

Nanoscale

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ARTICLE

***In-situ* evolution of bulk-active γ -CoOOH with immobilized Gd dopants enabling an efficient oxygen evolution electrocatalysis**Tianjue Hou,^{a†} Ruotao Yang,^{a†} Jiaxin Xu,^a Xiaodie He,^a Hongyuan Yang,^b Prashanth W. Menezes^{*b,c} and Ziliang Chen^{*a,b}Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Promoting the *in-situ* reconstruction of transition metal (TM)-based precatalysts into low-crystalline and well-modified TM (oxy)hydroxides (TMO_xH_y) during alkaline oxygen evolution reaction (OER) is crucial for enhancing their catalytic performances. In this study, we incorporated gadolinium (Gd) into the cobalt hydroxide precatalyst, achieving a deep reconstruction into cobalt oxyhydroxide (γ -CoOOH) while retaining incorporated Gd during the activation process of alkaline OER. The unconventional non-leaching Gd dopants endow the γ -CoOOH with reduced crystallinity, increasing the exposure of electrolyte-accessible Co atoms and enhancing bulk activity. Furthermore, modulation of the electronic structure of γ -CoOOH substantially boosts the intrinsic activity of the active Co sites. As a result, when supported on nickel foam, the catalyst exhibits remarkable alkaline OER performance, attaining a current density of 100 mA cm⁻² at a low overpotential of approximately 327 mV. Notably, an ultrahigh current density of 1000 mA cm⁻² is robustly maintained for 5 days, highlighting its immense potential for practical applications in large-scale hydrogen production.

Introduction

Hydrogen (H₂) is widely recognized as a promising alternative to fossil fuels, overconsumption of which induces the current severe energy and environmental crisis.^{1, 2} The sustainable energy-driven electrochemical water splitting, consisting of the anodic oxygen evolution reaction (OER) and the cathodic hydrogen evolution reaction (HER), has garnered significant attention because it can produce H₂ in an environmentally benign and non-carbon emission manner.^{3,4} However, the OER involves a complex four electron transfer step, with sluggish kinetics and hence reducing the overall efficiency of water electrolysis.^{3,5} Therefore, it is of high necessity to develop efficient electrocatalysts capable of accelerating OER. Industrially, the anode of alkaline water electrolysis is usually made of catalysts based on nickel (Ni) or its alloy (*e.g.*, Raney Ni), but their catalyst performance still needs further boosting.^{6, 7} In this regard, numerous efforts have been devoted to designing and synthesizing the new generation of low-cost non-noble transition metal (TM)-based catalysts, particularly those Fe, Co, Ni, and Mn-based compounds, with highly efficient alkaline OER capability to satisfy the requirements of practical applications.^{6–13}

When examining most TM-based compounds, including (oxyhydr)oxides, pnictides, chalcogenides, borophosphates, and intermetallics, in the alkaline OER in aqueous media, they tend to reconstruct into the associated higher-valence TM-based

(oxyhydr)oxides (TMO_xH_y), which serve as the real active structures.^{10, 14–17} Given the widespread observation of component oxidation into soluble oxyanions and subsequent leaching into electrolytes during OER, it's crucial to consider several key points.^{14–22} Firstly, among these single-phase OER-active TMO_xH_y, CoO_xH_y exhibits excellent corrosion resistance and notably, the highest electrical conductivity.^{23, 24} This makes Co-based materials promising precursors for efficient alkaline OER catalysts. Secondly, the alkaline OER capabilities of the pure CoO_xH_y are normally still far from satisfactory, likely due to the inadequate intrinsic activity of the redox active Co sites.²⁴ To address this issue, proper modifications are required for the *in-situ* reconstructed CoO_xH_y to increase the amount of the accessible redox active Co atoms with evidently improved inherent activity. Moreover, stabilizing the active Co sites with other components is of great significance to achieve the robust durability of CoO_xH_y, yet remains a challenge.^{25, 26} Within these conditions, incorporating elements that do not significantly leach out during alkaline OER in aqueous solutions into Co-based precatalysts may offer opportunities to effectively regulate the properties of *in-situ* evolved CoO_xH_y, eventually resulting in an enhanced oxygen evolution performance.^{25, 27}

On the other hand, the element doping has been widely proposed in previous works, as it can evidently promote the structural reconstruction of the TM-based precatalysts into the associated TMO_xH_y by reducing the reconstruction energy barrier or increasing the surface porosity.^{8, 28} However, the destabilization tendency of most doped atoms often results in their serving only as sacrificial agents, and the modulation effect cannot be maintained over prolonged OER electrochemistry. An intriguing observation is that the OER-active TMs themselves can be also utilized as the dopants, specially in the case of incorporating Fe into Ni- or Co-based catalyst systems where the resulting alkaline OER activity can be substantially improved.^{11, 29–33} However, the dissolution phenomenon during the operational OER process persists,^{8, 34} and therefore, the exact active sites responsible for alkaline OER are still under debate.³³ Based on these factors, one can envision that if a Co-based precatalyst can be incorporated by an OER-inactive but stable component, its *in-situ* deep reconstruction into a distinctive active CoO_xH_y phase could be

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



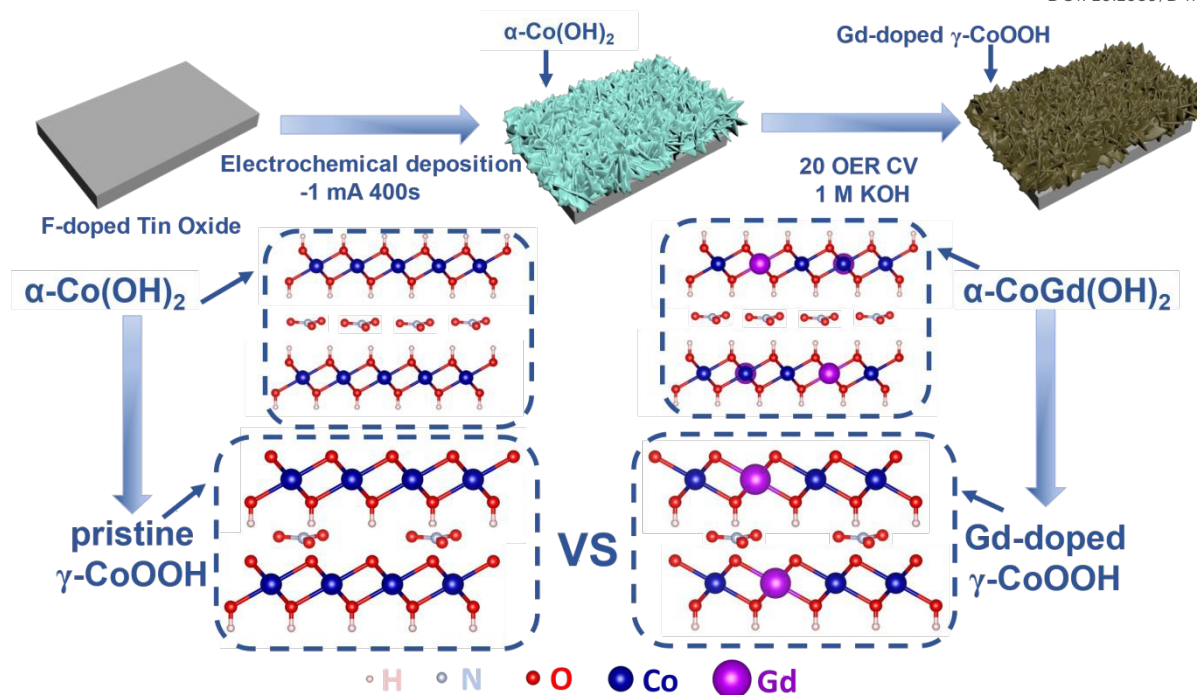


Fig. 1 Schematic representation of the synthesis for FTO-supported α -CoGd(OH)₂ and α -Co(OH)₂ and the activation of α -CoGd(OH)₂.

facilitated. Due to the regulation effect by the immobilized dopant, as well as the exclusion of the inferences from other potential active sites, such a CoO_xH_y could likely exhibit significantly improved alkaline OER performance. More importantly, this improvement can be explicitly attributed to the increased availability of redox active Co sites with optimized intrinsic activity.

Taking into account the aforementioned considerations, and to determine the role non-leaching feature of *f*-block rare earth metals under the alkaline OER conditions, we deliberately incorporate integrate *f*-block rare earth metals into cobalt hydroxide (α -CoGd(OH)₂) precatalyst.²⁷ Herein, gadolinium (Gd) was specifically chosen owing to its high chemical stability, strong corrosion resistance, and high conductivity.^{35, 36} As expected, compared with the pristine α -Co(OH)₂, the Gd-doping induced a deep OER-driven reconstruction into less-crystallinity γ -CoOOH with increased structural defects, facilitating the participation of more redox-active Co atoms in OER catalysis with enhanced bulk activity. Besides, the Gd dopants remained intact, enabling the regulation of the electronic structure of the γ -CoOOH host, thus boosting the intrinsic activity of the active Co sites. Benefiting from these advancements, the fully activated α -CoGd(OH)₂ exhibited strikingly superior OER performance compared to pristine α -Co(OH)₂ when deposited on both fluorine-doped tin oxide glass (FTO) and nickel foam (NF). Particularly noteworthy is the performance of α -Co_{0.95}Gd_{0.05}(OH)₂ on NF, requiring an overpotential of ~327 mV to achieve a current density of 100 mA cm⁻² which can then sustain an ultrahigh current density of 1000 mA cm⁻² for five days without visible degradation, displaying promising potential for further larger-scale application.

Result and discussion

Synthesis and characterizations of the as-prepared samples

The α -CoGd(OH)₂ precatalyst was directly grown on the FTO substrate (α -CoGd(OH)₂/FTO) through electrodeposition using a typical three-electrode system, in which, the FTO glass,

saturated calomel electrode (SCE), and Pt foil acted as the working electrode, reference electrode, and counter electrode, respectively. Co(NO₃)₂·6H₂O and Gd(NO₃)₃·H₂O were dissolved in deionized water as the deposition solution with a molar ratio of 0.95 : 0.05. After applying a constant current of -1 mA for a duration of 400 s, the targeted α -CoGd(OH)₂ supported on FTO was obtained. Subsequently, it was subjected to the OER activation using 20 cyclic voltammograms (CV) cycles, resulting in the *in-situ* to Gd-doped γ -CoOOH. The pristine α -Co(OH)₂/FTO was fabricated and activated using the same methods, except that no Gd sources were incorporated (details in Fig. 1 and the Experimental section).

Hereafter, the as-prepared α -CoGd(OH)₂/FTO and pristine α -Co(OH)₂/FTO, both before and after activation, were comprehensively characterized to acquire information about their morphology, phase, crystallinity, composition, and chemical state. Initially, field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) were employed to probe the morphology of such two as-prepared samples, from which the typical nanosheet-like morphology can be observed (Fig. 2a–d and Fig. S1a–c). High resolution TEM (HRTEM) imaging exhibited the lattice fringes with an interplanar distance of ~0.23 and ~0.20 nm for fresh α -CoGd(OH)₂, corresponding to the (105) and (108) plane of α -Co(OH)₂, respectively. Note that the distance was slightly larger than that of the theoretical value, indicating the lattice expansion induced by the incorporation of Gd atoms (Fig. 2e). Additionally, the selected area electron diffraction (SAED) pattern (Fig. 2f) uncovered the crystal facets (105), (102), and (110) of α -Co(OH)₂ (PDF #46-0605), providing further evidence of successful synthesis of α -Co(OH)₂ host phase. Similar observations were made for the pristine α -Co(OH)₂ sample without Gd incorporation (Fig. S1d, e). However, it is worth mentioning that the diffraction rings presented in the SAED pattern, as well as the lattice fringes shown in the HRTEM image, turned out to be more broken and indistinct for the α -CoGd(OH)₂



sample compared with those of the pristine α -Co(OH)₂, signifying the less crystallinity feature of host α -Co(OH)₂ after Gd doping. This formation of more structural defects could contribute to the OER-driven reconstruction promoting *in-situ* transformation could be realized by α -CoGd(OH)₂.^{28, 37} Additionally, the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) pattern and the energy-dispersive X-ray spectroscopy (EDS) elemental mapping images confirmed a uniform distribution of Co, Gd, and O within the selected region of the sample, directly indicating the successful Gd doping into the α -Co(OH)₂ phase (Fig. 2g–j and Table S1). Additionally, as shown in Table S2, inductively coupled plasma (ICP) was used to measure the atomic ratio of Co and Gd and delivered a similar result. Similar observations were made for the pristine α -Co(OH)₂ (Fig. S1f–h). The powder X-ray diffraction (XRD) technique was subsequently used to

examine the α -CoGd(OH)₂/FTO and pristine α -Co(OH)₂/FTO with the bare FTO as a reference. As depicted in Fig. 2k, in addition to the XRD peaks originating from the FTO substrate, the α -Co(OH)₂/FTO sample exhibited a discernible peak, which matched well with the most intensified (003) peak of a typical α -Co(OH)₂ pattern (PDF #46-0605).^{37, 38} However, such a peak in the case of α -CoGd(OH)₂/FTO appeared non-evident and negatively shifted. This is because the Gd-doping with a larger size compared with Co led to the slight lattice expansion, consequently reducing the crystallinity for the α -Co(OH)₂ host, which is in agreement with the above HRTEM and SAED data. Subsequently, the XRD patterns with 2 theta values below 10° for α -Co(OH)₂ and α -CoGd(OH)₂ together with the FWHM analysis on their respective (003) peak were also provided in Fig. S2, from which the broadening and negative shift of (003) peak can be easily identified, illustrating the crystallinity reduction

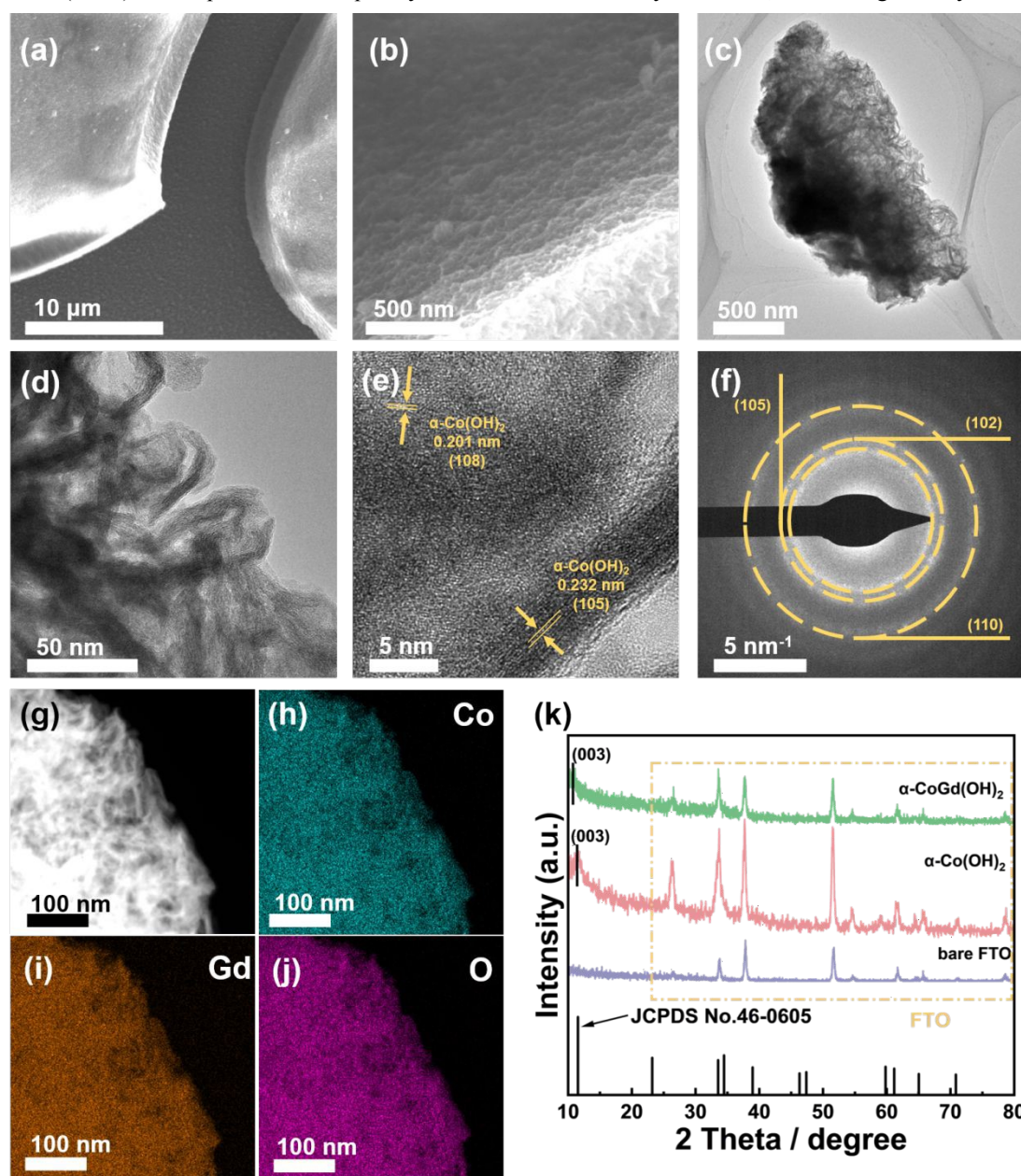


Fig. 2 (a, b) The FESEM images of α -CoGd(OH)₂/FTO. (c, d) The TEM images, (e) HRTEM image, and (f) SAED pattern together with the corresponding (g) HAADF pattern as well as the elemental mapping of (h) Co, (i) Gd, and (j) O for the α -CoGd(OH)₂ peeled from the FTO substrate. (k) The powder XRD patterns of the bare FTO, α -Co(OH)₂/FTO, and α -CoGd(OH)₂/FTO.



and lattice expansion induced by Gd introduction. Additionally, by employing calculations based on the Scherrer formula, it was determined that the average crystal size of α -Co(OH)₂ measured 7.27 nm, whereas α -CoGd(OH)₂ exhibited an average crystal size of 9.29 nm. These findings substantiated that successful Gd-doping can induce the increment of the average crystal size.³⁹ Afterward, we also used X-ray photoelectron spectroscopy (XPS) to gain more information on the chemical state and phase of the fresh α -CoGd(OH)₂/FTO and pristine α -Co(OH)₂/FTO. In Fig. S3a, the Co 2p_{3/2} spectrum in the latter sample can be fitted at ~781.1 and ~780.1 eV, corresponding to Co²⁺ and Co³⁺, respectively.²⁶ However, the fitted peaks indicative of Co²⁺ and Co³⁺ in the Co2p_{3/2} XPS spectrum for α -CoGd(OH)₂/FTO both shifted toward the higher binding energy, indicating the electronic interaction between Gd dopants and the Co atoms in the host lattice.^{7, 31} Moreover, the Gd 4d_{3/2} and 4d_{5/2} XPS peaks (Fig. S3b) can be fitted at ~148.1 and ~142.3 eV, respectively, illustrating the Gd was doped in the form of Gd³⁺.^{40, 41} In addition, the O 1s XPS spectrum of pristine α -Co(OH)₂/FTO was located at ~531.3 eV, similar to that previously reported for the α -Co(OH)₂ phase.⁴² Besides, a positive shift of O 1s XPS can be identified for the α -CoGd(OH)₂/FTO, further confirming the electronic modifications on the α -Co(OH)₂ induced by the introduction of Gd atoms (Fig. S3c).

Characterizations of the samples after OER activation.

The well-defined α -CoGd(OH)₂/FTO was fully activated using OER CV (details in the **Experimental section**) to enable the *in situ* evolution of the active oxyhydroxide that is responsible for the OER electrocatalysis. Notably, the optical images in **Fig. 3a** disclosed that the color of the α -CoGd(OH)₂ completely changed after activation, indicating a deep structural reconstruction. This

finding was further supported by the powder XRD patterns (Fig. 3b), where the broad (003) diffraction peaks of α -Co(OH)₂ can be found (except the peaks corresponding to the FTO substrate). We have further performed GI-XRD characterizations on both activated α -Co(OH)₂ and α -CoGd(OH)₂ while employing a beam knife to minimize air scattering in the low 2 theta region. In the former case free of Gd doping, the (003) diffraction peak of α -Co(OH)₂ was still easily identified. Conversely, such a peak was absent in the XRD pattern of the activated α -CoGd(OH)₂ (Fig. S4). This comparison clearly illustrated that the amorphization of α -CoGd(OH)₂ after activation mainly stemmed from the Gd doping instead of the pure anodic activation. The *in situ* Raman spectra were subsequently recorded to gain deeper insights into the phase reconstruction during activation. At open circuit potential (OCP), the spectrum of the α -CoGd(OH)₂ sample (Fig. 3c) exhibited two peaks at ~455 and ~518 cm⁻¹, attributed to the Co–O vibrations of α -Co(OH)₂ phase,⁴³ which were remained intact until 1.0 V (*vs.* RHE). Notably, the transformation of this precatalyst was initiated at 1.1 V (*vs.* RHE), where a hydrous Co(OH)₂ phase formed, as confirmed by a big peak at ~595 cm⁻¹.⁴⁴ Moreover, at 1.2 V (*vs.* RHE), the associated peaks at ~454 and ~518 cm⁻¹ almost disappeared and two new bands at ~462 and ~571 cm⁻¹ emerged. This indicated that the precatalysts reconstructed into γ -CoOOH phase.^{43, 44} Notably, the reconstructed γ -CoOOH got stabilized with increasing the applied potentials and returning to OCP. Moreover, for both α -CoGd(OH)₂/FTO and α -Co(OH)₂/FTO after OER activation, their Co 2p_{3/2} XPS spectra revealed an apparent increase in Co³⁺ concentration, aligning with the conclusion of the *in situ* evolution of higher-valence γ -CoOOH (Fig. 3d). Remarkably, the fitted peaks indexed to both Co³⁺ and Co²⁺ in the spectrum of

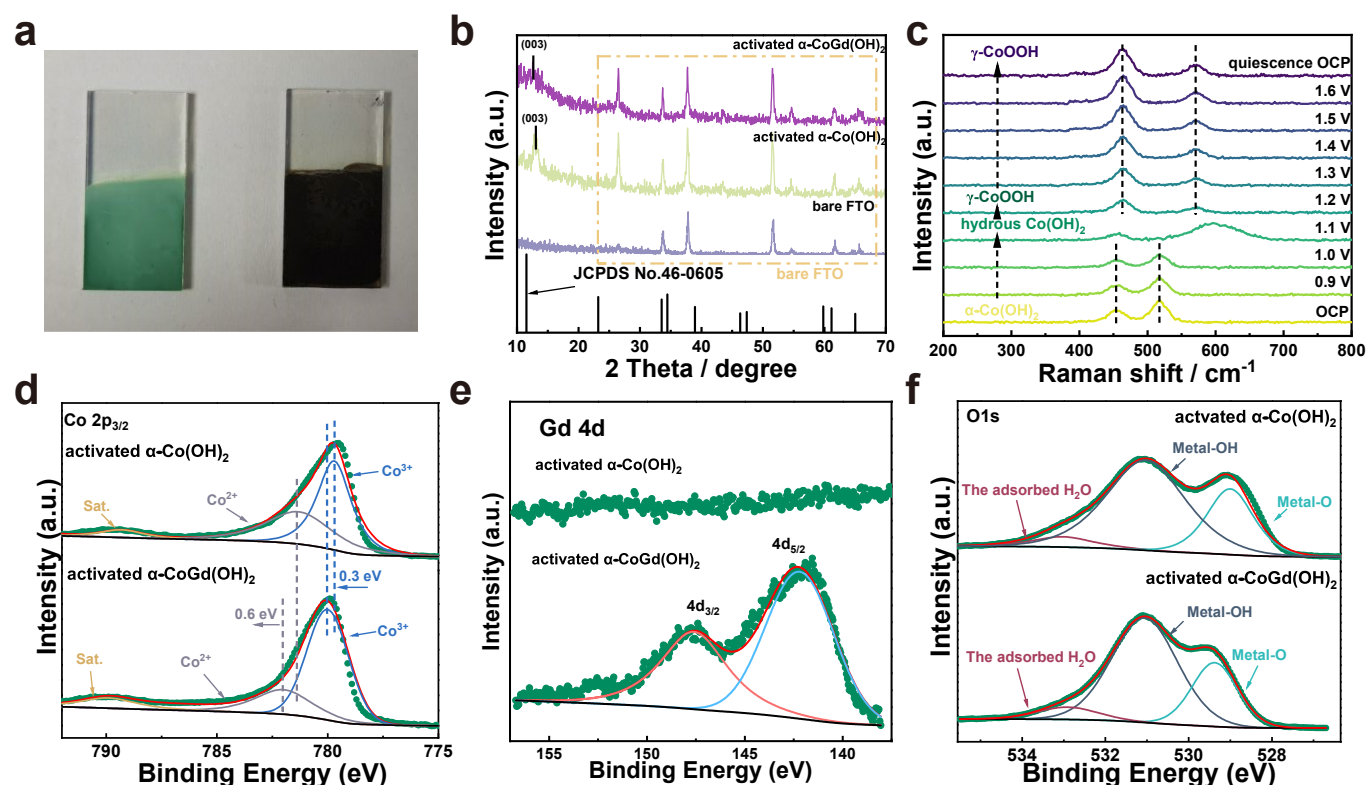


Fig. 3 (a) The optical images of α -CoGd(OH)₂ before and after activation. (b) The powder XRD patterns of the activated α -CoGd(OH)₂ and α -Co(OH)₂. Herein, the pattern of the bare FTO served as a reference. (c) *In situ* Raman spectra of the activated α -CoGd(OH)₂ at from 0.9 to 1.6 V *vs.* RHE, as well as the *ex situ* ones at OCP. (d) Co 2p_{3/2} XPS spectra of α -CoGd(OH)₂ and α -Co(OH)₂ after activation. (e) The Gd 4d XPS spectrum of α -CoGd(OH)₂ after activation. (f) The O 1s XPS spectrum of α -CoGd(OH)₂ and α -Co(OH)₂ after activation.



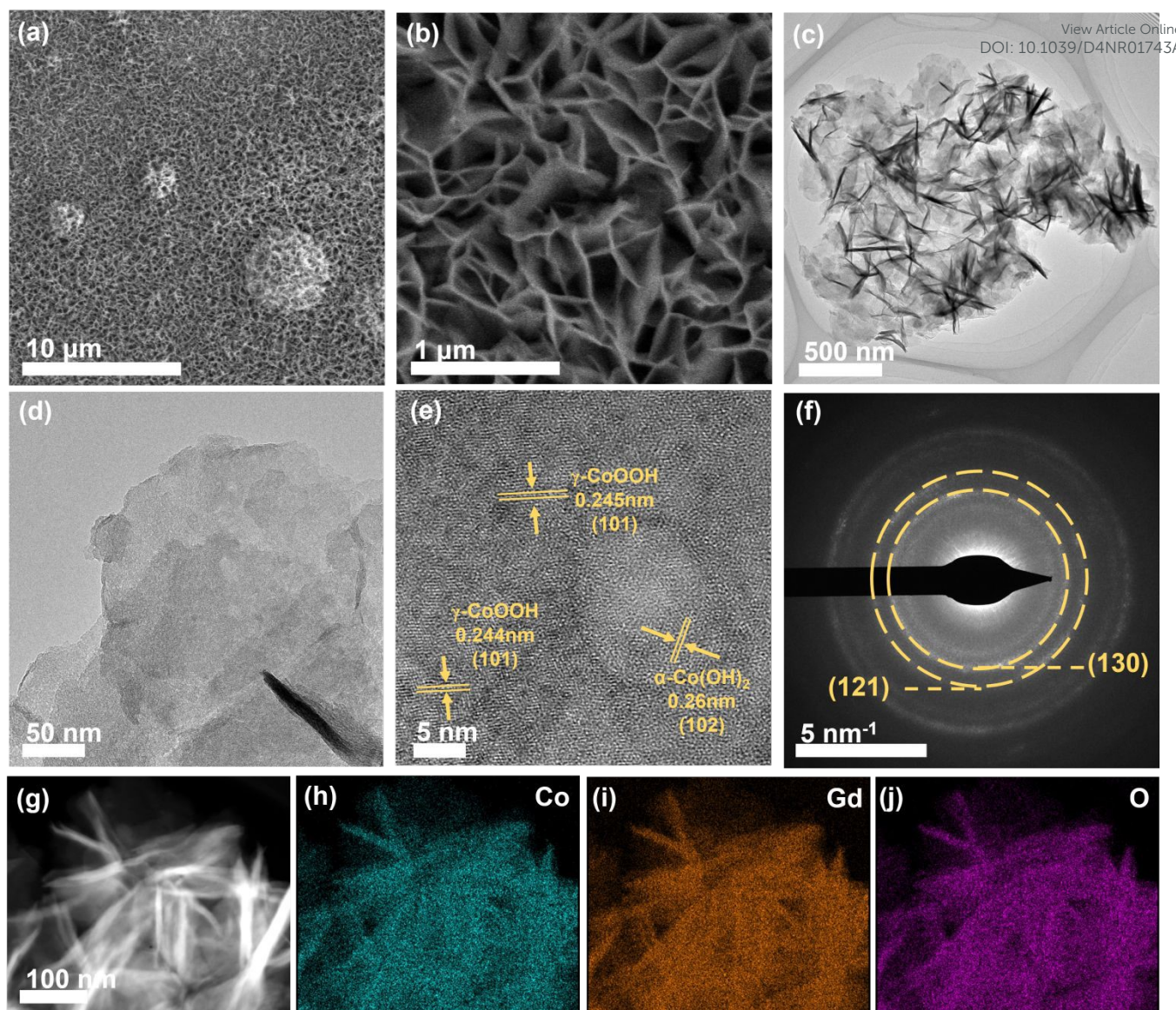


Fig. 4 (a, b) The FESEM images of α -CoGd(OH)₂/FTO after activation. (c, d) The TEM images, (e) HRTEM image, and (f) SAED pattern together with the corresponding (g) HAADF pattern as well as the elemental mapping of (h) Co, (i) Gd, and (j) O for the α -CoGd(OH)₂ after activation (peeled from the FTO substrate).

the former sample were located at higher binding energy positions, which implied a significant modification of the incorporated Gd. Fig. 3e displayed a clear Gd 4d XPS spectrum of the α -CoGd(OH)₂/FTO after activation, with fitted peaks assigned to 4d_{3/2} and 4d_{5/2} still representing the existence of Gd³⁺, affirming that the Gd was preserved during structural reconstruction, resulting in a Gd³⁺-doped high-valence γ -Co^{3+ δ} OOH active phase.^{40, 41} Also, there was no signal of Gd in α -Co(OH)₂ after activation. The O 1s XPS spectra in Fig. 3f further validated the evolution of oxyhydroxides for these two samples after OER activation.⁴⁵ The peak corresponding to the absorbed water, metal-OH and metal-O were attributed to \sim 532.9, \sim 531.1 and \sim 529.4 eV, respectively.⁴⁶ Based on the above data, it can be concluded that α -CoGd(OH)₂ deeply reconstructed into Gd-doped low-crystalline γ -CoOOH during OER activation, while the pristine α -Co(OH)₂ only achieved a lower degree of reconstruction, forming a pure γ -CoOOH with higher crystallinity. Analogically to most cases of TM-based precatalysts, the reconstruction of the pristine α -Co(OH)₂ occurs only on its surface because the transformed layer is usually densely stacked during the OER process. This will hinder the

penetration of the OH⁻ (reactants of alkaline OER) into the inner bulk, thereby limiting further reconstruction. Upon incorporating Gd into the α -Co(OH)₂ precatalyst to diminish crystallinity and create more structural defects, more exposed TM sites could be offered, thereby facilitating deeper penetration of OH⁻ reactants. Consequently, a deep surface transformation was induced.²⁵

The morphology of the activated α -CoGd(OH)₂/FTO and α -Co(OH)₂/FTO was investigated through the FESEM and TEM characterizations, revealing that both maintained nanosheet structures characteristic of oxyhydroxides (Fig.S5a–d and S5a–c). Furthermore, the HRTEM analysis in Fig. 4e confirmed that the lattice fringes of the α -CoGd(OH)₂ after OER activation were broken and indistinct. Whereas, within the short-range ordered region, the lattice fringes possessed an interplanar spacing distance of 0.24 nm, primarily attributed to the (101) plane of γ -CoOOH (PDF# 14-0673), suggesting the dominant presence of low-crystalline γ -CoOOH phase within the α -CoGd(OH)₂ after activation. This conclusion was supported by the SAED pattern of this sample (Fig. 4f). It's noteworthy that the measured interplanar distance was slightly larger than the ideal value of γ -CoOOH, possibly due to steady Gd



incorporation (Fig. 4e). Conversely, the activated pristine α -Co(OH)₂ sample (Fig. S5d, e) exhibited relatively unbroken lattice fringes in its HRTEM image. Meanwhile, its SAED pattern showed distinct diffraction rings, assigned to both reconstructed γ -CoOOH (PDF# 14-0673) and remaining α -Co(OH)₂ (PDF #46-0605). These findings highlight the pivotal role of Gd doping in structural reconstruction during alkaline OER. Furthermore, the HAADF-STEM pattern and the EDS elemental mapping images substantiated uniform distribution of that Co, Gd, and O throughout the selected region of the α -CoGd(OH)₂ after activation, indicating stable retention of incorporated Gd (Fig. 4g–j and Table S1), which was also well corroborated by the findings of ICP in Table S2. Note that the structure of CoO_xH_y materials is typically composed of

nanodomains formed by edge-sharing [MO₆] octahedral layers.⁴⁷ The large-sized nanodomains tend to be orderly arranged for the directly synthesized CoO_xH_y (such as the ones obtained from the electrochemical deposition in this study), resulting in limited access for the electrolyte to the bulk active sites.⁴⁸ As a result, only a near-surface activity can be achieved. Herein, the in-situ formation of low-crystallinity γ -CoOOH, facilitated by the stable incorporation of Gd, is believed to create more structural defects and voids. This enhances the penetration of the KOH electrolyte, thereby increasing the number of accessible redox-active Co atoms. Eventually, a higher bulk activity of the reconstructed active structure was realized. On the other hand, the stable incorporation of Gd dopants in the reconstructed γ -CoOOH could result in a distinctive gradient orbital coupling of Gd(4f)-

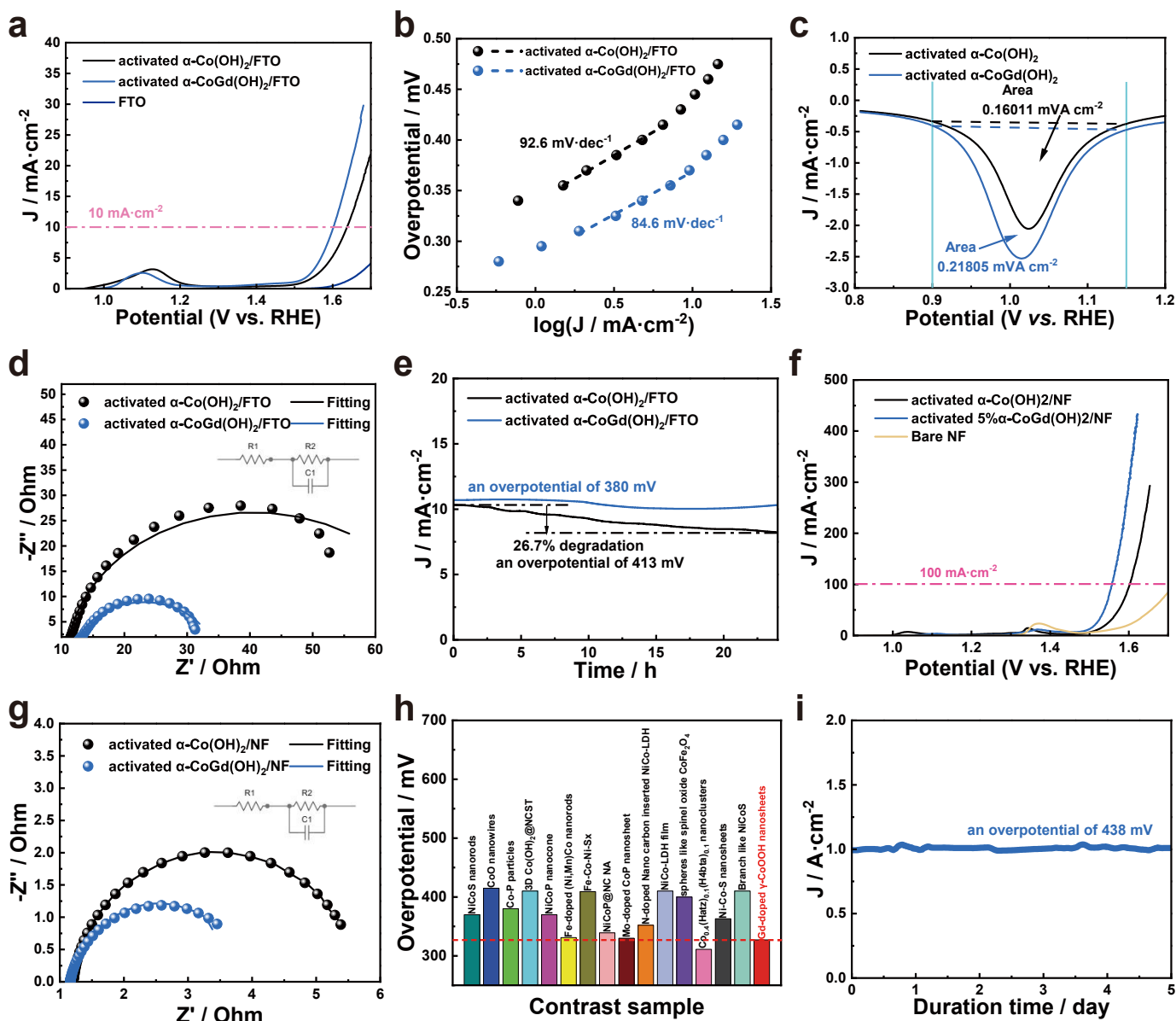


Fig. 5 (a) The LSV curves (together with the bare FTO reference), (b) Tafel slope plots, (c) integration of reduction peaks, (d) Nyquist plots obtained from EIS fitting to an equivalent circuit (inset) at an anodic potential of 1.6 V vs. RHE, (e) CA curves for α -CoGd(OH)₂/FTO and α -Co(OH)₂/FTO for 24 h. (f) The LSV curves (together with the bare NF reference) and (g) Nyquist plots obtained from EIS fitting to an equivalent circuit (inset) at an anodic potential of 1.55 V vs. RHE for α -CoGd(OH)₂/NF and α -Co(OH)₂/NF. (h) The activity comparison between α -CoGd(OH)₂/NF and other recently reported advanced Co-based catalysts for alkaline OER supported on NF. (i) The CA curve of α -CoGd(OH)₂/NF for 5 d. All the above electrochemistry was conducted after activating the studied samples using 20 cycles of OER CV.



O(2p)-Co(3d), increasing the electronic density and covalency of Co-O bond. Such an electron structure could optimize the adsorption energies towards the OER intermediates.^{11,35} Consequently, the intrinsic activity of the transformed active phase is significantly enhanced. The enhancements in both bulk and intrinsic activity of γ -CoOOH resulting from Gd doping are substantiated by a series of electrochemical analyses detailed in the following sections.

Alkaline OER electrochemistry of the activated samples and characterizations after stability test

After activation using CV cycles to ensure deep reconstruction into Gd-doped γ -CoOOH, all evaluations of the OER catalytic performances of α -CoGd(OH)₂/FTO were conducted in 1 M KOH (details in the **Experimental section**), with pristine α -Co(OH)₂/FTO after the same activation procedure used as a reference. The linear sweep voltammetry (LSV) tests were performed on α -CoGd(OH)₂/FTO with different Gd incorporation. Fig. S6a illustrated that among them, the sample prepared with a molar ratio between Co and Gd source of 0.95 : 0.05 exhibited optimum activity (the one characterized throughout the above sections). Notably, as is depicted in **Fig. 5a**, the activated α -CoGd(OH)₂/FTO required an overpotential of ~371 mV to afford 10 mA cm⁻² current density, substantially superior to that of the activated α -Co(OH)₂/FTO. The negligible OER activity of the bare FTO substrate indicated that the observed activity mainly originated from the deposited catalysts. Subsequently, steady-state measurements were conducted to determine the Tafel slope of α -CoGd(OH)₂/FTO and α -Co(OH)₂/FTO after activation.⁴⁹ As shown in Fig. 5b, α -CoGd(OH)₂/FTO exhibited a significantly lower Tafel slope, indicating that Gd incorporation promoted more favorable reaction kinetics of reconstructed γ -CoOOH. Additionally, the CV was performed on both activated α -CoGd(OH)₂/FTO and α -Co(OH)₂/FTO, and their respective reduction peak was analyzed to determine the number of redox active Co atoms that were involved in OER electrocatalysis.⁴⁷ Specifically, the former showed ~1.4 times more redox active Co sites than the latter (Figs. 5c and S7), which can be related to the lower crystallinity of the active γ -CoOOH induced by the immobilized Gd dopants. The lower crystallinity meant more structural defects, probably resulting in more disordered stacking of the edge-sharing [MO₆] octahedra layers, allowing greater electrolyte penetration.^{26, 50–52} As a result, more Co atoms can be accessed, and an enhanced bulk activity was achieved.^{7, 48} Based on this, we further normalized the current from the LSV data in Fig. 5a against such determined amounts of redox active Co atoms to evaluate their intrinsic activity.⁴⁶ As is shown in Fig. S8, the Gd-doped γ -CoOOH in the activated α -CoGd(OH)₂/FTO sample exhibited a distinctly higher inherent activity than that of the pure γ -CoOOH in the activated α -Co(OH)₂/FTO, which can be further verified by the higher turnover frequency (TOF) and mass-normalized activity of the activated α -CoGd(OH)₂/FTO (Figs. S11, S12).^{53, 54} Combining these results with the lower Tafel slope values (Fig. 5b), it can be concluded that the introduction of Gd atoms profoundly enhanced the intrinsic activity of the active sites of γ -CoOOH for alkaline OER. The electrochemical impedance spectroscopy (EIS) results (Fig. 5d and Table S3)

demonstrated an enhanced charge transfer ability of the reconstructed γ -CoOOH during OER upon doping Gd.¹⁷ The stability of activated α -CoGd(OH)₂/FTO and α -Co(OH)₂/FTO were further assessed through a 24 h chronoamperometry (CA) at a current density of ~10 mA cm⁻². As shown in Fig. 5e, negligible degradation was found for α -CoGd(OH)₂/FTO, whereas α -Co(OH)₂/FTO showed visible activity decline suggesting that Gd doping into γ -CoOOH might stabilize its alkaline OER activity. Considering CoO_xH_y typically features good electric conductivity and resistance to alkaline OER corrosion, the improvements on the reconstructed γ -CoOOH through doping Gd should primarily be attributed to the elevated bulk activity owing to the increased accessible redox active Co sites, as well as enhanced intrinsic activity of such catalytic atoms.²⁴ Moreover, through a set of characterizations, including (HR)TEM, SAED, HAADF-STEM, and EDS-elemental mapping, on the post-CA sample, the morphology, phase, crystallinity, composition content and distribution of the reconstructed Gd-doped γ -CoOOH was almost unchanged (Fig. S9), verifying the applicability and durability of the Gd incorporation.

Encouraged by the excellent OER catalytic performances of α -CoGd(OH)₂/FTO after activation, α -CoGd(OH)₂, together with the α -Co(OH)₂ reference, was further deposited on NF. After activation by CV cycles, the α -CoGd(OH)₂ peeled from the NF substrate exhibited similar features to the activated α -CoGd(OH)₂ extracted from the FTO (Fig. S10). The LSV (Fig. 5f), Tafel slope (Fig. S13), and EIS (Fig. 5g and Table S3) results for activated α -CoGd(OH)₂/NF and α -Co(OH)₂/NF exhibited a trend similar to that observed when deposited on FTO. Especially, as depicted in Fig. 5f and Fig. S13, the activated α -CoGd(OH)₂/NF can deliver a high current density of ~100 mA cm⁻² at only ~327 mV with a Tafel slope value of merely ~79.5 mV dec⁻¹. Furthermore, Fig. 5h and Table S4 demonstrated that its activity was superior or comparable to most of the recently reported advanced Co-based catalysts supported on NF for alkaline OER electrocatalysis. Finally, the possible industrial potential of the activated α -CoGd(OH)₂/NF was affirmed by subjecting it to an ultrahigh current density (~1000 mA cm⁻²) for 5 days without obvious decline (Fig. 5i). The material exhibited remarkable stability during this period, indicating its enormous promise for practical applications in industry.

Conclusions

In summary, our innovative Gd doping strategy has facilitated a significant transformation of the α -Co(OH)₂ precatalyst into γ -CoOOH, incorporating well-immobilized Gd during alkaline OER activation. The presence of stable Gd dopants led to low crystallinity of the reconstructed γ -CoOOH, thereby enhancing accessibility and increasing the number of redox active Co atoms. Consequently, a substantial increase in bulk activity was observed. Moreover, the inherent activity of these active Co atoms was largely enhanced due to profound modifications in the electronic structure of γ -CoOOH. As a result of these advantages, activated α -CoGd(OH)₂/NF achieved a remarkable current density of ~100 mA cm⁻² at only ~327 mV, and



impressively sustained an ultrahigh current density of 1000 mA cm⁻² for 5 days without noticeable activity degradation. Therefore, we believe that this newly developed α -CoGd(OH)₂ holds great potential for applications in large-scale green hydrogen production.

Experimental

Chemicals and Materials

The deionized water was used to carry out all the experiments. The potassium hydroxide (KOH, 95%) and cobalt nitrate (Co(NO₃)₂ · 6H₂O, 99.99%) were acquired from Sinopharm Group Co. Ltd. The gadolinium nitrate (Gd(NO₃)₃ · 6H₂O, 99.9%) was obtained from Macklin Biochemical Technology Co., Ltd. The electrode substrates NF and FTO were purchased from Merck & Co., Inc., respectively.

Synthesis of α -CoGd(OH)₂ with different Gd doping as well as their activation

In order to prepare α -CoGd(OH)₂, the electrodeposition was conducted in a standard three-electrode system, where the working electrode, counter electrode, and reference electrode were bare FTO, Pt foil, and SCE, respectively. Co(NO₃)₂ · 6H₂O and Gd(NO₃)₃ · 6H₂O were dissolved in 50 mL deionized water with a molar ratio of 0.95 : 0.05. Using the CHI760e electrochemical workstation, a constant applied current of -1 mA was maintained for a duration of 400 s. The resulting loading mass obtained was ~0.22 mg cm⁻². Furthermore, NF was employed as an alternative working electrode while keeping the rest of the deposition process consistent with that described above, eventually yielding a loading mass of ~0.68 mg cm⁻². Before all electrochemistry tests, the as-prepared α -CoGd(OH)₂ was activated using OER CV for 20 cycles in another three-electrode system (CHI760e electrochemical workstation). Note herein that the FTO- or NF-supported α -CoGd(OH)₂ was used as the working electrode, while Pt foil and Hg/HgO electrode acted as the counter and reference electrode, respectively. The electrolyte was 1 M KOH aqueous solution. Besides, the utilized potential window of the CV activation ranged from 0.9 to 1.5 V vs. RHE. Based on the same procedures abovementioned in the case of α -Co(OH)₂ (except that no Gd source was introduced), the pristine α -Co(OH)₂ deposited on FTO or NF were prepared and subsequently activated. In addition, another α -CoGd(OH)₂ with different Gd doping was fabricated by adjusting the molar ratio between Co(NO₃)₂ · 6H₂O and Gd(NO₃)₃ · 6H₂O, ranging from 0.975 : 0.025, 0.925 : 0.075, to 0.9 : 0.1. And these samples were denoted as 2.5% α -CoGd(OH)₂, 7.5% α -CoGd(OH)₂, and 10% α -CoGd(OH)₂, respectively.

Characterization

The phase information of the investigated samples was obtained using powder XRD on a Bruker D8 ADVANCE X-ray diffractometer, which used Cu K α radiation (λ = 1.5406 Å). The powder XRD in GI mode and equipped beam-knife was

characterized by the PANalytical X-ray diffractometer, which used Cu K α radiation. The calculation of average crystal size was supported by the Scherrer formula: $D = K \cdot \lambda / \beta \cdot \cos\theta$, where D is the crystallite size, K is the Scherrer constant (0.9), λ is the wavelength of the X-rays used (0.15406 nm), β is the FWHM, and θ is the peak position.³⁹ FESEM (Hitachi SU800 electron microscope, Tokyo, Japan) was utilized to acquire the morphology and structure of the target samples at an accelerating voltage of 10 kV. Furthermore, TEM (FEI Talos F200X and JEM F200) was used to further analyze the existence and distribution of its microstructure, phases, and components. The ICP (PerkinElmer, USA) was utilized to measure the compositions. XPS measurements were performed using a Thermo Scientific ESCALAB 250Xi spectrometer (USA), which had a power of 100 W (10 kV and 10 mA) and a monochromatic α X-ray source ($h\nu$ = 1486.65 eV). All samples were analyzed under vacuum conditions of less than 1.0 × 10⁻⁹ Pa, and the spectra were obtained with a 0.05 eV step size using Advantage software (version 5.979). Raman spectra were recorded using a Horiba LabRam HR Evolution confocal microscope, with a laser excitation wavelength of 473 nm, a laser power of 1.25 mW, and an objective magnification of 100× (NA = 0.95). The Raman spectrum was initially measured under the OCP using the Renishaw Raman system (in Via Qontorin, 532 nm laser), followed by *in situ* Raman testing from 0.9 V to 1.6 V, and finally the catalyst was re-measured after being placed in the OCP for an hour. The *in situ* Raman was performed on the Renishaw Raman system integrated with an electrochemical workstation (CHI, 760E).

Electrochemical measurements

The electrochemical experiments were performed using a CHI760e and EC-Lab electrochemical workstations in a typical three-electrode configuration. The working electrodes consisted of catalysts electrodeposited on different substrates, while a counter electrode made of Pt foil (1 × 1 cm) and a reference electrode composed of Hg/HgO was employed. The LSV, CV, CP, and CA experiments were carried out with an *iR* compensation of 90% on the CHI760e instrument. Furthermore, the CV and LSV tests were conducted at a scan rate of 5 mV s⁻¹. All measured potentials were calibrated with respect to RHE based on the following equation: E (vs. RHE) = E (vs. Hg/HgO) + 0.098 V + (0.059 × pH) V, where the pH value of 1 M KOH was adopted from our previous report.⁵⁵ The Tafel slope and EIS were conducted using the EC-Lab electrochemical workstation. The Tafel slope was determined through a steady-state measurement, *i.e.*, the CA was performed at each fixed potential for 3 minutes, and the applied potentials gradually increased with an interval of 15 mV.⁴⁹ The average current density obtained at each potential was used for the calculation of Tafel plots. The Tafel slope was determined according to the Tafel equation: $\eta = \log j + a$, where η , b , and j represent overpotential (V), Tafel slope (mV dec⁻¹), and current density (mA cm⁻²), respectively. In order to obtain the effective catalytic metal atoms of the catalyst, we determined the number of atoms capable of catalytic conversion using the formula: $n = A / s q$, which was achieved by analyzing the reduction peak area of a catalyst supported by



FTO with equivalent mass at a sweep rate of 5 mV s⁻¹. Here, n represents the number of transferred electrons, A denotes the reduction peak area, s signifies the sweep rate, and q represents the charge carried by a single electron.¹⁹ The EIS was recorded at 1.60 V (vs. RHE) for the catalysts deposited on FTO, as well as 1.55 V (vs. RHE) for the ones on NF. The amplitude of the sinusoidal wave was determined within a frequency range from 100 kHz to 1 mHz. The charge transfer resistance (R_{ct}) was reflected by the diameter of the semicircle in the Nyquist plots after fitting in the EC-Lab. The turnover frequency (TOF) was calculated by the formula: $TOF = j \cdot N_A / F \cdot n \cdot \Gamma$, where j is the current density, N_A is the Avogadro number, n is the number of electrons transferred for the evolution of a single O₂ molecule, F is the Faraday constant, and Γ is the surface concentration or the number of active Co sites.⁵³

Author Contributions.

T.H.: experimental data, writing-editing, characterization, analysis. R.Y.: characterization, experimental data, writing-editing. J.X.: experimental data. H.Y.: writing-editing. P.M.: conceptualization, writing-editing, funding acquisition. Z.C.: conceptualization, methodology, writing-editing, supervision, funding acquisition. The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is supported by National Natural Science Foundation of China (52201269), Natural Science Foundation of Jiangsu Province (BK20210735), Collaborative Innovation Center of Suzhou Nano Science & Technology, the 111 Project, and Suzhou Key Laboratory of Functional Nano & Soft Materials and Jiangsu Key Laboratory for Advanced Negative Carbon Technologies. Z.C. gratefully acknowledges the funding from Gusu leading talent plan for scientific and technological innovation and entrepreneurship (ZXL2022487). H. Yang thanks China Scholarship Council (CSC) for the Ph.D. fellowship. P. W. Menezes greatly acknowledges support from the German Federal Ministry of Education and Research in the framework of the project Catlab (03EW0015A/B) and project Prometh2eus (03HY105C).

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View Article Online
DOI: 10.1039/D4NR01743A



Data availability

- The data supporting this article have been included as part of the Supplementary Information.

