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Fe-facilitated dynamic active site generation on spinel CoAl_2O_4 with self-termination of surface reconstruction for water oxidation

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Abstract

The development of efficient and low-cost electrocatalysts for oxygen evolution reaction is critical for improving the water electrolysis efficiency. Here we report a strategy using Fe substitution to enable the inactive spinel CoAl_2O_4 to become highly active and superior to the benchmark IrO_2 . The Fe substitution is revealed to facilitate the surface reconstruction into active Co oxyhydroxides under OER conditions. It also activates the deprotonation on the reconstructed oxyhydroxide to induce negatively charged oxygen as active site, thus significantly enhancing the OER activity of CoAl_2O_4 . Furthermore, it promotes the pre-oxidation of Co and introduces great structural flexibility due to the uplift of the O 2p levels. This results in an accumulation of surface oxygen vacancy along with lattice oxygen oxidation that terminates as Al^{3+} leaches, preventing further reconstruction. We showcase a promising way to achieve tunable electrochemical reconstruction by optimizing the electronic structure for low-cost and robust spinel oxide OER catalysts.

1 Hydrogen has been proposed for long as an energy carrier for a sustainable and clean energy
2 infrastructure. However, such a hydrogen energy infrastructure has not been realized yet even so
3 many years have passed since its first proposal. One of the major reasons is the low efficiency and
4 high material cost of water electrolysis, which is a mean to sustainably produce hydrogen fuel from
5 water using the electrical energy generated by sustainable resources like solar panels.¹ The low
6 energy efficiency for such system is mainly caused by the sluggish reaction kinetics at the anode side
7 of water electrolyzer,² i.e. where water is oxidized and the oxygen evolution reaction (OER) occurs.
8 The benchmark anode electrocatalysts are noble metal-based oxides, such as IrO₂ and RuO₂,³⁻⁴ which,
9 however, aggravates the cost problem for water electrolysis. In recent years, great efforts have been
10 made to explore first-row 3d transition metal oxides as low-cost alternatives for OER.^{1,5} Toward that
11 goal, one important progress was made in identifying the active sites for some Co-containing oxides
12 as oxyhydroxides generated under operando condition.⁶⁻¹⁰ Specifically, many Co-based oxides were
13 reported to undergo surface self-reconstruction of Co sites to Co (III) oxyhydroxides, offering a
14 higher activity^{6, 9-10} arising from the di- μ -oxo bridged Co-Co sites.¹¹ However, despite revealing the
15 critical role of the surface reconstruction into oxyhydroxides, such reconstruction sometimes
16 compromises a stable OER catalysis due to instable surface chemistry.¹² In addition, how to properly
17 facilitate the surface reconstruction is still elusive.

18 Here, we report an approach to promote the surface reconstruction on inactive but low-cost CoAl₂O₄
19 (see Supplementary Note 1 for more about CoAl₂O₄) and to boost its OER performance by
20 substituting Al with a small amount of Fe. The partially substituted CoFe_{0.25}Al_{1.75}O₄ outperforms
21 IrO₂. We demonstrate here that a low level of Fe substitution is able to facilitate the surface
22 reconstruction of CoAl₂O₄ by activating the pre-oxidation of Co and optimizing the O 2p level of

oxide for greater structural flexibility. More importantly, a distinctive reconstruction behavior with self-termination has been revealed on $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$, which enables a stable surface chemistry. In addition, we suggest that, on the reconstructed surface, the Fe substitution facilitates a two-step deprotonation process, which leads to the formation of active oxygen sites at a low overpotential and thus greatly promotes the OER. Finally, the electrolysis application of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ as OER catalyst was demonstrated in membrane electrode assembly (MEA) configuration.

Results

Crystal structure characterization

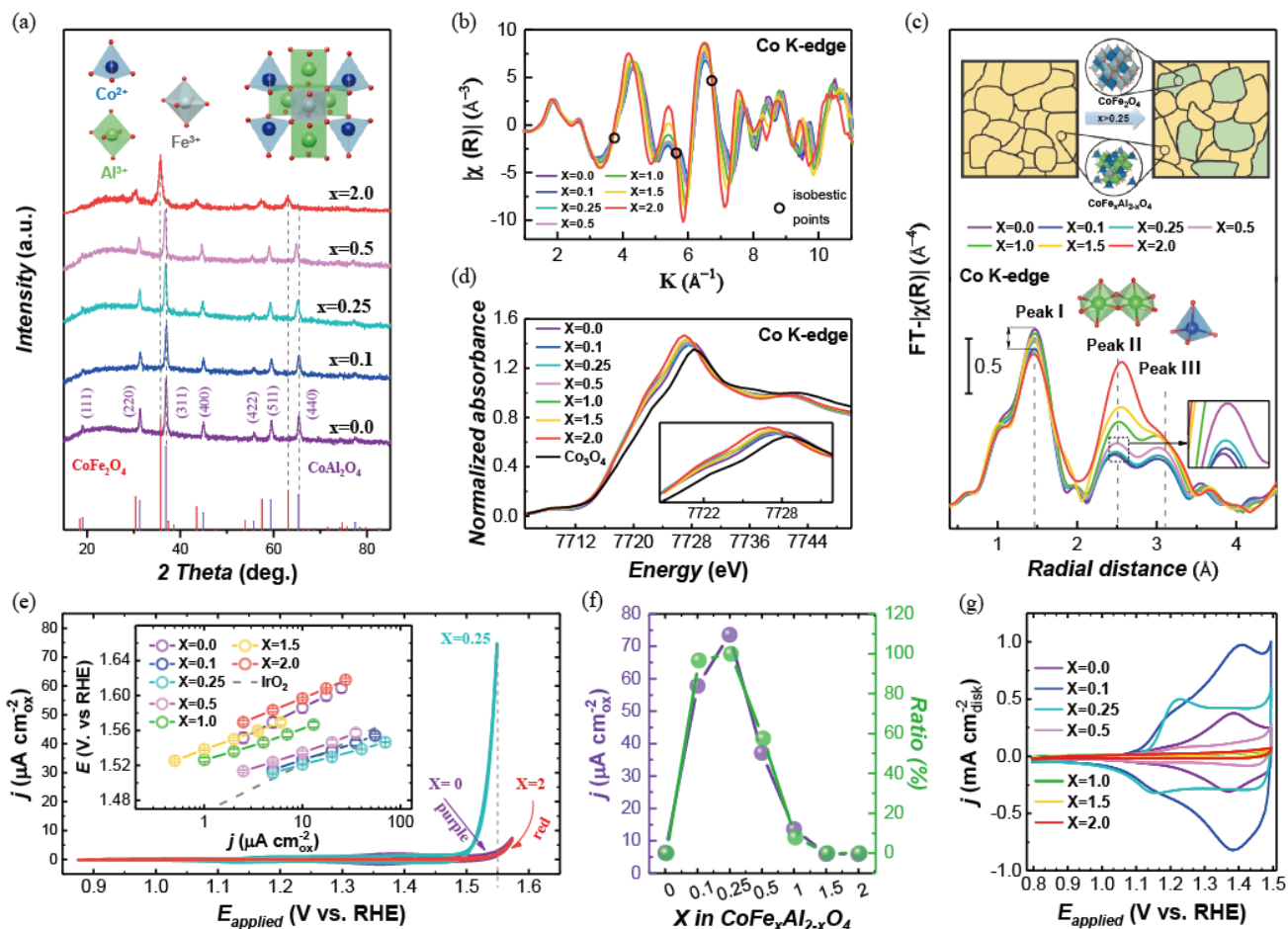
The $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0\sim 2.0$) oxides were synthesized by a sol-gel method. The crystal structures of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ oxides were characterized by powder X-ray diffraction (XRD). As displayed in Fig. 1a, the diffraction peaks of the as-prepared CoAl_2O_4 and CoFe_2O_4 match well with that of the standard cubic spinel (Fd-3m) oxides. $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ oxides with different Fe substitution amount remain in cubic spinel structure. Besides, the diffraction peak exhibits certain shift to lower angle with the increase of Fe substitution amount in the range of $0.25 < x < 2$ (Supplementary Fig. 1). Such peak shift could be ascribed to changes in lattice parameters induced by different ionic radius of Fe and Al cations and suggests a solid solution property. However, when the Co local atomic structure was investigated by EXAFS (Fig. 1b, Supplementary Fig. 2), certain isobestic points, such as at 4.5 \AA^{-1} , are remarkable, implying a complex property with Co in different components.²⁶ As further observed in Fourier transform (FT) Co K-edge EXAFS (Fig. 1c), two separated peaks, i.e. Peak II and Peak III, at $2.4\sim 3.1 \text{ \AA}$ are assigned to the features of Co_{Oh} (in octahedral site) and Co_{Td} (in tetrahedral site). At $x \leq 0.25$, no obvious changes are observed for peak II and peak III compared to pristine

44 CoAl_2O_4 , indicating that low-level Fe substitution does not change the occupation of Co. The obvious uplift of
45 these two peaks starts from $x=0.5$, which could be attributed to the segregation of a component that comprises
46 more octahedrally coordinated Co. This segregated component is inferred as CoFe_2O_4 which is in inversed
47 spinel structure where Co occupy the octahedral site.²⁷ Such inference is further evidenced by a Co K-edge
48 XANES linear combination fitting (LCF) with CoAl_2O_4 , CoFe_2O_4 and $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ as standard
49 (Supplementary Fig. 3). The fitting delivers an extremely low R factor, indicating that Co is primarily in
50 CoAl_2O_4 , CoFe_2O_4 and $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ components throughout the oxides.

51

52 In addition to the complex behavior of Fe-containing components throughout the oxides, the Fe substitution in
53 CoAl_2O_4 also alters the local atomic structure of Co. As observed in Co K-edge EXAFS (Fig. 1c), the
54 first-shell peak at $\sim 1.5 \text{ \AA}$, representative of the metal-oxygen bond, is weakened by Fe substitution, suggesting
55 lower metal-oxygen coordination number and more oxygen vacancy²⁸. Specifically, the EXAFS fitting result
56 (Supplementary Table 1) of the first-shell peak for $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ and CoAl_2O_4 reveals that Fe substitution
57 reduced the average coordination number by ~ 0.4 at maximum. Such effect, indicating an increase in oxygen
58 vacancy, is consistent with a decrease in cobalt valence state after Fe substitution which is evidenced by the
59 shift to lower energy of the Co K-edge XANES (Fig. 1d). The nominal Co valence states (Supplementary
60 Table 2) are indicated by the K-edge positions when compared to references CoAl_2O_4 and Co_3O_4 (see details
61 in SI). While Fe^{3+} is more electronegative than Al^{3+} , after Fe substitution, the K-edge energies of Co slightly
62 shift to lower absorption energy compared to CoAl_2O_4 , indicating a decrease in Co valence state. This
63 counterintuitive phenomenon could be rationalized by the creation of oxygen vacancies,⁵ which is also
64 supported by theoretical calculation (Supplementary Table 3). Indeed, the Fe substitution in CoAl_2O_4 was
65 found to reduce the formation enthalpy of oxygen vacancy, which indicates easier formation for oxygen

66 vacancy.



67

68 **Fig. 1 | Structural characterizations and OER performances of as-prepared $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ catalysts.** **a**,
69 The powder X-ray diffraction (XRD) patterns of as synthesized $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0.0\sim 2.0$) oxides. **b**, The Co
70 K-edge EXAFS spectra of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0.1\sim 2.0$). **c**, The Fourier transform (FT) $k^3\chi(R)$ Co K-edge
71 EXAFS of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0.1\sim 2.0$). The inset is schematics of the compositions in the $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ oxide.
72 **d**, The normalized Co K-edge XANES spectra of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ samples and the standard Co_3O_4 (Sigma
73 Aldrich) as the references. The K-edge position is determined by an integral method²⁹ as described in Methods,
74 and the details about edge positions and nominal valence state of Co and Fe are shown in Supplementary
75 Table 2. **e**, The cyclic voltammetry curves of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0, 0.25, \text{ and } 2$) in O_2 saturated 1 M KOH with a
76 scan rate of 10 mV s^{-1} . The inset is the corresponding Tafel plots after oxide surface area normalization,
77 capacitance correction, and iR correction. The error bars represent the standard deviation from three
78 independent measurements. The grey dashed line shows the best IrO_2 OER performance reported to date.⁴ **f**,
79 The OER current densities (left axis) of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ at 1.55 V vs. RHE. The composition ratio of
80 $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ component (right axis) in $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ oxides is plotted to show its correlation with the
81 OER activity. **g**, The cyclic voltammetry curves of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x = 0\sim 2$) in O_2 saturated 1 M KOH with a
82 scan rate of 10 mV s^{-1} between 0.8 and 1.5 V vs RHE. The upper limit of the potential window is capped to
83 show the pseudocapacitive behavior preceding to OER.

84

85

86 OER activity

87 The spinel $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ oxides were then measured for their electrocatalytic OER performances under
88 alkaline condition (see details in Methods). Supplementary Fig. 4 shows their steady OER cyclic voltammetry
89 (CV) curves. The current density was normalized to the surface area of oxides to present the intrinsic activity,
90 with the surface area of oxides being determined by Brunauer-Emmett-Teller (BET) measurements
91 (Supplementary Fig. 5 and Supplementary Table 4). Ohmic drop iR correction was applied to compensate the
92 potential loss from the resistance of the electrolyte solution. As observed in Supplementary Fig. 4, among these
93 spinel oxides, $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ is the best-performing one. Comparable OER performance is also observed for
94 low-level Fe substituted oxides at $x=0.1$ and 0.5 . In contrast, when further increasing the Fe substitution,
95 significant drop in activity is found as x exceeds 0.5 in $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$. Fig. 1e shows the selected OER CV
96 curves for $x=0, 0.25$, and 2 . Much better OER activity is found for $x=0.25$ than for $x=0$ and $x=2$. As seen in
97 the Tafel plots given in the inset of Fig. 1e, the OER overpotential for $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ (at $10 \mu\text{A cm}^{-2}_{\text{oxide}}$) is
98 approximately 70 mV lower than that for CoAl_2O_4 and CoFe_2O_4 (Supplementary Fig. 6). Such activity contrast
99 indicates a special role of Fe in oxides at the low substitution level. In addition, IrO_2 previously benchmarked
100 is also shown in the Tafel plot for comparison.⁴ As observed, the electrocatalytic activity of the
101 best-performing $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ outperforms the activity of the benchmark IrO_2 catalyst. Long-term stability
102 tests (Supplementary Fig. 7) of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0, 0.25$ and 2) oxides were carried out at constant current
103 density of $10 \mu\text{A cm}_{\text{ox}}^{-2}$ in 1 M KOH for 10 h . All measured samples exhibit negligible potential loss, which
104 indicates a good stability for these spinel catalysts under OER conditions. The best-performing catalyst,
105 $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$, was further carried Chronopotentiometry test for 48 hours under $20 \mu\text{A cm}_{\text{ox}}^{-2}$ ($\sim 3.5 \text{ mA}$
106 $\text{cm}_{\text{disk}}^{-2}$). As shown in the Supplementary Fig. 8 a, b, the $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ still shows negligible activity change
107 after 48-hour test, which demonstrates a superior stability of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ in alkaline for OER.

108

109 **Composition effect on OER**

110 We then investigate the OER promotion at low substitution level and the detrimental effect at higher
111 substitution level. Firstly, the $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ component may primarily contribute to the OER activity
112 according to the observed composition dependence. We then carried out LCF for the Co K-edge XANES using
113 $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ as standard in order to study the composition throughout the substituted oxides
114 (Supplementary Fig. 3 and Supplementary Table 5). As found by the LCF (Fig. 1f, green line), the composition
115 ratio of the $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ component is abundant at low substitution level such as $x=0.1$ and 0.25 but
116 become negligible as $x \geq 1$. This trend correlates well with the OER activities of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ oxides (Fig. 1f,
117 purple line). Thus, it suggests that the $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ component is primarily responsible for the significant
118 OER enhancement. Besides, the consistent trend is also observed for the pseudocapacitive charge in CV before
119 OER region (Supplementary Fig. 9) which is quantified from CVs (Fig. 1g) by previously reported
120 approaches.³⁰⁻³¹ The pseudocapacitive charge is particularly large at low substitution level but significantly
121 decrease at high Fe substitution ($x \geq 1$). The pseudocapacitive charge indicates the redox of surface active
122 sites,³¹ and its consistent trend with OER activities throughout the oxides suggests that the amount of active
123 sites is a dominating factor for OER activity in our case. Thus, the strong correlation between OER activity
124 and the composition ratio should be ascribed to the $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ component, which may govern the
125 formation of active sites.

126

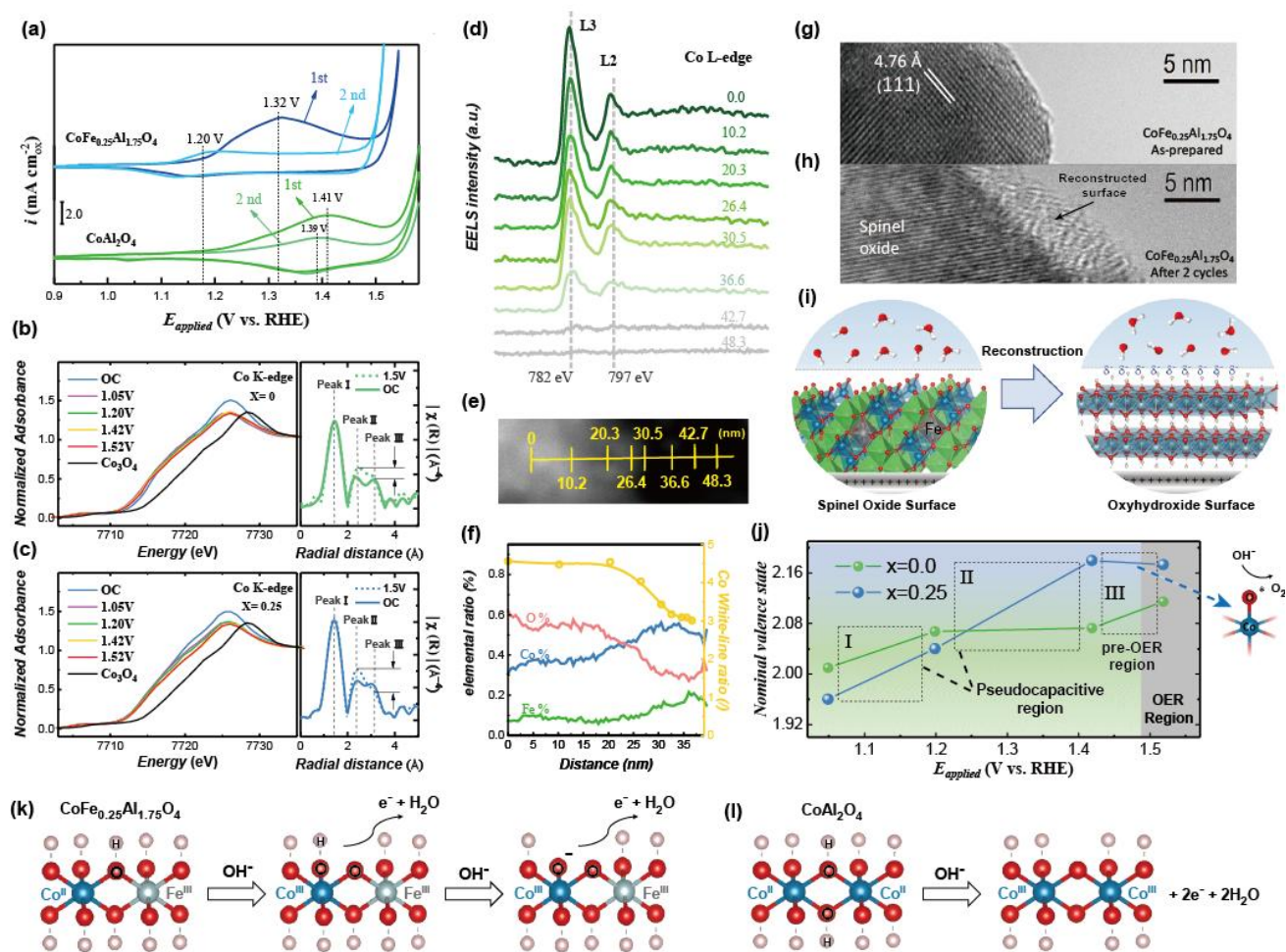
127 **Active site identification**

128 Attention was then paid on the dynamic changes at metal sites during the electrochemical process. Note that
129 there is nearly no change in the valency of Co and Fe in $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ (Fig.1d, Supplementary Fig. 10, and
130 Supplementary Table 2) and the local atomic structure of Fe site in $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ remains unchanged under

131 OER (Supplementary Fig. 11). The pre-oxidation of Co (II) in $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ during the potential sweeps is
132 proposed to play a critical role in evolving active species (the preclusion of the pre-oxidation of Fe (III) to
133 evolve active species is shown in SI). Earlier studies have revealed the importance of pre-oxidation of Co (II)
134 in oxides for OER, where Co (II) is inclined to be oxidized to Co (III) or higher oxidation state, which is
135 believed to be a critical step to generate active oxyhydroxide sites for OER.³²⁻³³ To study the pre-oxidation of
136 Co (II) in CoAl_2O_4 and $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$, their cyclic voltammeteries (1st and 2nd cycles) are investigated (Fig.
137 2a). For both CoAl_2O_4 and $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$, the 1st cycle display a larger pseudocapacitive charge than 2nd
138 cycle and the CV profiles exhibit negligible changes during subsequent cycles (Supplementary Fig. 12). Such
139 electrochemical behaviors suggest that the surface of catalysts might undergo an irreversible surface
140 reconstruction into, as reported, the oxyhydroxide¹⁰, evolving a stable catalytic surface for OER. In addition,
141 we found that the oxyhydroxide formation here displays different pseudocapacitive behaviors depending on
142 the presence or not of Fe. To be specific, the anodic peak in 1st cycle appears at ~1.32 V for $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$,
143 while a much more anodic one is observed for CoAl_2O_4 (~1.41 V), suggesting a promoting effect of Fe on the
144 pre-oxidation of Co (II) and facilitating the subsequent formation of Co oxyhydroxide. For $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$,
145 significant differences are observed between the 1st cycle and 2nd cycle in oxidation peak as well as the
146 pseudocapacitive charge, indicating a change in surface chemistry, while no such marked contrast was
147 observed for CoAl_2O_4 . Thus, a more thorough reconstruction may happen on the surface of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$.
148 According to the aforementioned pseudocapacitive behaviors, such reconstruction should be ascribed to the
149 presence of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ component. Then, as observed in the OER region, the overpotential for triggering
150 the OER by $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ is greatly reduced at 2nd cycle while almost no such difference is detected
151 between 1st and 2nd cycle for CoAl_2O_4 , indicating that the reconstruction process in the presence of Fe is a
152 critical step for OER. In the 2nd and subsequent cycles, reversible redox peaks are observed for CoAl_2O_4 and

153 $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ in pseudocapacitive range, suggesting reversible redox reactions on the reconstructed
154 surfaces. For CoAl_2O_4 , the major anodic peak appears at ~ 1.38 V, which could be assigned to Co (III) / Co (IV)
155 transition as suggested in previous literature³⁴. However, the Co (III) / Co (IV) transition cannot be
156 rationalized without an earlier notable Co (II) / Co (III) anodic features (should appear at ~ 1.2 V vs RHE).
157 Besides, its high intensity also contradicts the fact that only a small portion of Co cation in Co-based oxides
158 could be reached and oxidized into Co (IV)^{33, 35}. Considering that the surface has reconstructed during the 1st
159 cycle, we believe that this anodic peak at ~ 1.38 V should be primarily attributed to the delayed Co (II) / Co
160 (III) transition. Since the anodic process on oxyhydroxide surface can be viewed as deprotonation process
161 with oxidation of metal cation,³⁶ the delayed Co (II) oxidation for CoAl_2O_4 suggests a difficult deprotonation
162 process. For $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$, an obvious anodic wave is observed at ~ 1.2 V which is assigned to Co (II) / Co
163 (III) transition.^{9, 34} This observation suggests an easier deprotonation process and activated Co (II) oxidation
164 due to the Fe substitution. Such Co (II) / Co (III) redox is followed by a double layer charging response,
165 which may result from the large surface area of the reconstructed surface and suggests a diffusion of a
166 distribution of protons on the surface³⁷. After such anodic redox of Co species, $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ exhibit a much
167 lower overpotential required for triggering OER than that for CoAl_2O_4 (~ 70 mV lower as indicated in Fig. 1e).
168 Thus, it is clear that in the presence of Fe, highly active oxyhydroxides would be induced along with the
169 reconstruction of oxide surface. Therefore, the Fe substitution is inferred to activate the Co pre-oxidation at
170 low potential, facilitating both the surface reconstruction and the subsequent evolution of surface active sites.
171 Such inference is further substantiated by *in-situ* XANES and the active species as identified by *in-situ*
172 EXAFs.

173



174

175 **Fig. 2 | *in-situ* investigation on pre-OER behaviors of catalysts and schematic illustration of surface**
 176 **reconstruction and deprotonation process.** **a**, The pseudocapacitive behavior in the 1st and 2nd
 177 $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ and CoAl_2O_4 during the cyclic voltammetry cycling. **b,c**, The normalized in-situ Co K-edge
 178 XANES (left) under the different potentials of 1.05, 1.20, 1.42, and 1.52 V (vs. RHE) with Co_3O_4 (Sigma
 179 Aldrich) as the references, as well as the in-situ Fourier transform (FT) $k^3\chi(R)$ Co K-edge EXAFS (right)
 180 under open circuit (OC) and 1.5 V (vs. RHE): **(b)** CoAl_2O_4 and **(c)** $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$. The peak I, II, and III in
 181 FT-EXAFS are assigned to M-O, $\text{M}_{\text{OH}}\text{-M}_{\text{OH}}$, and $\text{M}_{\text{OH}}\text{-M}_{\text{Td}}$ radial distance, respectively. **d**, The Co L-edge
 182 EELS spectra along with the line pathway as shown in **e**, scanning transmission electron microscopy (STEM)
 183 of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ after 100 cycles. The mark points denote the scanning distance along with the path way
 184 (nm): 0, 10.2, 20.3, 26.4, 30.1, 36.6, 42.7 and 48.3. **f**, The elemental ratio of O, Co, Fe (left axis) and the
 185 white-line ratio of Co L-edge (right axis) along with the line pathway. The white-line ratio is determined by
 186 the intensity of L3 and L2 peaks in EELS spectra.³⁸ **g,h**, The HRTEM images to show the surface regions for
 187 (g) as-prepared $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$; (h) $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ after 2 cycles **i**, The reconstruction process from spinel
 188 $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ into oxyhydroxide with activated negatively charged oxygen ligand. **j**, The *in-situ* Co
 189 oxidation state of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ and CoAl_2O_4 (i.e. $x=0$) under the different potentials of 1.05, 1.20, 1.42, and
 190 1.52 V (vs. RHE). **k,l**, The proposed deprotonation mechanism before OER are shown for **(k)** $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$
 191 and **(l)** CoAl_2O_4 .

192

193

194 In Fig. 2b and 2c (right diagram), the *in-situ* Co K-edge Fourier transform (FT) EXAFS spectra without and

195 with an applied potential of 1.5 V (vs RHE) are shown for $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ and CoAl_2O_4 ($x=0$). At open circuit,
196 the FT-EXAFS profiles for $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ and CoAl_2O_4 ($x=0$) are quite similar. The Peak I at ~ 1.5 Å is
197 referred to an average metal-oxygen bond length. Two separated peaks, i.e. Peak II and Peak III at 2.4 Å and
198 3.1 Å, respectively, are assigned to the radial distance of Co_{Oh} (Co in octahedral site) and Co_{Td} (Co in
199 tetrahedral site) to their neighboring metal atoms. Because the Co fraction does not change in $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$
200 with the Fe substitution, the ratio of Peak II to Peak III represents the composition ratio of Co_{Oh} and Co_{Td} in
201 these oxides. Compared with the profiles collected at open circuit, the Peak II of Co K-edge in both
202 $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ and CoAl_2O_4 increase with the applied potential of 1.5 V. Such increase of the Peak II
203 indicates an accumulation of Co atoms in edge-sharing octahedral coordination⁸, which is attributed to the
204 formation of Co oxyhydroxide which is in edge-sharing CoO_6 octahedral structure.³³ Notably, a much higher
205 ratio of Peak II / Peak III is observed for $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ as compared to that for CoAl_2O_4 , suggesting a
206 consistent conclusion as our observation in 1st cycle of CV that the reconstruction into oxyhydroxide is more
207 thorough for $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$. Such reconstruction of Co on the surface for $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ is also evidenced
208 by STEM-EELS (Fig. 2d and 2e) and HRTEM (Fig. 2g and 2h) at the reconstructed surface. Under
209 STEM-EELS, a notable increase of elemental ratio of Co (Co%) at the near surface of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$
210 particles is detected (Supplementary Fig. 13 and Fig. 2f), which would be a result of Co oxyhydroxide
211 formation on surface. The white-line ratio for Co L edge (Fig. 2f) decreases and indicates increased oxidation
212 state³⁹, which could be an effect of irreversible of electrochemical oxidation of Co (II) to form Co (III)
213 oxyhydroxide during the 1st cycle. Under HRTEM, the generated oxyhydroxide can be observed on the
214 reconstructed surface of oxide. Thus, the surface chemistry of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ is changed by reconstruction
215 from oxide into oxyhydroxide (Fig. 2i). As reported that Co oxyhydroxides evolved as the active species for
216 many Co-based oxide catalysts,^{7, 9-10, 32} we thus believe that the reconstruction facilitated by Fe substitution is

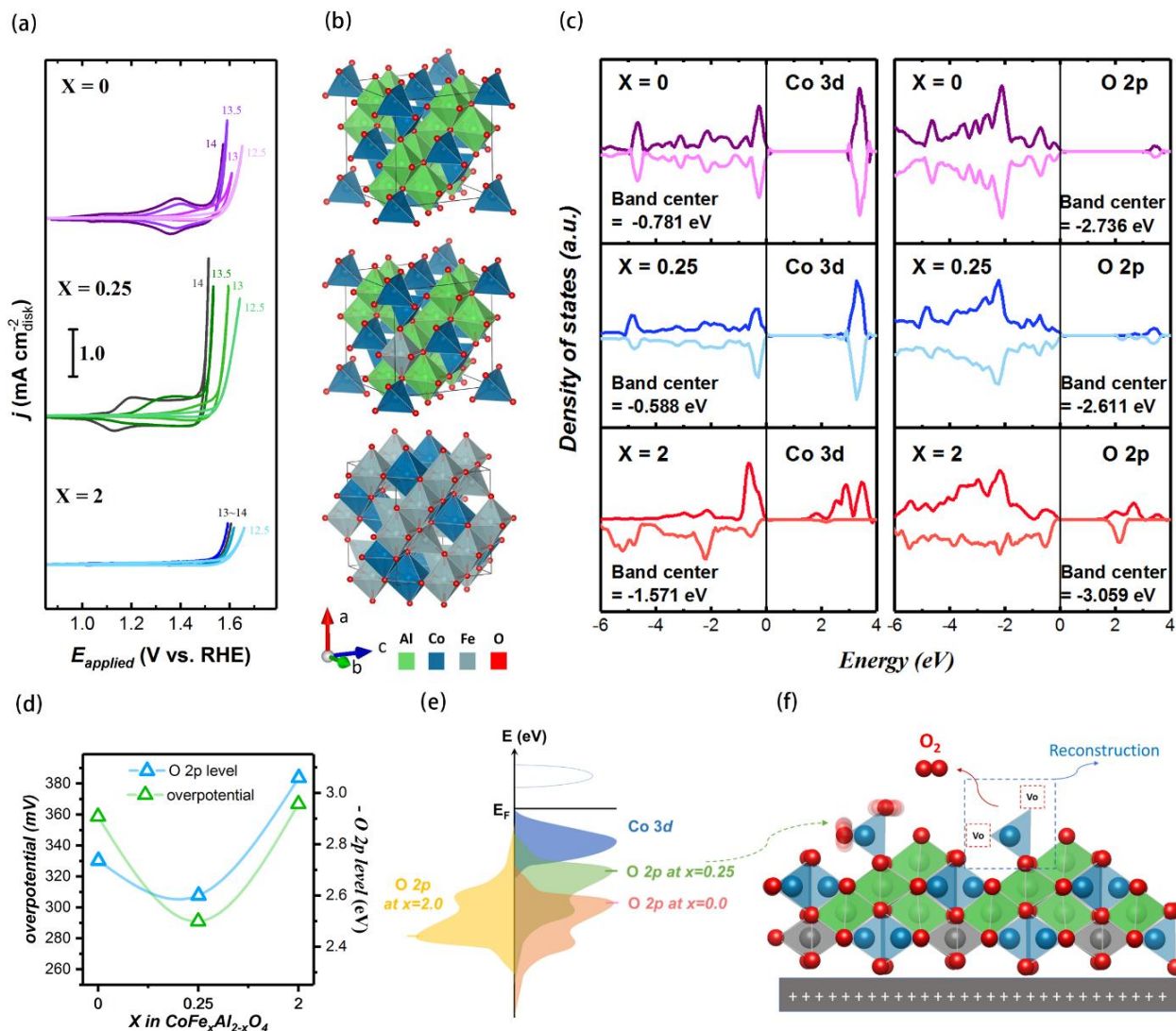
217 the most critical step for evolving active surface oxyhydroxide.

218

219 **Fig.**

220 In the cases of active oxyhydroxides, some studies proposed a so-called active oxygen species,^{21-22, 40} which is
221 created during the deprotonation (anodic sweep) step, as the ultimate active site. Thus, considering the
222 observed alternation of anodic peak by Fe substitution in 2nd CV cycle, the dynamic valence state of Co during
223 the anodic sweep was then examined by *in-situ* XANES. Fig. 2b and 2c (left diagram) display the Co K-edge
224 XANES of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ and CoAl_2O_4 ($x=0$) oxides recorded at 1.05, 1.20, 1.42, and 1.52 V (vs. RHE),
225 respectively. The K-edges in XANES of both oxides shift to higher energy, indicating the oxidation of Co. The
226 corresponding nominal valence states of Co in $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ and CoAl_2O_4 under each applied potential are
227 plotted in Fig. 2j. The valency increment in the pseudocapacitive region could be primarily observed in region
228 I (1.05 – 1.20 V) and region II (1.20 – 1.42 V), and the Co behavior in pre-OER stage can be found in region
229 III (1.42 – 1.52 V). The increase of Co valency could be viewed as deprotonation process on the reconstructed
230 surface of catalysts. As observed, in pseudocapacitive range (region I and region II), the $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$
231 exhibits an increase of valency in both region I and region II. Whereas, the valency for CoAl_2O_4 increases only
232 in region I, suggesting a limited deprotonation process. Its next deprotonation process is only observed at
233 higher potential in the region III. Thus, the Fe substitution is likely to facilitate the deprotonation process at
234 low potential to form active oxygen species on the surface, which accounts for the OER activity enhancement.
235 Here, to illustrate the role of Fe in deprotonation process, we propose two proton/electron transfer processes
236 for evolving active oxygen sites on $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ surface. As shown in the Fig. 2k, the first deprotonation
237 process on $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ should start at the bridged OH linked to both Co and Fe center, which is
238 responsible for the valency increment of Co (II) cation, and such process on bridged OH could be facilitated

239 by its neighboring Fe^{3+} center. The first deprotonation process is followed by another deprotonation process at
240 terminal OH linked to Co or Fe center. Similar deprotonation process was also reported for NiFe_xOOH ²².
241 Unlike NiFe_xOOH where the Fe substitution anodically shifts the Ni oxidation peak^{22, 36}, an opposite behavior
242 was observed here for Fe substituted CoAl_2O_4 . The suppressing effect of Fe on Ni oxidation was explained by
243 the kinetics barrier for the deprotonation of terminal OH linked to Fe center.³⁶ Thus, on the basis of the
244 activated Co oxidation in our study, we believe that the second deprotonation process should be at the terminal
245 OH linked to Co center, and the activated Co oxidation is ascribed to the reduced kinetic barrier for the proton
246 abstraction at Co site. The second process with one proton abstraction is not compensated by the metal
247 oxidation but rather by negatively charged oxygen ligand (O^*) that serves as active site. However, for
248 CoAl_2O_4 , during the corresponding pseudocapacitive range, it merely undergoes deprotonation process on
249 bridged OH (Fig. 21). The following deprotonation for CoAl_2O_4 on the terminal OH is greatly delayed and
250 OER does not occur till the second deprotonation happens, suggesting this process as a prerequisite for OER.
251 Thus, the critical role of Fe is to facilitates the deprotonation process to generate active oxygen site at lower
252 potential on $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$, thereby leading to a lower overpotential for OER. It should be noted that the
253 redox reaction on the reconstructed oxyhydroxide surface would be greatly affected by the reconstruction
254 process in the 1st cycle. As also observed in our pH dependence measurement (Fig. 3a), the redox peak is
255 greatly altered, not simply shifted, by changing the pH of electrolyte. Especially, the redox peak is even muted
256 at $\text{pH} \leq 13$. Clearly, such alternation is led by a pH-sensitive surface reconstruction, which results in forming
257 surface oxyhydroxide in different state with varied pH. Such pH-sensitive surface reconstruction suggests that
258 it may include certain decoupled proton/electron transfer process such as lattice oxygen oxidation⁴¹ which is
259 further demonstrated in the following section.



260

261 **Fig. 3 | Electronic interpretation of the effect of Fe substitution on surface reconstruction.** a, Cyclic
 262 Voltammetry (CV) of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0.0, 0.25$ and 2.0) scanned in O_2 -saturated KOH (pH= 12.5~14) at a
 263 scan rate of 10 mV s^{-1} . b, The computational models of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$: (top) $x=0$, (middle) $x=0.25$, (Bottom)
 264 $x=2$. c, The computed Co 3d, O 2p density of state (PDOS) of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0, 0.25$ and 2.0). d, The OER
 265 overpotential at $10 \mu\text{A cm}^{-2}_{\text{oxide}}$ and the O 2p band center relative to Fermi level ($-\text{O } 2p$) for $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$
 266 ($x=0.0, 0.25$ and 2.0) e, The schematic band diagrams of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0, 0.25$ and 2.0). The Co 3d-band in
 267 the diagram represents the highest occupied state and the lowest unoccupied state. f, The schematic diagram of
 268 a surface reconstruction mechanism for $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$.

269

270

271 Interpretation of O 2p

272 As aforementioned, the active oxygen site is generated by the deprotonation on the oxyhydroxide surface and

273 the reconstruction for forming surface oxyhydroxide serves as the prerequisite for efficient OER catalysis. We

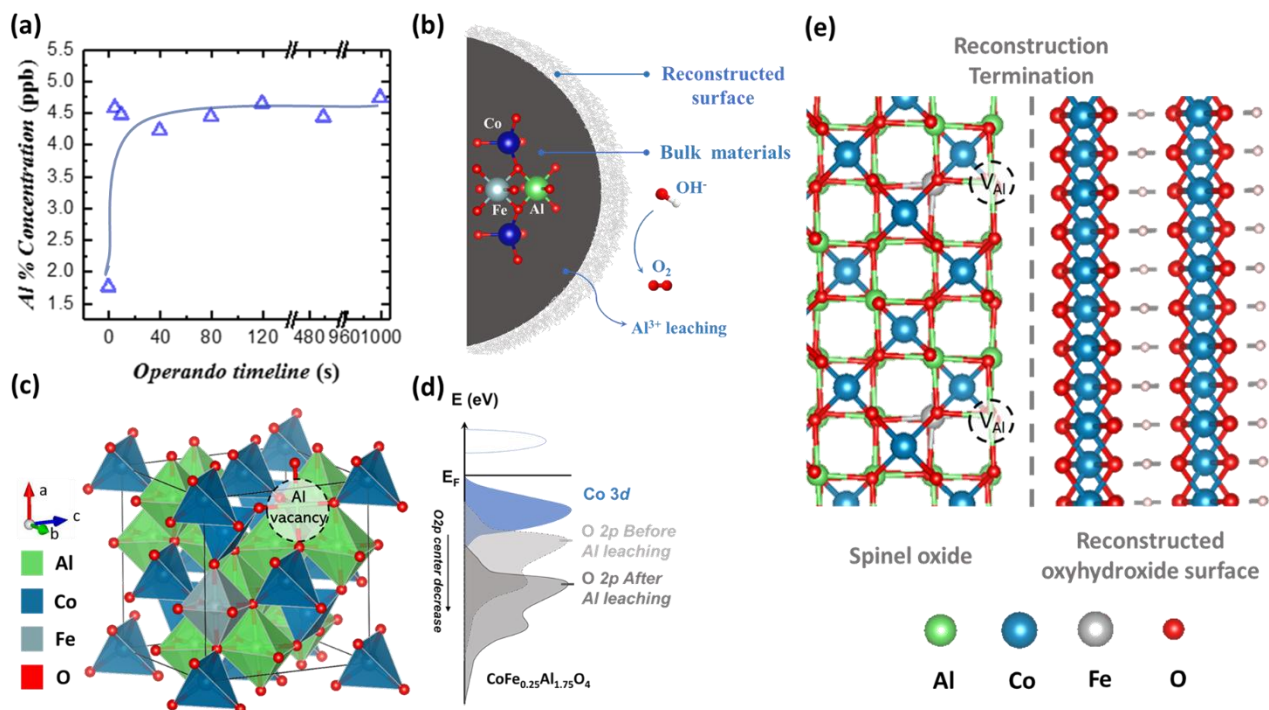
274 have also mentioned that the Fe-facilitating reconstruction is dominated by the $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ component
275 and may involve certain decoupled proton/electron transfer process. The inner driving force for the
276 reconstruction is further studied by density functional theory (DFT) calculation. The electronic density of state
277 (DOS) calculation is adopted to examine the alternation in electronic structure of oxides by Fe substitution.
278 The computational models for $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0, 0.25, \text{ and } 2$) are shown in Fig. 3b (see modelling and
279 calculation details in SI). The projected density of state (pDOS) of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0, 0.25, \text{ and } 2$) oxides and
280 their band center energies are given in Fig. 3c (see more details in Supplementary Table 6). As found for band
281 center energies, the Fe substitution in CoAl_2O_4 uplifts the O 2p-band center in energy closer to the Fermi level.
282 However, as Al^{3+} is fully replaced by Fe^{3+} to form CoFe_2O_4 , it becomes an inverse spinel structure and the O
283 2p-band center greatly moves down in energy. The PDOS results reveal that Fe substitution could either uplift
284 or downshift the O 2p level depending on the substitution level. Moreover, the position of O 2p-band center
285 relative to Fermi level shows consistent trend with the OER activity of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ oxides ($x=0, 0.25 \text{ and } 2$)
286 (Fig. 3d). It is also noteworthy that the OER activity of $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ oxides is greatly affected by their
287 reconstruction process under OER conditions. Thus, the O 2p level is likely an influential factor to the surface
288 reconstruction. Earlier studies have revealed that the O 2p-band level relative to the Fermi level was always
289 associated with some activity-related structural parameters for perovskite oxides.^{14, 42-44} For example, a linear
290 relationship was established between the O 2p-band level and the oxygen vacancy ($V_{\text{O}}^{\bullet\bullet}$) formation energy in
291 some perovskite oxides, in which the low $V_{\text{O}}^{\bullet\bullet}$ formation energy could be predicted by high O 2p level close to
292 Fermi level.^{14, 42} Given that spinel structure contains octahedral MO_6 unit as well as that of perovskite oxides,^{5,}
293⁴⁵ the uplifted O-2p band center by Fe substitution should also facilitate the $V_{\text{O}}^{\bullet\bullet}$ formation in spinel oxides.
294 Consistent results have been revealed above in the structural analysis of substituted oxides where Fe
295 substitution lowers the metal-oxygen coordination number and decrease the Co valence state, suggesting an

296 increased oxygen vacancy concentration. In addition to the influential role of O 2p level on bulk $V_O^{\bullet\bullet}$
297 formation, it is also governing the lattice oxygen oxidation mechanism for oxides.^{41, 46-47} With the uplifted O
298 2p center closer to Fermi level, the oxygen character in the antibonding state below Fermi level becomes more
299 dominant (Fig. 3e). As an anodic potential is applied, the Fermi level shifts deeper into O 2p state and the
300 holes in oxygen state are created as the O_2/H_2O redox potential is aligned with the O 2p state energy in the
301 oxide, which leads to the oxidation of lattice oxygen.^{41, 48} Thus, credited to the uplifted O 2p level, the
302 oxidation of lattice oxygen in $CoFe_{0.25}Al_{1.75}O_4$ should be more favorable than that in $CoAl_2O_4$ and $CoFe_2O_4$.
303 Note that the lattice oxygen mediated OER mechanism should not dominate the OER here. This is also
304 confirmed by a cycling test of $CoFe_{0.25}Al_{1.75}O_4$ oxides over 100 cycles (shown in Supplementary Fig. 12). The
305 lattice oxygen-mediated OER is always featured with unstable oxide due to cation leaching on catalysts and
306 thus leading to activity increase with cycling.⁴⁷ For example, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) as well-identified
307 oxygen active-perovskite catalysts exhibit ~4-fold current increase over 50 cycles.¹² In contrast, the
308 $CoFe_{0.25}Al_{1.75}O_4$ did not exhibit marked OER current variation during CV cycling, suggesting that the
309 reconstructed surface is stable and the involvement of lattice oxygen is not notable during the OER catalysis.
310 This is further evidenced by the electrochemical study on active surface area and HRTEM (Fig. 2g, 2h and
311 Supplementary Fig. 14) of $CoFe_{0.25}Al_{1.75}O_4$ after reconstruction and 100 cycles. The reconstruction in 1st cycle
312 is found merely at limited depth (~5 nm) on the surface of $CoFe_{0.25}Al_{1.75}O_4$ and the reconstructed surface
313 keeps quite stable during subsequent cycling. Please also see detailed discussion in Supplementary Note 2.
314 Thus, the stable surface chemistry after reconstruction excludes the involvement of lattice oxygen in OER
315 catalysis on the reconstructed surface, and also keeps the accuracy of the estimation of the specific activity
316 normalized to BET surface area. However, we believe that the surface reconstruction should start with the
317 lattice oxygen oxidation, which results in the aforementioned pH-sensitive reconstruction (Fig. 3a). According

318 to early report, high $V_{O^{\bullet\bullet}}$ (oxygen vacancies) concentration (especially $V_{O^{\bullet\bullet}}$ on the surface) would grant
319 structural flexibility for surface reconstruction on oxides.⁶ As a further step, even though the induced $V_{O^{\bullet\bullet}}$
320 grants certain structural flexibility in oxides, these $V_{O^{\bullet\bullet}}$ are actually stabilized in the bulk crystal. In another
321 word, such flexibility has to be triggered by additional perturbation such as the lattice oxygen oxidation. This
322 is also evidenced by our theoretical study and XANES result of $CoFe_2O_4$, where $CoFe_2O_4$ exhibits the lowest
323 enthalpy for oxygen vacancy formation (Supplementary Table 3) and experimentally possessing the highest
324 oxygen vacancy concentration (Supplementary Table 2) compared to $CoAl_2O_4$ and $CoFe_{0.25}Al_{1.75}O_4$. However,
325 neither an obvious reconstruction-related current response in the first cycle nor a redox peak subjected to
326 oxyhydroxide during the second cycle can be observed for $CoFe_2O_4$ in CV (Supplementary Fig. 15). Besides,
327 compared to $CoAl_2O_4$ and $CoFe_{0.25}Al_{1.75}O_4$, $CoFe_2O_4$ shows the weakest pH-dependent OER performance (Fig.
328 3a) and the lowest O 2p band center. Thus, we believe that the lattice oxygen oxidation at the pristine surface
329 to creating more surface $V_{O^{\bullet\bullet}}$ should be a critical trigger for the surface reconstruction. This is further
330 evidenced by the elemental ratio on the surface of $CoFe_{0.25}Al_{1.75}O_4$ after 100 cycles obtained by STEM-EELS
331 (Fig. 2f). The O% greatly decreases along with notable Co enrichment on the reconstructed surface, which
332 implies the critical role of creating surface oxygen vacancy on triggering Co reconstruction. Thus, it is
333 believed that, along with the lattice oxygen oxidation,⁴¹ a great structural instability emerges as the oxygen
334 vacancies further accumulate on the oxide surface and induce the surface reconstruction (Fig. 3f) into
335 oxyhydroxides that is more stable in alkaline.¹⁹⁻²⁰ As a result, such dynamic instability in electrochemical
336 process can be electronically indicated by the O 2p level.

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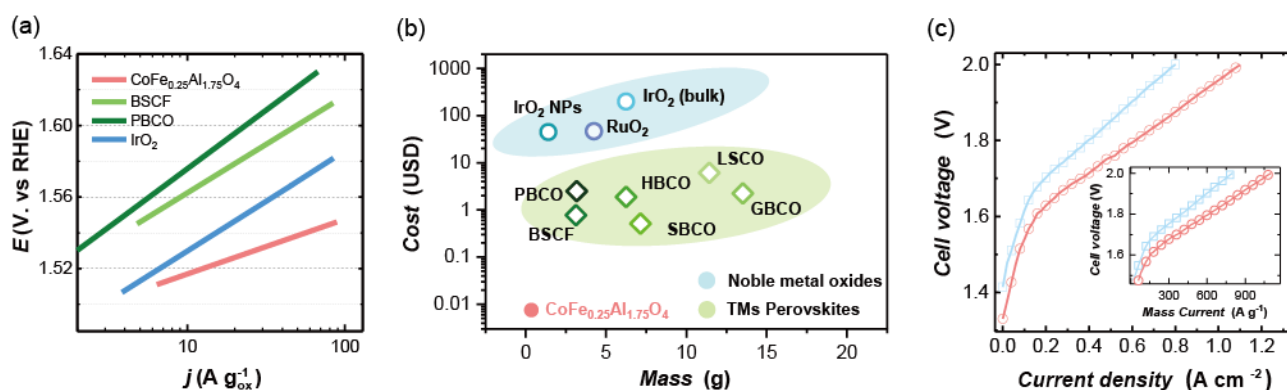
340 **Fig. 4 | Reconstruction terminating mechanism with Al³⁺ leaching.** **a**, ICP-MS test of the electrolyte for
 341 CoFe_{0.25}Al_{1.75}O₄ cycling under operation time of 0~1000s (in 1 M KOH under 20 μA cm_{ox}⁻²). The dissolubility
 342 of Al in terms of Al(OH)₄⁻ is far beyond the concentration of Al³⁺ in our tested electrolytes. **b**, The
 343 schematic of Al³⁺ leaching along with surface reconstruction of spinel oxide. **c**, The computational model for
 344 CoFe_{0.25}Al_{1.75}O₄ after Al³⁺ leaching. The spinel structure beneath reconstructed surface was confirmed under
 345 HRTEM (Supplementary Fig. 14b). **d**, The schematic band diagrams of CoFe_{0.25}Al_{1.75}O₄ with and without Al³⁺
 346 vacancy. **e**, The schematic of CoFe_{0.25}Al_{1.75}O₄ that terminates its surface reconstruction due to the termination
 347 of lattice oxygen oxidation.

348

349

350 Also importantly, while many reconstructable catalysts like Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} exhibit unstable surface
 351 chemistry and become notably amorphous after cycling¹², CoFe_{0.25}Al_{1.75}O₄ is distinguished for its stable
 352 surface chemistry after reconstruction as discussed above. The reconstruction triggered by lattice oxygen
 353 oxidation was terminated after 1st cycle and the reconstructed surface is highly active and stable in the
 354 subsequent cycles. To investigate the mechanism of such reconstruction termination, we carried ICP test on
 355 the electrolyte used for CoFe_{0.25}Al_{1.75}O₄ cycling. It was found that the leaching of Al cations was notable while
 356 Co and Fe cations both exhibited negligible leaching (Supplementary Table 7). Besides, observed under
 357 operando timeline, the Al leaching was found quickly finished as the OER happened, and no notable Al

358 leaching is found thereafter (Fig. 4a), which is consistent with the reconstruction process observed in CV.
 359 Hence, we believe that the leaching of Al is closely associated with the reconstruction process. As Al leached
 360 with the reconstruction at the very beginning, such leaching would alter the local electronic structures of oxide
 361 to prevent further reconstruction (Fig. 4b). We further employed DFT to study the local electronic structure for
 362 the lattice with Al vacancy (Fig. 4c). As illustrated in Fig. 4d and Supplementary Fig. 16, the O 2p level
 363 decreases in energy as Al vacancy is introduced in the lattice. As a result, the lattice oxygen oxidation would
 364 be terminated as O 2p level is low in energy, and the reconstruction thus stops accordingly as no more oxygen
 365 vacancies created (Fig. 4e). Such termination mechanism makes $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ a discernable catalyst which
 366 shows a stable surface chemistry after reconstruction and is capable to carry efficient and stable OER catalysis
 367 on reconstructed surface.



368 **Fig. 5| Competitive potential in electrolyzers application.** **a**, Mass activity of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$,
 369 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCF)¹, $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ (PBCO)⁴⁴ and IrO_2 nanoparticles (NPs)⁴. **b**, The material mass
 370 and cost for delivering a current of 10 A at overpotential of 0.3 V by $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$, $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$
 371 (BSCF)¹, $(\text{Pr}_{0.5}\text{Ba}_{0.5})\text{CoO}_{3-\delta}$ (PBCO)⁴⁴, $(\text{Sm}_{0.5}\text{Ba}_{0.5})\text{CoO}_{3-\delta}$ (SBCO)⁴⁴, $(\text{Gd}_{0.5}\text{Ba}_{0.5})\text{CoO}_{3-\delta}$ (GBCO)⁴⁴,
 372 $(\text{Ho}_{0.5}\text{Ba}_{0.5})\text{CoO}_{3-\delta}$ (HBCO)⁴⁴, IrO_2 nanoparticles (NPs)⁴, IrO_2 (bulk, Premetek Co.)⁴⁹ and RuO_2 ⁵⁰. The cost is
 373 evaluated by the cost of metal elements in oxides. **c**, The polarization curves of the electrolyzer with
 374 $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ (1 mg cm^{-2}) and IrO_2 (Premetek Co., 1 mg cm^{-2}) as anode catalyst and Pt/C (TKK 47.1 wt% Pt, 1
 375 mg cm^{-2}) as cathode catalyst. Inset is the polarization curves of $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ and IrO_2 in mass current density.
 376 Cell temperature was maintained at 60 °C. The experimental details are shown in Methods.
 377

378
 379 With all advantages discussed above, $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ exhibits competitive potential in alkaline electrolyzer
 380 applications. Its mass activity (Fig. 5a) outperforms IrO_2 and the benchmarked transitional metal oxides (e.g.
 381 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ ¹ and $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{CoO}_{3-\delta}$ ⁴⁴). Its cost for given performance is lower than that of noble

382 metal oxides and other reported transition metal perovskites by orders of magnitude (Fig 5b). $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$
383 was further examined in a homemade membrane electrode assembly (MEA) electrolysis cell with an anion
384 exchange membrane as the solid electrolyte (Supplementary Fig. 17). The $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ exhibited a notable
385 higher mass efficiency as well as higher areal activity than IrO_2 (Fig. 5c). Its performance in MEA is also
386 better than that reported for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ under similar condition (Supplementary Fig. 18).⁶

387

388 **Conclusion**

389 In summary, we show a promoted surface reconstruction on CoAl_2O_4 by Fe substitution. $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ is
390 proven to be a critical component in the $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0.0\sim 2.0$) series as it undergoes surface
391 reconstruction. The surface reconstruction has been investigated by HRTEM, EELS, and XAFS. Evidenced by
392 operando XAFS, Fe activates two deprotonation processes in reconstructed oxyhydroxides, leading to the
393 formation of active oxygen species at a low overpotential. We interpret that the uplift of O 2p level by Fe
394 substitution facilitates the creation of surface oxygen vacancies ($\text{V}_\text{O}^{\bullet\bullet}$) along with the lattice oxygen oxidation
395 under OER condition and grants a greater structural flexibility for reconstruction. The O 2p moves down as
396 Al^{3+} leaches at the beginning of reconstruction and further terminates the surface reconstruction for a stable
397 surface chemistry. Under this strategy, $\text{CoFe}_{0.25}\text{Al}_{1.75}\text{O}_4$ exhibits outstanding intrinsic activity, mass efficiency,
398 and stability toward OER. Its high performance has been also demonstrated in MEA configuration. On the
399 basis of this work, more alternative strategies would be explored to tune the active sites formation by
400 adjusting its dynamic reconstruction to develop robust and low-cost OER catalysts.

401

402 **Methods**

403 **Materials synthesis and characterization.** $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0, 0.1, 0.25, 0.5, 1, 1.5, 2$) powders were prepared by the sol-gel method
404 using citric acid as a chelating agent and urea as combustion agent. Firstly, cobalt acetate ($\text{Co}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$), Iron(III) nitrate
405 nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), aluminum nitrate ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$) in specific molar ratio were dissolved in diluted nitric acid,
406 followed by the addition of citric acid and urea. The mixture was stirred and heated up at 80-100 °C to generate highly viscous gel.
407 Then, the gel was then transferred to an oven to decompose and dry in the air at 170 °C for 12 hours. Finally, followed by the
408 calcination at 400 °C for 6 hours, the spinel $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ ($x=0, 0.1, 0.25, 0.5, 1, 1.5, 2$) oxides were obtained. The High resolution
409 TEM (HRTEM) and STEM-EELS were taken on a JEOL JEM- 2100F microscope at 200KV. The X-ray diffraction (XRD) patterns of

410 bulk $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ were recorded on Bruker D8 diffractometer at a scanning rate of 2° min^{-1} , using Cu-K_α radiation ($\lambda = 1.5418 \text{ \AA}$).
411 The BET (Brunauer-Emitter-Teller) surface area was analyzed on ASAP Tristar II 3020 from single-point BET analysis performed
412 after 12 h outgassing at 170°C (**Supplementary Table 4**).

413

414 **Electrochemical characterization under three-electrode system.** The working electrode was fabricated by drop casting method. The
415 as-prepared catalysts which first mixed with acetylene black (AB) at a mass ration of 5:1, then were dispersed in isopropanol/water
416 ($v/v=1:4$) solvent followed by the addition of Na^+ -exchanged Nafion as the binder and ultrasonicated for 20min to form homogeneous
417 ink. The glassy carbon electrode was polished to a mirror finish with 50 nm $\alpha\text{-Al}_2\text{O}_3$ and ultrasonicated in IPA and water to completely
418 clean up. At last, 10 μl of the as-prepared ink was dropped onto a glassy carbon (GC) electrode (0.196 cm^2) and dried overnight at
419 room temperature to yield a final loading mass of $255 \mu\text{g}_{\text{ox}} \text{ cm}^{-2}$.

420 The electrochemical tests were carried out by three-electrode method using $\text{CoFe}_x\text{Al}_{2-x}\text{O}_4$ as working electrode, platinum plate (1×2
421 cm^2) as the counter electrode, Hg/HgO (1M KOH, aqueous, MMO) as the reference in O_2 -saturated 1.0 M KOH by using Bio-logic SP
422 150 potentiostat. All potentials are converted to RHE scale and $i\text{R}$ corrected by the resistance of electrolyte. The conversion between
423 the potentials vs. RHE and vs. MMO was performed by the following equation: $E \text{ (vs. RHE)} = E \text{ (vs. MMO)} + E_{\text{MMO}} \text{ (vs. SHE)} +$
424 $0.059 \times \text{pH}$. $E_{\text{MMO}} \text{ (vs. SHE)} = 0.098 \text{ vs. SHE}$ at 25°C . The Cyclic Voltammetry(CV) was obtained under potentials from 0.875V to
425 1.575V (vs. RHE) at a scan rate of 10 mV s^{-1} . Besides, the CV was also conducted for all samples under potentials from 0.695V to
426 1.495V (vs. RHE) to investigate the pseudocapacitive charge preceding the OER region. The chronopotentiometry measurement was
427 performed by holding the specific current density of $10 \mu\text{A cm}^{-2}_{\text{oxide}}$ for 10 hours. Electrochemical impedance spectra(EIS) was
428 recorded at 1.525V (vs. RHE) under 10 mV of amplitude from 100 KHz to 0.01Hz.

429

430 **X-ray absorption spectroscopy.** X-ray absorption near edge spectroscopy (XANES) and extended X-ray absorption fine structure
431 (EXAFs) were performed under transmission mode at Singapore Synchrotron Light Source, XAFCA beamline. The Co and Fe K-edge
432 position obtained by an integrate method²⁹ is shown in Supplementary Table 2. The Co nominal valence state is obtained by using
433 as-prepared CoAl_2O_4 (+2.0, 7717.41 eV) and standard Co_3O_4 (+2.67, 7719.96 eV) as benchmark. The Fe nominal valence is obtained
434 by using standard Fe_3O_4 (+2.67, 7121.71 eV) and standard Fe_2O_3 (+3, 7122.82 eV) as benchmark. Noted that the as-prepared CoAl_2O_4
435 well match with the standard CoAl_2O_4 , and Co valence state in standard CoAl_2O_4 is +2. The nominal oxygen vacancy concentration is
436 calculated on the basis of the nominal valence state of Co, Al (III) and Fe. The in-situ XAS measurements were performed in
437 fluorescence-transmission geometry, where the spectra of samples and references were measured in fluorescence mode. The catalysts
438 were sprayed on carbon paper at a loading of 2 mg cm^{-2} as working electrode. The measurement was carried out under the same
439 condition as OER measurement in a homemade cell. The *in-situ* XANES measurement was applied after one cycle. The *in-situ* XAFS
440 measurement was taken on the as-prepared catalysts without any additional electrochemical treatment. Acquired XAFS data were
441 processed in ATHENA program and analysed in ARTEMIS program integrated with IFEFFIT software package⁵¹.

442

443 **Density functional theory calculations.** The calculation was carried out by Vienna ab initio Simulation package (VASP) using
444 spin-polarized density functional with the Hubbard model (DFT+U).⁵²⁻⁵³ The projector augmented wave (PAW) model with
445 Perdew-Burke-Ernzerhof (PBE) function was used to describe the interactions between core and electrons, and the value of the
446 correlation energy (U) was fixed at 3.3, 4.3 eV for the 3d orbits of Co and Fe, respectively.⁵⁴⁻⁵⁵ An energy cutoff of 500 eV was used
447 for the plane-wave expansion of the electronic wave function. The Brillouin zones of all systems were sampled with Gamma-point
448 centered Monkhorst-Pack grids. A $7 \times 7 \times 7$ Monkhorst Pack k-point setup were used for bulk geometry optimization, while $9 \times 9 \times 9$ for
449 electronic structures calculation. The force and energy convergence criterion were set to 0.02 eV \AA^{-1} and 10^{-5} eV , respectively. All
450 models are created by comparing the stability of spinel with normal or inversed structure in a unit cell, and the structures at lower
451 energy are selected for study. The CoAl_2O_4 (Supplementary Table 7) prefer the normal spinel structure with Co^{2+} located on tetrahedral
452 sites and the Al^{3+} located on octahedral sites ($[\text{Co}]_{\text{Td}}[\text{Al}]_{\text{Oh}}[\text{Al}]_{\text{Oh}}\text{O}_4$). The $\text{CoFe}_{0.25}\text{Fe}_{1.75}\text{O}_4$ model was established by replacing two
453 Al^{3+} atom in CoAl_2O_4 unit cell with two Fe atoms. The CoFe_2O_4 (Supplementary Table 8) prefers inverse spinel with Co^{2+} at

454 octahedral sites and Fe³⁺ both at tetrahedral sites and octahedral sites ([Fe]_{Td}[CoFe]_{Oh}O₄).

455

456 **Membrane electrode assembly (MEA) electrolyzer.** A homemade MEA electrolysis cell with an anion exchange membrane was
457 employed to evaluate the performance of the as-prepared CoFe_{0.25}Al_{1.75}O₄ catalyst. The cell includes two titanium end plates, on
458 which a single serpentine flow field (area: 6.25 cm², 1.0 mm in width, 0.5 mm in depth, and 1.0 mm in rib) was machined. The
459 titanium end plates were coated with a gold layer (thickness: 200 nm) to reduce the contact resistance. The CoFe_{0.25}Al_{1.75}O₄ was first
460 mixed with high surface area carbon (HSAC, Ketjen black EC-600J, carbonization treatment) with a weight ratio of 1:1. The
461 composite powder was then mixed with PTFE suspension (60 wt% PTFE dispersion in water from Chemours), isopropyl alcohol and
462 water to prepare the anode catalyst ink. The PTFE content in the catalyst layer was controlled with 10 wt%. The catalyst ink was
463 ultrasonicated for 30 minutes at room temperature and manually spread onto a corrosion-resistant stainless-steel mesh (SSL mesh,
464 #500). The catalyst loading on the as-prepared electrode was 1 mg cm⁻². The cathode Pt electrode was fabricated with the same
465 procedure without the addition of HSAC. A catalyst ink, consisting of commercial Pt/C catalyst (TKK, TEC10EA50E 47.1 wt% Pt,
466 3.22 nm in mean particle size), PTFE suspension, isopropyl alcohol and water, was manually spread onto a carbon paper (Toray 060).
467 The catalyst loading on the electrode was 1 mg cm⁻². The PTFE content in the catalyst layer was 10 wt%. The IrO₂ anode was
468 fabricated with commercial IrO₂ powder (Premetek Co) by the same procedure as for preparing the CoFe_{0.25}Al_{1.75}O₄ electrode. An
469 anion exchange membrane (A901, 11 μm, Tokuyama) was employed as the membrane. To reduce the contact resistance, the membrane
470 sandwiched by the anode electrode and cathode electrode was pressed at a pressure of 1 MPa for 5 minutes at room temperature. 0.1 M
471 KOH was pumped into the electrode channels by a peristaltic pump at a constant flow rate of 2 ml min⁻¹. The cell temperature (60 °C)
472 was maintained by an electric heating plate and measured by a thermocouple placed near the anode and cathode current collectors. The
473 polarization curves were measured with an electrochemical workstation (Solartron 1470E). The water electrolysis was performed
474 under constant current mode, in which the current was increased by 0.125 A (20 mA cm⁻²) and retained for 5 minutes for each step
475 until the cell voltage was reached 2.0 V. Before the water electrolysis, the as-fabricated MEA was activated by a potentiostatic mode
476 with a scan rate of 0.5 mV s⁻¹ and a terminal voltage of 2.0 V.

477

478

479 **Data availability**

480 The data related to this study is available from the authors upon reasonable request.

481

482

483 **References**

484

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602

603 **Author contributions**

604 T.W., S.S. A.G. and Z.X. conceived the original concept and initiated the project. T.W. prepared the materials and
605 performed electrochemical and XRD measurements. S.S. help designed the set-up for in-situ XAS measurement. S.X.
606 and T.W. carried out the XAS measurement. Y.D. and T.W. processed and analyzed the XAS data. J.S. worked on the
607 DFT calculations and analysis. W.S., G.L., and B.C. carried HRTEM and STEM-EELs investigation. L.Z. conducted the
608 measurement in MEA system. L.Z., H.W., H.L., and G.S. analyzed the MEA result. T.W. wrote the manuscript with the
609 input from all authors, and Z.X., A.G., and S.S. revised manuscript.

610

611 **Competing interests**

612 The authors declare no competing interests.

613

614 **Additional information**

615 Supplementary information is available for this paper at

616