f), Co3O4, Co3O4−*x*, and Ru/Co3O4−*x* samples possess specific surface areas of 54.7, 63.2, and 65.7 m2/g, respectively. The large surface area of Ru/Co3O4−*x* is due to the continuous ultrasonication and stirring treatment, illustrating that this synthetic strategy could not alter the surface areas greatly. Therefore, the enhancement of the electrocatalytic activities of Ru/Co3O4−*x* should originate from the coexistence of oxygen vacancies and Ru atoms rather than the changes in the surface area.



To analyze chemical compositions and electronic properties of as-prepared electrocatalysts, X-ray photoelectron spectros- copy (XPS) measurements are performed, as shown in [Figures](#_bookmark3) [4](#_bookmark3) and [S11−S14](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf). In survey spectra ([Figure S11](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf)) of Co3O4, Co3O4−*x*, and Ru/Co3O4−*x*, Co and O elements are detected in all the samples, whereas Ru is only observed in the Ru/ Co3O4−*x* sample, thereby confirming the introduction of Ru via the defect-induced in situ deposition strategy. Moreover, the content of Ru in Ru/Co3O4−*x* according to the XPS quantitative analysis is approximately 3 wt %, which is higher

fitted peaks, the ratio of Co2+/Co3+ is increased, suggesting the existence of more oxygen vacancies in Co3O4−*x*. For the Ru/ Co3O4−*x*, the binding energy of Co 2p3/2 ([Figure 4](#_bookmark3)c) positively shifted from 779.3 to 779.7 eV owing to electron transfer from Ru to Co sites, stating the strong electron coupling effect between Ru atoms and Co3O4−*x* substrates. In O 1s spectra of Co3O4 and Co3O4−*x* ([Figure 4](#_bookmark3)d,4e), the increased peak intensity of Co3O4−*x* at 531.0 eV suggests that abundant oxygen vacancies are generated on the material surfaces caused by NaBH4 solution treatment. Notably, the amount of oxygen vacancies in Ru/Co3O4−*x* is reduced ([Figure 4](#_bookmark3)f) after Ru atom loading, thereby further certifying the reaction between oxygen vacancies and Ru3+, which is in good accordance with EPR results. Ru 3p spectra in [Figures S12−S14](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf) show that the peaks of Ru species at 461.7 and 483.8 eV are only clearly detected in the Ru/Co3O4−*x* sample. Interestingly, the binding energies of Ru species in Ru/Co3O4−*x* are higher than those of Ru0 but lower than those of Ru4+,35 thereby indicating that a special state of Ru*δ*+ in Ru/Co3O4−*x* originated from the spontaneous redox reaction between Ru3+ and oxygen vacancies. To further

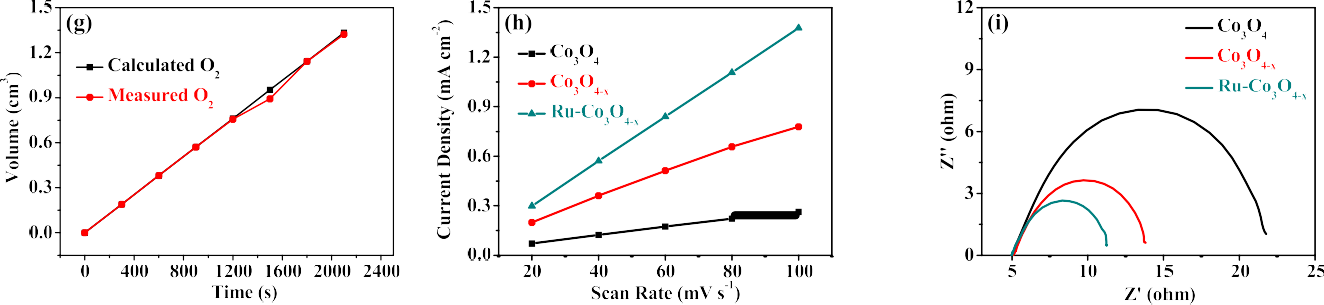


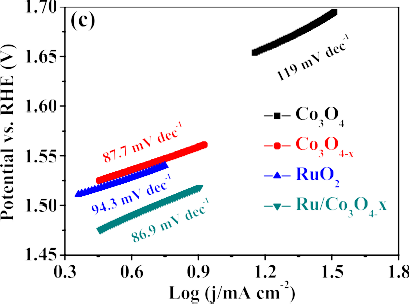
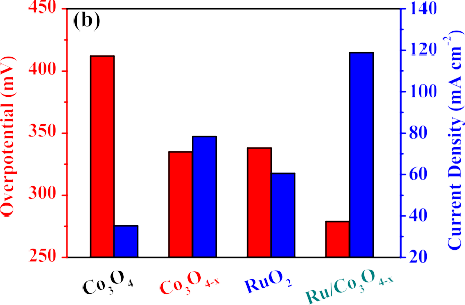
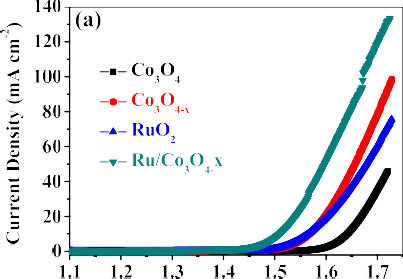
Figure 5. Electrochemical oxygen evolution performance. (a) OER polarization curves; (b) overpotentials at a current density of 10 mA cm−2 and corresponding current densities at potential of 1.7 V; and (c) Tafel slope of Co3O4, Co3O4−*x*, Ru/Co3O4−*x*, and commercial RuO2. (d) TOF values of Co3O4, Co3O4−*x*, Ru/Co3O4−*x*. (e) *i*−*t* curve, (f) multistep chrono−potentiometric curve, and (g) measured and theoretical yields of O2 over Ru/Co3O4−*x*. (h) Double-layer capacitances (*C*dl) and (i) electrochemical impedance spectroscopy of Co3O4, Co3O4−*x*, and Ru/Co3O4−*x*.

explore the chemical state and atomic structural information of Ru in Ru/Co3O4−*x*, X-ray absorption near-edge structure (XANES) analysis was performed at the Ru K-edge. [Figure 4](#_bookmark3)g shows that the energy absorption edge of Ru/Co3O4−*x* is

up to 118.8 mA cm−2, which is better than those of Co3O4 (35.1 mA cm−2), Co3O4−*x* (78.4 mA cm−2), and commercial RuO2 (60.5 mA cm−2), demonstrating that oxygen vacancies and atomically dispersed Ru could synergistically boost the

located between the Ru foil and RuO2, suggesting the state of

OER performance. The Ru/Co3O4 sample without oxygen

positively charged Ru*δ*+ species. In [Figure 4](#_bookmark3)h, no Ru−Ru bond at a distance of 2.32 Å was detected in the extended X-ray absorption fine structure (EXAFS) of Ru/Co3O4−*x*, which directly proves the absence of Ru clusters or Ru nanoparticles. Based on the EXAFS ([Figure 4](#_bookmark3)h) and fitting curve results ([Figure 4](#_bookmark3)i), prominent peaks from Ru−O and Ru−Co contributions are observed, further confirming the feasibility of the defect-induced in situ deposition strategy for anchoring atomically dispersed Ru onto defect-rich Co3O4−*x*.

The electrocatalytic activities of the OER over as-prepared electrocatalysts were measured in oxygen-saturated 1 M KOH solution using a three-electrode system. The linear sweep voltammetry (LSV) curve of Ru/Co3O4−*x* ([Figure 5](#_bookmark4)a) exhibits a sharp increase in the anodic current beyond potential at 1.41 V vs. RHE, manifesting the best catalytic performance among all the samples. The Ru/Co3O4−*x* needs one overpotential of 280 mV to achieve a current density of 10 mA cm−2, which is smaller than Co3O4 (412 mV), Co3O4−*x* (338 mV), and commercial RuO2 (335 mV). Moreover, the current density ([Figure 5](#_bookmark4)b) at high potential (1.7 V) over Ru/Co3O4−*x* reaches

vacancies was also prepared, and the corresponding LSV curve ([Figure S15](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf)) shows the poor OER activity of Ru/Co3O4, which further proves the synergistic effect of oxygen vacancy and atomically dispersed Ru for enhanced OER. In addition, Ru/Co3O4−*x* exhibits a small Tafel slope ([Figure 5](#_bookmark4)c) of 86.9 mV dec−1, lower than Co3O4 (119 mV dec−1) Co3O4−*x* (87.7 mV dec−1), and commercial RuO2 (94.3 mV dec−1), which suggests its favorable OER kinetics. Based on the amount of metal sites, the turnover frequency (TOF) values of Co3O4, Co3O4−*x*, and Ru/Co3O4−*x* are shown in [Figure 5](#_bookmark4)d. Similar to the aforementioned results, the Ru/Co3O4−*x* displays a TOF value of 0.056 s−1, which is higher than Co3O4−*x* (0.025 s−1) and Co3O4 (0.006 s−1), thereby further demonstrating that the oxygen vacancies and Ru atoms could synergistically enhance the OER performance of Co3O4. The amperometric *i*−*t* test in [Figure 5](#_bookmark4)e shows a negligible performance degradation, indicating its good stability of Ru/Co3O4−*x* in alkaline media, which is benefited by the strong electron coupling effect between Ru atoms and Co3O4−*x* substrates. [Figure 5](#_bookmark4)f shows a multistep chrono−potentiometric curve over Ru/Co3O4−*x*

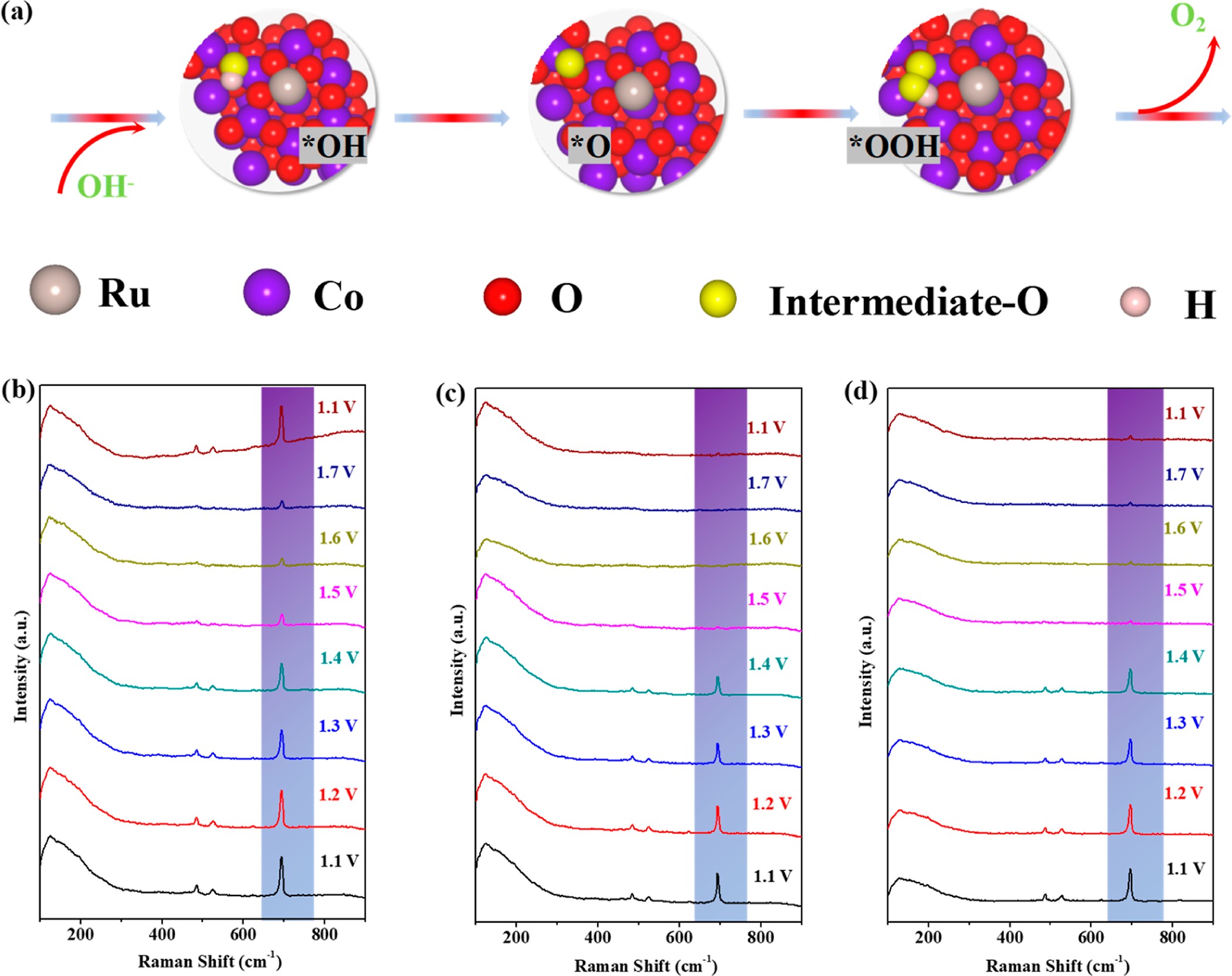


Figure 6. (a) OER process over the Ru/Co3O4−*x* in an alkaline electrolyte. In situ Raman spectra of (b) Co3O4, (c) Co3O4−*x*, and (d) Ru/Co3O4−*x* measured at different anodic potentials.

with current densities that range from 10 to 60 mA cm−2, where the corresponding potential immediately changes at the beginning current density and remains unchanged for each step, indicating the excellent mass transports and stability of the Ru/Co3O4−*x*. In addition, the yield of produced O2 over the Ru/Co3O4−*x* electrocatalyst in [Figure 5](#_bookmark4)g reveals a high Faradic efficiency of 99% during the OER, declaring these obtained catalytic currents originate exclusively from the

Surface reconstruction could occur over metal-based electrocatalysts at high applied potentials during the OER process.[36](#_bookmark8)−[38](#_bookmark8) Depending on intrinsic properties of the electrocatalysts and their catalytic mechanism, surface reconstruction can be reversible or irreversible.[39](#_bookmark8),[40](#_bookmark8) Operando Raman measurements were conducted to investigate the surface reconstruction and active sites of Co3O4, Co3O4−*x* and Ru/Co3O4−*x* electrocatalysts ([Figure S19](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf)). [Figure 6](#_bookmark5)a

oxygen evolution. Double-layer capacitances (*C*dl) are

displays the conceivable OER process over Ru/Co3O4−*x*.

measured ([Figures S16−S18](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf) and [5](#_bookmark4)h) to explore the nature of the OER activity promotion of Ru/Co3O4−*x*. Ru/Co3O4−*x* shows a large *C*dl value of 13.6 mF cm−2, which is higher than Co3O4−*x* (7.27 mF cm−2) and Co3O4 (2.41 mF cm−2), indicating more active centers on Ru/Co3O4−*x* are generated from oxygen vacancies and Ru atom doping. Furthermore, the Nyquist plot in [Figure 5](#_bookmark4)i shows that Ru/Co3O4−*x* possesses a lower frequency range semicircle diameter (6.3 Ω), which is smaller than Co3O4−*x* (8.8 Ω) and Co3O4 (16.7 Ω), implying the faster charge transfer over the Ru/Co3O4−*x* electrocatalyst. Accordingly, the coexistence of atomically Ru atoms and

During the OER process, the Raman peaks of the Co3O4 electrocatalyst in [Figure 6](#_bookmark5)b gradually decrease above a potential of 1.4 V, and no newly evolved Raman peak is observed, suggesting that the surface of Co3O4 was transferred into amorphous species during OER steps.[27](#_bookmark7),[41](#_bookmark8) Moreover, Raman characteristic peaks of Co3O4 recovered at the end of OER suggest that the surface reconstruction is reversible over Co3O4. As for the Co3O4−*x* ([Figure 6](#_bookmark5)c) and Ru/Co3O4−*x* ([Figure 6](#_bookmark5)d) electrocatalysts, the Raman signals also attenuate as the potential increases beyond 1.4 V. However, surface reconstruction phenomena become irreversible because of the

oxygen vacancies contributes to more active sites and faster

existence of oxygen vacancies.42 The XRD of Ru/Co3O4−*x*

charge transfer, thereby greatly improving the OER perform- ance of Ru/Co3O4−*x*.

after OER was conducted, and the pattern in [Figure S20](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf) displays that the main crystal phase of Ru/Co3O4−*x* did not

change, which proves that the reconstruction has occurred on the surfaces of electrocatalysts. More importantly, the Raman characteristic peaks of Ru/Co3O4−*x* measured at 1.5, 1.6, 1.7, and 1.1 V at the end of the OER are higher than those of Co3O4−*x*, confirming that Ru atoms could improve the durability of Co3O4−*x* during OER due to the strong electron coupling effect between Ru atoms and Co3O4−*x* substrates.43 The XPS of Ru/Co3O4−*x* after OER is also performed and shown in [Figure S21](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf). Likewise, the Co−OH bond was detected in the O 1s spectrum, confirming the reconstruction on the surface during OER.44 Operando Raman measurements illustrate the irreversible transformation into amorphous species on Ru/Co3O4−*x* surfaces during OER, which leads to more active sites while the Ru atoms enhance the electro- catalytic stability.

# CONCLUSIONS

In summary, defect-induced in situ single-atom deposition strategy was reported to construct electrocatalysts with oxygen vacancy and single-atom catalysts for enhanced OER perform- ances. During this process, atomically dispersed Ru has been

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directly anchored onto oxygen vacancy-rich cobalt oxides

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based on the spontaneous redox reaction between Co3O4−*x* and Ru3+ ions. Noticeably, the as-prepared Ru/Co3O4−*x*

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electrocatalyst with oxygen vacancy defects and Ru single

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atom exhibited excellent OER performance, which is much better than those of Co3O4, Co3O4−*x*, and commercial RuO2. Moreover, owing to the strong interaction between Ru atoms and Co3O4−*x* supports, outstanding long-term durability was also achieved over this Ru/Co3O4−*x* electrocatalyst. DFT calculation revealed that the electron decentralization and d- band center of Co3O4 can be synergistically tailored by oxygen vacancies and Ru atoms, thereby leading to optimized

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adsorption of oxygen-based intermediates and lowered

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reaction barriers. This defect-induced in situ single-atom deposition strategy paves a new route to construct electro- catalysts with oxygen vacancy and single atoms for enhanced electrocatalytic oxygen evolution.

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# ASSOCIATED CONTENT

\***sı Supporting Information**

The Supporting Information is available free of charge at

[https://pubs.acs.org/doi/10.1021/acscatal.2c04946](https://pubs.acs.org/doi/10.1021/acscatal.2c04946?goto=supporting-info).

Materials’ synthesis, materials’ characterizations, electro- chemical measurement, DFT computational calculations and corresponding additional data including optimized configurations, formation energies, SEM, TEM, XPS, CV, LSV, XRD, in situ Raman, and OER performance comparison ([PDF](https://pubs.acs.org/doi/suppl/10.1021/acscatal.2c04946/suppl_file/cs2c04946_si_001.pdf))

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**Notes**

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