A Co-Doped Nanorod-like RuO$_2$ Electrocatalyst with Abundant Oxygen Vacancies for Acidic Water Oxidation

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HIGHLIGHTS
A Co-doped RuO$_2$ electrocatalyst with an abundance of oxygen vacancies was synthesized.
The compound exhibits ultra-high OER performance in acidic media.
The oxygen vacancies contribute to the high OER performance.
A Co-Doped Nanorod-like RuO₂ Electrocatalyst with Abundant Oxygen Vacancies for Acidic Water Oxidation

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SUMMARY
Active and highly stable electrocatalysts for oxygen evolution reaction (OER) in acidic media are currently in high demand as a cleaner alternative to the combustion of fossil fuels. Herein, we report a Co-doped nanorod-like RuO₂ electrocatalyst with an abundance of oxygen vacancies achieved through the facile, one-step annealing of a Ru-exchanged ZIF-67 derivative. The compound exhibits ultra-high OER performance in acidic media, with a low overpotential of 169 mV at 10 mA cm⁻² while maintaining excellent activity, even when exposed to a 50-h galvanostatic stability test at a constant current of 10 mA cm⁻². The dramatic enhancement in OER performance is mainly attributed to the abundance of oxygen vacancies and modulated electronic structure of the Co-doped RuO₂ that rely on a vacancy-related lattice oxygen oxidation mechanism (LOM) rather than adsorbate lattice reaction mechanism (ALM), as revealed and supported by experimental characterizations as well as density functional theory (DFT) calculations.

INTRODUCTION
Hydrogen is considered an ideal clean energy carrier to store electrical energy derived from renewable, intermittent power sources that has evoked significant interest and stimulated intensive investigations in the scientific literature. Furthermore, the conversion of hydrogen back into electrical energy can be efficiently performed in fuel cells to effectively harness the energy initially stored. Electrochemical water splitting, including hydrogen evolution reaction and oxygen evolution reaction (OER), provides an efficient and environmentally friendly way for large-scale hydrogen production with high purity. To date, alkaline water splitting technologies have been well established and are commercially available for industrial H₂ production (Lin et al., 2016; Suen et al., 2017; Zheng et al., 2016; Wang et al., 2018a, 2018b; Zhuang et al., 2019; Zhou et al., 2019). Nevertheless, compared with alkaline water splitting, acidic water splitting using proton exchange membrane (PEM) electrolyzer offers great advantages such as higher ionic conductivity, fewer unfavorable reactions, high voltage efficiency, and faster system response (Nong et al., 2015; Sardar et al., 2014). However, the scarcity of highly active and stable OER electrocatalysts in acidic condition greatly hinders the widespread commercialization of acidic water splitting. IR oxide-based materials are considered as the state-of-the-art electrocatalysts for OER under acidic condition. For example, IR-based double perovskites (Diaz-Morales et al., 2016), IrOₓ/StrIrO₃ hybrid (Seitz et al., 2016), and pyrochlore-structured Ir-based oxide (Kim et al., 2017) were recently reported to be active and stable OER electrocatalysts in acidic condition. Unfortunately, their potential for commercialization is greatly hindered by the low production and high price of IR. A possible alternative to IR is the much cheaper Ru, which also shows high OER catalytic activity in acidic condition, such as the typical rutile-structured RuO₂ (Lee et al., 2012). However, many Ru-based electrocatalysts suffer from low stability in acidic condition owing to the over-oxidation of Ru into soluble RuO₃ moieties under the demanding oxidative environment (Kotz et al., 1983). Therefore, elaborate design or optimization of Ru-based systems with improved activity and stability is a matter of utmost urgency and a prospective area of research for the development of efficient and environmentally attractive acidic water splitting. To address this problem, in our previous work, we focused on altering RuO₂ surface atom arrangement and/or electronic structures that are pivotal to the catalytic performances. Accordingly, we fabricated hollow porous RuO₂ polyhedra (Su et al., 2018) and CrO₂-RuO₂ solid solution (Lin et al., 2019) materials that exhibit excellent OER performance. Specifically, CrO₂-RuO₂ solid solution possess a very low overpotential of 178 mV at 10 mA cm⁻² and galvanostatic stability test of 10 h at the same current density in 0.5 M H₂SO₄. Recently, Lotsch and co-workers reported RuO₂ nanosheets with enhanced acidic OER activity and stability ascribing the increase in reactivity to the surface edges of RuO₂ (Laha et al., 2019).
Besides metal doping and morphological control, oxygen vacancies in transition metal oxides have been reported to enhance the electrocatalytic process. For example, Xu et al. created oxygen vacancies on Co$_3$O$_4$ nanosheets via a plasma-engraving strategy, revealing that the vacancies can significantly enhance the alkaline OER activity of the nanosheets (Xu et al., 2016, 2018). The authors proposed that the oxygen vacancies on the Co$_3$O$_4$ nanosheets surface could improve the electronic conductivity and create more active sites for OER. Very recently, Wang et al. (Huang et al., 2019) and Kolpak et al. (Yoo et al., 2018) proposed a vacancy-related lattice oxygen oxidation mechanism (LOM), which could bypass the limitation of the most commonly reported adsorbate evolution mechanism (AEM) having a minimum theoretical overpotential of 0.37 eV. In light of these studies, we attempted to synthesize RuO$_2$-based electrocatalyst that has abundant oxygen vacancies with optimized electronic structure for enhanced OER performance in acidic media. To achieve this target, we proposed to use some alien metal ions with different valence state to replace the Ru ions, which can simultaneously create oxygen vacancies and alter the electronic structures. Herein we chose Co because the lower oxidation states of Co dopants in the RuO$_2$ lattice require less $O^2-$ ions to appropriately balance the charge, thus yielding oxygen vacancies. Metal-organic frameworks (MOFs) have been demonstrated to be versatile templates or precursors to prepare highly active electrocatalysts (Liu et al., 2017), such as N-doped porous carbon (Ma et al., 2016; Xia et al., 2016), metal oxides nanocomposites (Cai et al., 2017; Salunkhe et al., 2017), and carbon-coated nanosized metal alloys (Su et al., 2017). Based on this platform, we have successfully prepared a Co-doped RuO$_2$ nanorod electrocatalyst by annealing a Ru-exchange ZIF-67 amorphous composite. We selected ZIF-67 as a candidate because of its high surface area, accessible porosity that can facilitate ion exchange, and ease of synthesis (Banerjee et al., 2008; Gross et al., 2012; Qian et al., 2012). The synthetic route is briefly illustrated in Scheme 1. The resulting Co-doped RuO$_2$ nanorod exhibits an extremely low overpotential of 169 mV for OER in acidic environment at 10 mA cm$^{-2}$ and excellent stability with a chronopotentiometry performance of over 50 h at the same current, outperforming the most active OER electrocatalysts reported to date. Based on the density functional calculations, we propose that the OER process on the compound undergoes a vacancy-related LOM, which enhances both the activity and stability.

**RESULTS AND DISCUSSIONS**

**Synthesis and Characterization of Ru-ZIF-67 and Co-Doped RuO$_2$ Nanorods**

ZIF-67 was synthesized via a facile procedure previously reported (Feng and Carreon, 2015) (see details in **Methods** section). The powder X-ray pattern (PXRD) and scanning electron microscope (SEM) image of the as-prepared product confirms that a pure ZIF-67 phase was obtained (Figures S1 and S2). The Co ions in ZIF-67 were exchanged by Ru ion (RuCl$_3$ was used as the Ru ion source) in THF solvent at room temperature.
to obtain Ru-exchanged ZIF-67 (Ru-ZIF-67). The Ru content in the resulting product can be varied by controlling the amount of RuCl₃ reactant used for the exchange reaction. The resulting Ru-ZIF-67 is amorphous as revealed by the PXRD pattern and SEM image (Figures S3 and S4), which could be attributed to the significantly different coordination manner and environment of Ru and Co. In fact, crystal structure is not necessary for the following annealing treatment, which is associated with pyrolysis and atom rearrangements. Co-doped RuO₂ nanorods with different Co/Ru ratio can be obtained through further thermal decomposition of the as-prepared Ru-ZIF-67 powders in air at 350°C. Based on inductively coupled plasma-mass spectroscopy (ICP-MS) measurements, the formulas of the as-prepared RuO₂ samples are Co₀.₂₇Ru₀.₇₃O₂·₈, Co₀.₃₈Ru₀.₆₂O₂·₈, Co₀.₁₁Ru₀.₈₉O₂·₈, and Co₀.₀₄Ru₀.₉₆O₂·₈ (δ is used to balance the valence), respectively. Figure 1A shows the PXRD patterns of these samples, in which the major phase can be identified as rutile RuO₂ (JCPDS. No. 43-1027). Notably, the PXRD signals that belong to RuO₂ shift to the right when the Co content in the sample increases, suggesting that Co atoms have been successfully incorporated into the RuO₂ crystal lattice to form a rutile Co-doped RuO₂ phase with a concomitant lattice shrink. Figures 1B and S5 show the planes of RuO₂ corresponding to the labeled PXRD peaks. The d-spaces of these planes decrease after the insertion of Co atoms that have a smaller size than that of the Ru atom. We further varied the annealing temperature for Co₀.₁₁Ru₀.₈₉O₂·₈ to investigate the structural evolution of Co-doped RuO₂ nanocrystals. As shown in Figure S6, the content of metallic Ru can be decreased by increasing the annealing temperature and becomes negligible when the annealing temperature is increased to 500°C. The higher annealing temperatures lead to better crystallinity for the Co-doped RuO₂ as seen from the higher peak intensity and increased sharpness of the PXRD signals.

Transmission electron microscopy (TEM) was employed to characterize the morphology and structure of the Co-doped RuO₂ powders. As shown in Figures 2A–2D and S7–S9, all of the as-prepared Co-doped RuO₂ samples display nanorod-like shape morphology with a diameter of ~8 nm and length of ~20 nm. High-resolution TEM (HR-TEM) image (Figure 2E) clearly shows lattice fringes, indicating the high crystallinity of the Co-doped RuO₂ samples. Both the HR-TEM and the selected area electron diffraction (SAED) characterization (Figure 2F) confirm the rutile RuO₂ structure of Co-doped RuO₂ nanorods. High-angle annular dark-field scanning transmission microscopy (HAADF-STEM) was employed to analyze the elemental distribution over a single nanorod. As shown in Figure 2G, the elements of Ru, Co, and O were uniformly distributed over an entire single nanorod crystal, demonstrating the formation of rutile Co-doped RuO₂ phase (the mapping images for a wider region are shown in Figure S10), consistent with the finding from PXRD characterization.

In addition, Co₀.₁₁Ru₀.₈₉O₂·₈ (350) displays a typical type II isotherm with an H1 type hysteresis loop (Figure S11), which is characteristic for the aggregation of small particles. The calculated surface area for Co₀.₁₁Ru₀.₈₉O₂·₈ (350) is 31.3 m² g⁻¹, larger than that of RuO₂ (8.9 m² g⁻¹).

OER Activity in Strong Acidic Media

The OER activity of Co-doped RuO₂ powders was investigated in a strong acidic media (0.5 M H₂SO₄) by use of a typical three-electrode electrochemical system containing a Pt wire as counter-electrode and an
Hg/Hg₂SO₄ reference electrode (see details in Methods section). The Co-doped RuO₂-based electrodes were prepared by drop-casting a water/ethanol and Nafion-based ink of Co-doped RuO₂ on glassy carbon disk. We measured linear sweep voltammetry (LSV) curves at a scan rate of 5 mV s⁻¹. The Ohmic potential drop (iR) correction was performed to all experimental data to eliminate the effect of solution resistance, and the potentials were calibrated to the reversible hydrogen electrode (RHE) for comparison. Initially, we investigated the OER performance of Co-doped RuO₂ powders with different Co content to emphasize the effects of Co content on the OER catalysis of RuO₂ and to obtain a sample with optimum OER activity for further exploration. Figure 3A presents the LSV curves of Co₀.27Ru₀.73O₂₋ₓ, Co₀.18Ru₀.82O₂₋ₓ, Co₀.11Ru₀.89O₂₋ₓ, and Co₀.03Ru₀.97O₂₋ₓ annealed at 350°C, where the rising current indicates the evolution of oxygen. As seen in Figure 3A, the OER activity is inversely proportional to Co content when the Co/Ru ratio is higher than 0.11:0.89, suggesting that the Ru atom is the catalytic center. Reasonably, a higher Co content will decrease the number of exposed catalytic Ru sites. However, when the Co/Ru ratio reduces to 0.04:0.96, the OER activity becomes relatively poor, thus emphasizing the significant role of Co dopant, which can induce oxygen vacancy and modify the electronic structure of Ru. Clearly, Co₀.11Ru₀.89O₂₋ₓ (350) exhibited the best OER activity among the samples, with an overpotential of 169 mV at 10 mA cm⁻². We thus further altered the annealing temperature of Co₀.11Ru₀.89O₂₋ₓ to realize the best annealing temperature for Co₀.11Ru₀.89O₂₋ₓ to maximize the OER performance. As shown in Figure 3B, along with the rise of annealing temperature, the OER activity decreases successively. This decrease can be assigned to the lattice strain effects and/or reduced active crystal defects under higher annealing temperature and is supported by the increase in PXRD intensity and sharpness. Electrochemical impedance spectroscopy (EIS) measurements were also performed to assess the electrical resistance of Co₀.11Ru₀.89O₂₋ₓ samples annealed at
As shown in Figure 3C, all the Nyquist plots display a depressed semicircle, suggesting a charge-transfer process during the OER. These Nyquist plots were further fitted to analyze the electrical resistance by a simple equivalent electrical circuit as shown in the inset in Figure 3C (Audichon et al., 2016; Harrington and van den Driessche, 2011). Co$_{0.11}$Ru$_{0.89}$O$_2$ displays the smallest semicircle radius compared with other catalysts, implying the smallest electric resistance and fastest charge transfer rate for OER kinetics at the interface.

As demonstrated by the above results and discussion, Co$_{0.11}$Ru$_{0.89}$O$_2$ is the optimized material as it possesses the highest OER performance among those samples with varying Co content or annealing temperatures. We further tested the stability of Co$_{0.11}$Ru$_{0.89}$O$_2$ by cycling the catalyst between 1.2 and 1.6 V at a sweep rate of 100 mV s$^{-1}$ in 0.5 M H$_2$SO$_4$ for 10,000 cycles. As shown in Figure 3D, after 10,000 cycles, the overpotential of Co$_{0.11}$Ru$_{0.89}$O$_2$ was 184 mV, only a 15-mV increase relative to the initial overpotential. For further comparison, the OER performance of commercial RuO$_2$ with a particle size of 30 nm was also tested at identical conditions. RuO$_2$ displays much lower OER activity, with an overpotential of 273 mV to drive the current density of 10 mA cm$^{-2}$. Moreover, after 10,000 cycles, the OER activity...
of RuO₂ is dramatically reduced and becomes negligible compared with the initial OER activity, revealing poor stability for OER in acidic media. These results for commercial RuO₂ are consistent with those seen in the literature (Kim et al., 2017; Audichon et al., 2016; Li et al., 2017). In addition, considering that the OER activity is correlated to the number of exposed sites, we further plotted the LSV of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) and RuO₂ with respect to the calculated surface areas (Figure S12). The results show that the enhanced OER performance of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) is not merely increased by the surface area. In contrast, the enhanced intrinsic activity arises from oxygen vacancies and the Co dopant plays a much more important role.

Figure 3E shows the Tafel plots of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) and RuO₂ before and after 10,000 cycles. The Tafel slope for RuO₂ of the initial cycle is 63 mV dec⁻¹ and dramatically rises to 98 mV dec⁻¹ after 10,000 cycles. For Co₀.₁₁Ru₀.₈₉O₂₋₃ (350), the Tafel slope slightly decreases from 49 to 47 mV dec⁻¹ after 10,000 cycles, implying that the OER kinetics of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) after 10,000 cycles is slightly faster than that of initial Co₀.₁₁Ru₀.₈₉O₂₋₃ (350). The smaller and unchanged Tafel slope of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) suggests a faster and much more stable OER kinetic rate than RuO₂. Ultimately, to further confirm the big difference in stability of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) and RuO₂, chronopotentiometry was examined under a constant current density of 10 mA cm⁻². Figure 3F presents the corresponding potential change for both Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) and RuO₂. Clearly, RuO₂ loses OER activity in less than 3 h; on the contrary, Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) remains essentially stable throughout the 50-h galvanostatic stability test. We also measured the chronopotentiometric curve under a higher current density of 50 mA cm⁻². As shown in Figure S13, Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) remains essentially stable throughout the 8-h galvanostatic stability test. Furthermore, as shown in Figure S14, the Co/Ru ratio before cyclic voltammetry (CV) is 0.124/0.876, generally consistent with the ICP result (Co/Ru = 0.11/0.89). After CV cycles, the Co/Ru ratio shows a very slight decrease, with a value of 0.107/0.893 (Figure S15), indicating the high stability of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350). In addition, the morphology of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) after 10,000 CV cycles remains unchanged (Figure S16). These results demonstrate that Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) is stable in 0.5 M H₂SO₄ at the oxidizing potential during the OER process. For comparison, we summarized the reported materials with high OER activity in acidic media in Table S1. Notably, Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) presents a record low overpotential and outperforms IrO₂-based catalysts, which represent the state-of-the-art electrocatalyst for OER in acidic media.

Origin of OER Activity and Stability

We first carried out X-ray photoelectron spectroscopy (XPS) analysis to assess the surface chemical state of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350). For comparison, XPS of commercial RuO₂ was also measured. As shown in Figure 4A, the XPS peaks for Ru 3d of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) and RuO₂ can be deconvoluted into two sets of doublet peaks for Ru 3d₅/₂, 3d₃/₂, their satellite peaks, and two single peaks for C₁s (arising from corrosion carbon) (Morgan, 2015). For RuO₂, the primary Ru 3d₅/₂ and 3d₃/₂ peaks of RuO₂ center at 280.6 and 284.8 eV, respectively, consistent with those reported in the literature (Sarma and Rao, 1980; Shen et al., 1991). As for Ru 3d of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350), a small shift to higher binding energy can be clearly observed, which may be attributed to a higher electron density at the Ru sites. As mentioned earlier, there is a small portion of metallic Ru in our sample as determined by PXRD characterizations. However, the corresponding XPS peaks for metallic Ru are nearly invisible possibly because the majority of species in the outer surface are aggregated Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) particles in the RuO₂ phase. In the annealing process, the outer surface of the sample is directly exposed to air largely increasing the probability of generating metal oxides. The Co 2p spectrum of Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) is shown in Figure S17. For comparison, we also prepared a sample by annealing pure ZIF-67 using the same procedure for preparing Co₀.₁₁Ru₀.₈₉O₂₋₃ (350). The structure of the resulting powder is identified as Co₃O₄ (Figure S18). As shown in Figure S14, the main peak of Co 2p is shifted toward higher binding energy state compared with that of Co₃O₄ derived from ZIF-67, suggesting a relatively higher oxidation state of Co doped into Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) attributed to the electron withdrawing effect of Ru⁴⁺ in the lattice. O 1s spectra for Co₀.₁₁Ru₀.₈₉O₂₋₃ (350) and RuO₂ are shown in Figure 4B. For RuO₂, the O 1s XPS peak can be deconvoluted into four peaks, corresponding to different type of O species. The main peak centered at 529.2 eV corresponds to the Ru–O in the lattice, and the shoulder peak centered at 530.5 eV can be assigned to the OH⁻ ions that integrated into the outer surface of RuO₂. The higher binding energy peak centered at 531.9 eV is attributed to the surface oxygen vacancies species, which is often observed on metal oxides (Dupin et al., 2000; Uhlenbrock et al., 1992). The small peak centered at 533.3 eV originates from the adsorbed H₂O molecules (Dupin et al., 2000). For Co₀.₁₁Ru₀.₈₉O₂₋₃ (350), the O 1s peak can be deconvoluted into three peaks, corresponding to the Ru–O, OH⁻, and oxygen vacancy species, respectively.
We can find that the peak for oxygen vacancy species is much stronger than that of RuO$_2$, suggesting that a larger number of oxygen vacancies exist on the Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ surface. The increase of oxygen vacancies on Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ arises from the lower oxidation state of Co dopants in the RuO$_2$ lattice that require less O$^{2-}$ ions to appropriately balance the charge. In many cases, oxygen vacancies species can significantly enhance the OER activity by dramatically improving the electronic conductivity that leads to the creation of more active sites (Xu et al., 2016). In addition, compared with RuO$_2$, Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350) shows a broadened valence band (VB) spectra (Figure 4C), suggesting that the incorporation of Co dopants not only introduces the oxygen vacancies but also modulates the electronic structure of RuO$_2$. The XPS wide-scan spectrum of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350) is shown in Figure S19. In addition, we also measured the XPS spectra for Co and Ru elements of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350) after stability test. As shown in Figures S20 and S21, the XPS spectra of Co and Ru after stability test remained generally unchanged in both position and shape, indicating the high stability of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350).

To investigate the local structure of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350), X-ray absorption spectroscopy (XAS) characterization was further employed (Figure S22). The Fourier transformed (FT) radial structure based on the k$^2$-weighted extended X-ray absorption fine structure (EXAFS) is displayed in Figure 4D. The peak at ~1.5 Å corresponds to Ru-O bonds. Interestingly, compared with RuO$_2$, the intensity of this peak for Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350) distinctly decreased, which is ascribed to the coordination deficiency from Ru, revealing the existence of abundant oxygen vacancies in Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350). Note that the Ru-Ru peak is also present, which is consistent with the PXRD results.

Figure 4. Chemical State and Structure Analysis of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350)
(A) Ru 3d XPS profiles of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350) and RuO$_2$.
(B) O 1s XPS profiles of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350) and RuO$_2$.
(C) Valence band XPS profiles of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350) and RuO$_2$.
(D) Fourier transformed EXAFS spectra of Ru K-edge for Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350), RuO$_2$, and Ru foil.
Finally, we carried out density functional theory (DFT) calculations to gain more insights into the excellent OER activity of Co-RuO$_2$. Based on previous studies that RuO$_2$ (110) was identified as the most stable surface with the lowest surface energy among various facets (Su et al., 2018; Fang and Liu, 2010; Wei and Liu, 2011), we constructed a (110) surface model of Co$_x$Ru$_{1-x}$O$_{2-x}$ ($x = 0.1$) to simulate the experimentally obtained material. O vacancy is created to maintain the total charge balance induced by different valence states of Co and Ru atoms. As shown in Figure S23, two possible types of O vacancies were located on different sites: O$_{v I}$ formed by the substitution of 6-coordinated Ru and O$_{v II}$ formed by the substitution of 5-coordinated Ru. The comparison of the formation energies indicates that O$_{v I}$ vacancy sites are dominant and mainly participate in the subsequent OER process owing to its 0.50 eV lower formation energy than that of O$_{v II}$ sites.

To address the role of oxygen vacancies in OER, the activity of the neighbored 5-coordinated Ru is definitely inevitable to be compared. Therefore, two possible competing OER processes via O$_{v I}$ in LOM and 5-coordinated Ru in AEM were comparatively investigated to explore the preferred lower free energy path. As demonstrated in Figure 5A, five elementary steps are taken into account involving four electrochemical electron transfer steps ($\Delta G_1$ ~ $\Delta G_4$) and one non-electrochemical O$_2$ desorption step ($\Delta G_5$) in both processes. For the initial adsorption of upcoming H$_2$O molecule, the intermediate L1 (O$_{v I}$-OH) in LOM and intermediate A1 (Ru-OH) in AEM were formed on O$_{v I}$ and 5-coordinated Ru sites, respectively. The lower adsorption energy (0.71 eV) of L1 than A1 reveals that H$_2$O preferred to react with O$_{v I}$ vacancy rather than the Ru site. It is well reasonable because O$_{v I}$ vacancy between the two unsaturated cations (Ru1 and Co1 in Figure S24) on
the surface possesses lower electron depletion (blue contour) in Figure 5B to bind with H2O molecules, thus yielding lower adsorption energy of L1 to proceed the following OER steps in LOM mechanism.

Another important factor to evaluate the effect of O vacancy on OER process is free energy variation of the rate-determining step (RDS) in both LOM and AEM, as plotted in Figure 5C. Along the LOM reaction path, the formation of Ru(OH)-Ov(1OH) after the second H2O attacking was identified as RDS, which yielded a free energy barrier of 0.71 eV versus RHE. The RDS in AEM occurred on the formation of *OOH on the 5-coordinated Ru with yielding a free energy barrier of 0.95 eV versus RHE. Clearly, the corresponding 0.24 eV lower energy barrier of RDS in LOM suggested that the OER would preferentially undertake O vacancy site rather than the 5-coordinated Ru site. Moreover, we believe that the enhanced stability is also associated with the LOM pathway. The participation of O vacancy can effectively avoid the over-oxidation of Ru to the soluble RuO4, which is deemed as the major reason for the instability of RuO2 electrocatalyst governed by AEM in the acidic conditions.

The density of states of RuO2 and Co-doped RuO2 were compared and provided in Figure S25 to further understand the inherent electron variation on O vacancies. The binding region between −2.0 eV and the Fermi level was obviously broadened in the Co-doped RuO2, which was well consistent with the observed XPS VB results. Actually, both IrO2 and Cu-doped RuO2 electrocatalysts were previously found to promote OER activity by broadening the binding regions (Su et al., 2018; Sun et al., 2015). It is well accepted that the p-band center of O is an effective descriptor to evaluate OER performance (Grimaud et al., 2013). Our calculated p-band centers were −4.57 eV in RuO2 and −3.03 eV in Ru1−xCoxO2−x, showing a higher energy shift toward the Fermi level upon the creation of O vacancy by Co dopant. According to p-band center theory, Ru1−xCoxO2−x with p-band center closer to the Fermi level exhibits higher OER catalytic activity.

Conclusion
In summary, by use of Co-based MOF, we have developed a nanorod-like Co-doped RuO2 electrocatalyst with superior OER performance in acidic condition. Impressively, this compound outperforms the state-of-the-art IrO2-based electrocatalyst and the currently reported RuO2-based electrocatalysts by demonstrating an ultralow overpotential (169 mV) and excellent stability. The abundance of oxygen vacancies together with the modulated electronic structure contribute to the superior OER activity, as revealed by both experimental characterizations and DFT calculations. We show that the OER preferentially proceeds via the LOM pathway by passing a lower RDS barrier (0.24 eV) in the assistance of O vacancies than reacting on 5-coordinated Ru. This OER enhancement is attributed to larger charge depletion on O vacancies and higher energy shift toward the Fermi level of p-band center. Our study puts forward the potential of using doped RuO2-based materials to confront the challenges in acidic OER process.

Limitations of the Study
Based on the combination of XPS, XAS, and DFT, oxygen vacancy has been interpreted as a key contributor to the excellent acidic OER activity and stability. However, to get an in-depth sight of the effect of oxygen vacancy, an in situ characterization of the oxygen vacancy is still needed but is very challenging.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.100756.

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AUTHOR CONTRIBUTIONS
L.C. and Y.L. designed the project and wrote the manuscript; Y.T. and Y.L. carried out the experiments; S.W. and Q.Z. carried out DFT calculations; Q.Z. wrote the computational part of the manuscript; L.Z. performed
the XAS experiments and data analysis. E.V., L.C., and X.L. provided helpful suggestions and polished the manuscript. All authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

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Supplemental Information

A Co-Doped Nanorod-like RuO₂
Electrocatalyst with Abundant Oxygen Vacancies for Acidic Water Oxidation

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Figure S1. PXRD pattern of as-prepared ZIF-67. Related to Scheme 1.

Figure S2. SEM image of as-prepared ZIF-67. Related to Scheme 1.
Figure S3. PXRD pattern of Ru-ZIF-67-C. Related to Figure 1.

Figure S4. SEM images of Ru-ZIF-67-B and C. Related to Figure 1.
Figure S5. Crystal structure of RuO$_2$ viewed along different direction. The yellow planes represent the crystal facets of RuO$_2$. Related to Figure 1.

Figure S6. PXRD patterns of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ annealed at different temperatures. Related to Figure 1.
Figure S7. TEM image of Co$_{0.27}$Ru$_{0.73}$O$_{2-\delta}$ annealed at 350 °C. Related to Figure 2.

Figure S8. TEM image of Co$_{0.18}$Ru$_{0.82}$O$_{2-\delta}$ annealed at 350 °C. Related to Figure 2.
Figure S9. TEM image of Co_{0.04}Ru_{0.96}O_{2-δ} annealed at 350 °C. Related to Figure 2.

Figure S10. HAADF-STEM image and the corresponding element mapping images. Related to Figure 2.
Figure S11. N₂ adsorption-desorption isotherms of Co₀.₁₁₉₀₈₉O₂₋₆₃₅₀ and RuO₂ at 77 K. Related to Figure 2.

Figure S12. Intrinsic surface area based LSV curves of Co₀.₁₁₉₀₈₉O₂₋₆₃₅₀ and commercial RuO₂ before and after CV cycling measurements. Related to Figure 3.
Figure S13. Chronopotentiometry test of $\text{Co}_{0.11}\text{Ru}_{0.89}\text{O}_2$ (350) at the current density of 50 mA cm$^{-2}$. Related to Figure 3.

Figure S14. TEM-EDS of $\text{Co}_{0.11}\text{Ru}_{0.89}\text{O}_2$ (350) before stability test. Related to Figure 3.
Figure S15. TEM-EDS of $\text{Co}_{0.11}\text{Ru}_{0.89}\text{O}_{2-\delta}$ (350) after stability test. Related to Figure 3.

Figure S16. TEM image of $\text{f Co}_{0.11}\text{Ru}_{0.89}\text{O}_{2-\delta}$ (350) after stability test. Related to Figures 2 and 3.
Figure S17. Co 2P XPS profiles of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ and Co$_3$O$_4$. Co$_3$O$_4$ was synthesized by annealing pure ZIF-67 at 350 °C. Related to Figure 4.

Figure S18. PXRD pattern of the product obtained from annealing pure ZIF-67. The reference patterns of Co$_3$O$_4$ were obtained from Jade 2004 (JCPDS No. 43-1003).
Related to Figure 4.

Figure S19. The XPS wide-scan spectra of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$(350). Related to Figure 4.

Figure S20. XPS spectra for Co of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350) before and after 10000 CV cycles. Related to Figure 4.
Figure S21. XPS spectra for Ru of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$ (350) before and after 10000 CV cycles. Related to Figure 4.

Figure S22. Normalized Ru K-edge XAS spectra of Co$_{0.11}$Ru$_{0.89}$O$_{2-\delta}$(350), RuO$_2$ and Ru foil. Related to Figure 4.
Figure S23. The formation of O vacancy for different Co doping sites. Related to Figure 5.

Figure S24. The intermediates along LOM and AEM processes. Related to Figure 5.
Figure S25. Calculated density of states (DOS) of bulk RuO$_2$ and Co-doped RuO$_2$. Related to Figure 5.

Table S1. The comparison of overpotentials of representative OER electrocatalysts in acidic media. Related to Figure 3.

| Catalyst       | substrate | Electrolyte | Overpotential at 10 mA cm$^{-2}$ (mV) | Chronopotentiometry at specific current density | Ref.                                      |
|----------------|-----------|-------------|----------------------------------------|------------------------------------------------|-------------------------------------------|
| Co-RuO$_2$     | GCE       | 0.5 M H$_2$SO$_4$ | 169                                    | 50 h @ 10 mA cm$^{-2}$                           | This work                                 |
| Cr$_{0.6}$Ru$_{0.4}$O$_2$(550) | GCE | 0.5 M H$_2$SO$_4$ | 178                                    | 10 h @ 10 mA cm$^{-2}$                          | Nat. Commun. 2019, 10:162                  |
| Ba[Co-PO M]    | CP        | 1 M H$_2$SO$_4$ | 361                                    | --                                              | Nat. Chem. 2018, 10, 24                    |
| 6H-IrO$_2$     | GCE       | 0.5 M H$_2$SO$_4$ | 248                                    | 30 h @ 10 mA cm$^{-2}$                          | Nat. Commun. 2018, 9:5236                 |
| IrCoNi PHNCs   | GCE       | 0.1 M HClO$_4$  | 303                                    | 3.3 h @ 5 mA cm$^{-2}$                         | Adv. Mater. 201, 729, 1703798,           |
| IrNiCu         | GCE       | 0.1 M HClO$_4$  | 300                                    | --                                              | ACS Nano. 2017,                           |
| Material                  | Electrode | Solution          | Potential, Current Density | Reference                                      |
|--------------------------|-----------|-------------------|----------------------------|-----------------------------------------------|
| DNF                      |           |                   |                            |                                               |
| Ir                       | GF        | 0.5 M H$_2$SO$_4$ | 290 10 h@10 mA cm$^{-2}$  | *Nano Energy*. 2017, 40, 27.                |
| Ni$_{0.5}$Mn$_{0.5}$Sb$_{1.5}$O$_y$ | ATO       | 1 M H$_2$SO$_4$   | ~672 170 h@10 mA cm$^{-2}$ | *Energy Environ. Sci*. 2017, 10, 2103.     |
| W$_{0.57}$Ir$_{0.43}$O$_{3-\delta}$ | FTO       | 1 M H$_2$SO$_4$   | 370 0.6 h@10 mA cm$^{-2}$  | *Energy Environ. Sci*. 2017, 10, 2432.     |
| Co$_3$O$_4$              | FTO       | 0.5 M H$_2$SO$_4$ | 570 12 h@10 mA cm$^{-2}$   | *Chem. Mater*. 2017, 29, 950.               |
| Y$_3$Ru$_2$O$_{7-\delta}$ | GCE       | 0.1 M HClO$_4$    | 270@1 mA cm$^{-2}$ 8 h@1 mA cm$^{-2}$ | *J. Am. Chem. Soc*. 2017, 139, 12076.    |
| IrO$_2$-RuO$_2$ @Ru      | GCE       | 0.5 M H$_2$SO$_4$ | 281 --                      | *J. Mater. Chem. A*. 2017, 5, 17221.        |
| NiFeP                    | Free-standing | 0.05 M H$_2$SO$_4$ | 540 12 h@10 mA cm$^{-2}$       | *Adv. Mater*. 2017, 29, 1606570.         |
| IrNi NCs                 | GCE       | 0.1 M HClO$_4$    | 280 2 h@5 mA cm$^{-2}$        | *Adv. Func. Mater*. 2017, 27, 1700886.     |
| Co-IrCu ONC              | GCE       | 0.1 M HClO$_4$    | 290 --                      | *Adv. Func. Mater*. 2017, 27, 16046888.    |
| IrO$_x$-Ir               | GC plates | 0.5 M H$_2$SO$_4$ | 290 100 h@2 mA cm$^{-2}$      | *Angew. Chem. Int. Ed*. 2016, 55, 752.    |
| IrO$_x$/SrIrO$_3$        | SrTiO$_3$ | 0.5 M H$_2$SO$_4$ | 270-290 30 h@10 mA cm$^{-2}$ | *Science*. 2016, 353, 1011.               |
| BaYIrO$_6$               | Au        | 0.1 M H$_3$ClO$_4$| ~315 1 h@10 mA cm$^{-2}$      | *Nat. Commun*. 2016, 7, 12363.            |
| Ir-Ni Oxide              | Ti        | 0.1 M HClO$_4$    | ~270 --                      | *J. Am. Chem. Soc*. 2015, 137, 13031.     |
| IrNiO$_x$                | ATO       | 0.05 M H$_2$SO$_4$| ~330 --                      | *Angew. Chem. Int. Ed*. 2015, 54, 2975.   |
| IrO$_2$                  | GCE       | 0.1 M H$_3$ClO$_4$| ~430 --                      | *J. Electrochem. Soc*. 1983, 130, 825.    |
**Transparent Methods**

**Materials.** All reagents are of analytical grade and used as received. The commercial RuO₂ and Nafion (5 wt% solution) were purchased from Sigma-Aldrich.

**Synthesis of ZIF-67.** The ZIF-67 nanoparticles were synthesized via a procedure reported in literature. Cobalt nitrate hexahydrate (0.3 g) and 2-methylimidazole (0.66 g) were dissolved in methanol (11.3 g). The two solutions were then mixed and stirred at room temperature at 600 rpm for 24 h. The resulting purple precipitate was separated from the solution by centrifugation at 4000 rpm for 10 minutes and washed three times with methanol and dried overnight at 80 °C. The sample was further dried at 100 °C under vacuum for 12 h for future use.

**Synthesis of Ru-ZIF-67.** Typically, ZIF-67 (0.1 g) powder and desired amount of RuCl₃·xH₂O were added into 15 mL tetrahydrofuran (THF) and allowed to stir for 24 h. The resulting precipitate was centrifuged and washed with 3 times with THF, then dried at 80 °C in air. To obtain different Ru content Ru-ZIF-67, the amount of RuCl₃·xH₂O added was 0.2 g, 0.3 g, 0.4 g and 0.6 g respectively. For clearness, we denoted these samples as Ru-ZIF-67-A, Ru-ZIF-67-B, Ru-ZIF-67-C, and Ru-ZIF-67-D, respectively.

**Synthesis of Co-doped RuO₂ nanorods.** Co-doped RuO₂ powders were obtained by annealing Ru-ZIF-67 precursors in air at temperatures of 300~500 °C for 4 h. Typically, 20 mg of Ru-ZIF-67-C were placed in crucible and put into a muffle, and then annealed in air with a heating rate of 10 °C min⁻¹ to 350 °C, and held at 350 °C for 4 h.

**Characterizations.** Powder X-ray diffractions (PXRD) characterization of the samples were performed on a D8-Advance Bruker AXS diffractometer with Cu_Kα (λ=1.5418 Å)
radiation at a voltage of 40 kV and 40 mA. The sample morphologies were characterized using a field-emission scanning electron microscope (SEM) (Hitachi, S-4800). SEM specimens were prepared by depositing sample powders onto carbon adhesive tapes. Transmission electron microscopy (TEM) images and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were carefully recorded on Talos F200X and JEM-ARM200F. The chemical composition and bonding states were measured by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS ULTRA^{DLD} instrument with a monochromatic Al-Kα X-ray source ($h\nu=1496.6$ eV). The power was 120 W and the X-ray spot size was set to 700×300 μm. The pass energy of the XPS analyzer was set as 20 eV. The base pressure of the analysis chamber was better than $5\times10^{-9}$ Torr. The nitrogen adsorption-desorption isotherm was measured on ASAP 2020M apparatus at 77 K. Before the measurements, the samples were outgassed under vacuum at 160 °C for 12 hours. Raman spectra were recorded on a Renishaw inVia Reflex spectrometer. Inductively coupled plasma-mass spectroscopy (ICP-MS) measurements were carried on NexION 300 (Perkin-Elmer).

**Electrochemical measurements.** In a typical procedure, 4 mg of Co-RuO$_2$ powder was added to 1 mL of water/ethanol (3:1, v/v) containing 15 μL Nafion aqueous solution (5%, Sigma-Aldrich), and dispersed by sonication under shaking for 30 min to generate a homogeneous black ink. 5 μL of the prepared catalyst ink was drop-cast on a glassy carbon electrode (Geometric area: 0.07065 cm$^2$) and dried at room temperature to form a thin film working electrode. A three-electrode system, contained a glassy carbon working electrode, a counter electrode made of platinum wire (diameter: 0.5 nm), and a saturated Hg/Hg$_2$SO$_4$
reference electrode, were used to measure the electrochemical properties. All measurements were performed in 0.5 M H₂SO₄ acidic solution. The Hg/Hg₂SO₄ reference electrode was calibrated with a Pt wire electrode in H₂-saturated 0.5 M H₂SO₄ solution. The results showed that the potential difference between the Hg/Hg₂SO₄ reference electrode and reversible hydrogen electrode was 0.645 V. Cyclic voltammograms (CVs) tests were collected at a scan rate of 100 mV s⁻¹ typically between 1.2 and 1.6 V. Chronopotentiometric measurements were carried out by applying a constant current of 10 mA cm⁻² for up to 50 h. Electrochemical impedance spectroscopy (EIS) were performed at 1.4 V. The EIS results were presented in the form of Nyquist plot and fitted using ZView software with a representative equivalent electrical circuit. We carried out iR correction according to the literatures reported.[Zheng et al. 2017; Li et al. 2017] The potential was manually corrected using Ohm’s law: \( E = E_{\text{app}} - iR_{\text{s}} \times 0.85 \), where \( R_s \) (solution resistance) is determined to be 9 Ω by EIS (Figure 3c).

**Calculation details**

All DFT calculations are carried out by using the Vienna ab-initio Simulation Package (VASP) [Kresse, et al. 1996] to optimize geometry structures and energies. The exchange–correlation functional is performed within the generalized gradient approximation proposed by Perdew–Burke–Ernzerh (GGA-PBE).[Perdew, et al. 1996; Perdew, et al. 1992; ] The core electrons is described by the Projector Augmented Wave (PAW) potential,[Blochl, et al. 1994] and the cut-off kinetic energies for the plane waves are set to 500 eV,[Kresse, et al. 1994] The convergence criteria of energy and force on each atom after relaxation are less than 10⁻⁴ eV.
and 0.02 eV/Å², respectively. The RuO₂(110) is built with 2*2 supercell with fixing two bottom layers in the geometry optimization. The Brillouin zone is sampled by Gamma point [Hendrik, et al. 1976] and a vacuum distance of 15 Å along z direction was set to ensure sufficient vacuum on surface. The Thermal and zero point energy (ZPE) corrections are further calculated by DFT-D3 to obtain the Gibbs free energy (ΔG), which is determined following \[ \Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S, \] according to the standard hydrogen electrode (SHE) model proposed by Nørskov et al.[Peterson, et al. 2010] Grimme’s DFT-D3 scheme are expected to provide dispersion correction in van der Waals (vdW) interactions.[Grimme, et al. 2010; Grimme, et al. 2011] ΔE, ΔE_{ZPE} and ΔS are the electronic total energy differences, the differences in the zero point energy and the change of entropy, respectively. T is the temperature set to 298.15 K.

Free energy calculations: The Gibbs free energy changes are calculated by the following equations (1) to (4) for AEM while those for LOM are calculated by the equations (5) to (8) [Rossmeisl, et al. 2005].

\[ \Delta G_1 = \Delta G_{O^-} - \Delta G_{OH^+} - eU + \Delta G_{H_+} (pH) \]  

\[ \Delta G_2 = \Delta G_{OOH^+} - \Delta G_{O^-} - eU + \Delta G_{H_+} (pH) \]  

\[ \Delta G_3 = \Delta G_{OO} - \Delta G_{OOH^+} - eU + \Delta G_{H_+} (pH) \]  

\[ \Delta G_4 = 4.92 eV + \Delta G_{OH^-} - \Delta G_{OO} - eU + \Delta G_{H_+} (pH) \]  

\[ \Delta G_5 = \Delta G_{[Ov-OH]} - \Delta G_{[Ov-OO]} - eU + \Delta G_{H_+} (pH) \]  

\[ \Delta G_6 = \Delta G_{[OH-Ov-OH]} - \Delta G_{[Ov-OOH]} - eU + \Delta G_{H_+} (pH) \]  

\[ \Delta G_7 = \Delta G_{[OOH]} - \Delta G_{[OH-Ov-OH]} - eU + \Delta G_{H_+} (pH) \]
\[ \Delta G_\circ = 4.92 \text{eV} + \Delta G_{(Ov-OO)^*} - \Delta G_{(Ov-OOH)^*} - eU + \Delta G_{H^+} (pH) \] (8)

where \( U \) is the potential determined against by normal hydrogen electrode (NHE) at standard condition (\( T = 298.15 \text{ K}, P = 1 \text{ bar}, \text{pH} = 0 \)) [Nørskov et al. 2004]. The free energy changes of the protons relative to the above-specified electrode at non-zero \( \text{pH} \) is represented by Nernst equation as \( \Delta G_{H^+} (pH) = -k_B T \ln(10) \times p\text{H} \). The Gibbs free energy differences of these intermediates include zero-point energy (ZPE) and entropy corrections according to \( \Delta G = \Delta E + \Delta \text{ZPE} - T \Delta S \), where the energy differences \( \Delta E \) are calculated with respect to \( \text{H}_2\text{O} \) and \( \text{H}_2 \) (at \( U = 0 \) and \( \text{pH} = 0 \)). The theoretical overpotential is defined as the lowest potential at which all reaction steps are thermodynamically downhill [Man, et al. 2011; Doyle, et al. 2015]

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