Superb water splitting activity of the electrocatalyst Fe₃Co(PO₄)₄ designed with computation aid

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For efficient water splitting, it is essential to develop inexpensive and super-efficient electrocatalysts for the oxygen evolution reaction (OER). Herein, we report a phosphate-based electrocatalyst [Fe₃Co(PO₄)₄@reduced-graphene-oxide(rGO)] showing outstanding OER performance (much higher than state-of-the-art Ir/C catalysts), the design of which was aided by first-principles calculations. This electrocatalyst displays low overpotential (237 mV at high current density 100 mA cm⁻² in 1 M KOH), high turnover frequency (TOF: 0.54 s⁻¹), high Faradaic efficiency (98%), and long-term durability. Its remarkable performance is ascribed to the optimal free energy for OER at Fe sites and efficient mass/charge transfer. When a Fe₃Co(PO₄)₄@rGO anodic electrode is integrated with a Pt/C cathodic electrode, the electrolyzer requires only 1.45 V to achieve 10 mA cm⁻² for whole water splitting in 1 M KOH (1.39 V in 6 M KOH), which is much smaller than commercial Ir-C//Pt-C electrocatalysts. This cost-effective powerful oxygen production material with carbon-supporting substrates offers great promise for water splitting.
The oxygen evolution reaction (OER) is a fundamental reaction in electrochemical energy conversion processes, which is the basis of water splitting, batteries, and photo-electrochemical cells [3,4]. The water splitting is considered as a promising and renewable method for producing hydrogen and oxygen gases [5]. However, the efficiency of water splitting in basic electrolyte is largely hindered by sluggish kinetics of the oxidative half-cell OER reaction [6] and so commercial water splitting usually works at a high voltage of 1.8–2.0 V [7]. Recently, noble metal-based compounds such as IrO2 and RuO2 exhibit good catalytic activities toward OER [8]. However, the widespread practical application of these noble metal-based compounds is restricted due to their skyrocketing price and scarcity [9]. Therefore, the development of cost-effective catalysts with high electrocatalytic activity and stability for OER is in high demand, which would lead to a cost-effective production of oxygen via water splitting. In this regard, inexpensive earth-abundant transition metal-based OER electrocatalysts would be a good choice not only because of their high abundance and low cost but also due to their high electrocatalytic activity and stability in wide pH ranges [11-13].

Over the past decade, transition metal-based OER electrocatalysts (for instance, cobalt phosphate, surface-oxidized steels, NiFe-layered double hydroxide/nickel foam, oxo-hydroxides, oxide, perovskites, cobalt phosphate composites, and CoO2, etc.) have been explored due to their high potential for water oxidation, high durability under basic condition, and their benign environmental nature [5,7-9,12-14]. Nevertheless, these materials exhibit large overpotential (η) for OER [5,7-9,12]. Therefore, effective designing of state-of-the-art electrocatalyst and clear understanding of OER catalytic mechanism remain challenging tasks.

Herein, we report a phosphate-based electrocatalyst of Fe3Co(PO4)4/reduced-graphene-oxide (rGO) (1) for OER, which is predicted to be highly active by density functional theory (DFT). The as-synthesized 1 indeed serves as a highly active electrocatalyst for OER in basic media with overpotential of ~237 mV at 100 mA cm−2, and long-term durability (5000 cycles). On the basis of theoretical modeling and experimental observations, the high OER activity of the designed electrocatalyst is ascribed to the PO4-induced positive shift of the redox potential. The efficient mass and charge transfer due to defects/dislocations in the PO4-induced mixed phase and large Brunauer–Emmett–Teller (BET) surface area also help in the OER activity. When it was integrated into asymmetric two-electrode water-splitting cells, the electrolyzer required a potential ~1.45 V in 1 M KOH (or ~1.39 V in 6 M KOH), to drive a current density of 10 mA cm−2 for whole water splitting, which is much smaller than that of the integrated commercial Ir-C/Pt-C electrocatalysts (~1.53 V in 1 M KOH).

Results and discussion

Theoretical model. Inexpensive Fe and Co hybrids with inorganic species (such as P or O) can show good OER performance [15-17] in that the covalent strength of Fe-CoOx in a Fe-Co-X linkage is controlled by the inductive effect [16]. Positive shift of the redox potential for transition metal oxide catalysts can lead to high catalytic activity [18]. In consideration of the inductive effect, we have considered various phosphorus oxides P2O5 as a better alternative for P/O. Given that O is highly electronegative, substituting O with phosphate would be a good choice for OER. Thus, tuning the O catalytic effect would be possible by substituting O with phosphate and further fine-tuning by optimizing the Fe/Co ratio. In many cases, Fe and Co behave similarly with similar ionization potentials EIP(Fe/Co) ≈ 7.87/7.86 eV but they show a large difference in valence electron configurations [Ar]3d74s2/[Ar]3d74s2 and electron affinities EEA(Fe/Co) = 0.15/0.66 eV.

Therefore, their cations with varying Fe/Co ratio give different electrochemical properties with different induction effects. This led us to theoretically investigate the OER performance of stable cage structures of Fe3nCo8−nO12 (m = 0,2,4,6,8) and Fe6Co2−n(PO4)4 (n = 0–4) (Fig. 1a) at varying compositions of Fe and Co (a few varying Fe/Co ratios of 4/0, 3/1, 2/1, 1/3, and 0/4). DFT calculations were performed to understand their electronic structure (Supplementary Figs. 1–4) and O2/OH free energies (ΔGO/ΔGOH) and theoretical overpotentials (ηtheory) required for OER (Fig. 1) at various compositions (Supplementary Table 1), where Δ denotes an active site. We found that the metal substrate of rGO, although significantly beneficial for durability and conductivity (Supplementary Fig. 5), does not give significant effects on H-adsorption energies of Fe6Co2−n(PO4)4 (n = 0–4). To study the catalytic effect, here we have focused on the most stable (010) surface of Fe6Co2−n(PO4)4 (Supplementary Table 2) rather than Fe6Co2−n(PO4)4@rGO for the realistic model.

The optimal catalytic activity is found from the Fe/Co ratio of 3 for the Fe6Co2−n(PO4)4 models of clusters and (010) surfaces. For Fe/Co mixed-metal phosphates, the ηtheory at Fe sites is the smallest at n = 3, i.e., Fe6Co2(PO4)4, whereas the ηtheory of Co sites is not small, remaining almost same for n = 0–4 (Supplementary Table 1). In the Fe6Co2−nO12 (m = 0,2,4,6,8) model, the substitution effect of Co for Fe improves the ηtheory at Fe sites but not at Co sites. Thus, in both models, a small amount of Co that substitutes Fe is effective on Fe sites but not so on Co sites, and the optimized Fe/Co ratio at Fe sites in Fe6Co2−n(PO4)4 is 3. The binding energies of intermediate states at Fe sites become weaker if they are surrounded by many Co atoms. As a result, those local Fe sites become less active. The Fe sites of Fe6Co(PO4)4 are predicted to show excellent activity with ηtheory = 0.24 V. The Fe and Co sites are tri-coordinated in clusters and penta-coordinated in (010) surfaces. The binding energies of intermediate states become weaker on the penta-coordinated Fe sites constantly (~0.5 eV) than on the tri-coordinated Fe sites. Yet, their free-energy changes between O-adsorption and OH-adsorption (ΔGO–ΔGOH) behave similarly, except for this constant difference, and so their overpotentials are similar in both models. It seems that the binding energies of all the intermediate states also become weaker at more coordinated sites on surfaces by almost the same magnitude (~0.5 eV) than on clusters.

To sum up, the electronic structure calculations reveal that the phosphate and the Fe/Co ratio (optimal value of 3/1) are important in tuning the redox potential. As compared with Fe3CoO4 (0001), the phosphate group in Fe3Co(PO4)4 (010) lowers the metal oxide antibonding state and positively shifts the redox potential with the inductive effect (Supplementary Fig. 1). As Co (which is slightly more electronegative than Fe) pulls down the metal oxide antibonding state energy levels and thereby positively shifts the redox potential (Supplementary Fig. 2), tuning the Fe/Co ratio can be exploited for better OER performance.

DFT calculations show that 1 exhibits the optimal ΔGO−ΔGOH free energy (Fig. 1a). At the O-adsorbed metal sites of 1, the bond strength between Fe/Co 3d and O 2p orbitals becomes weaker than at those of Fe6Co2−nO12 (Supplementary Fig. 3). Thus, we investigate the energetics of all intermediates (OH, O, OOH adsorption) and evaluate the theoretical overpotentials for OER (ηtheory) of catalyst Fe6Co2−n(PO4)4 (010) and clusters of Fe3Co(PO4)4, FeCo3(PO4)4, Fe6Co2O12, and Fe2Co6O12 (Fig. 1). Iron-cobalt oxide clusters are also studied to understand their ratio effect on catalytic activity. We calculate ηtheory for the Fe3Co2−n(PO4)4 cluster and Fe2Co(PO4)4 (010) surface models, and other cases with different Fe/Co ratios. The ηtheory at Co site of Fe3Co2−n(PO4)4 (010) is 0.49 V, which is larger than the ηtheory by 0.24 V at Fe site of Fe6Co2(PO4)4. The Fe site in the Fe3Co2−n(PO4)4 cluster, FeCo3(PO4)4, Fe6Co2O12, and Fe2Co6O12 models of clusters and (010) surfaces.
Fe\(_6\)Co\(_2\)O\(_{12}\) cluster, vi: Fe\(_2\)Co\(_6\)O\(_{12}\) cluster) at Fe (gray circle) and Co (dark gray triangle) active sites.

Δenergies

Source data for Fe and Co sites of Fe\(_3\)Co(PO\(_4\))\(_4\) (010). OER typically undergoes a four-electron step process in alkali media. In an ideal case, the free-energy changes by Δ\(G\) = 0.6 eV.

Optimized geometries of the *O, *OH, and *OOH intermediates on the Fe sites of Fe\(_3\)Co(PO\(_4\))\(_4\) (010) (Supplementary Table 1). ΔG\(_{\text{OH}}\) of Fe\(_3\)Co(PO\(_4\))\(_4\) (0.24 V) and Co site (1.76 V). The improvement in ΔG\(_{\text{OH}}\) overpotentials at both step (black line). The conversion of *OH to *O is the rate-determining step on both Fe site

Fig. 1 DFT-predicted structures, overpotentials, and free-energy profiles. a 2D color-coded map of theoretical overpotential \(\eta^{\text{theory}}\) as function of free energies Δ\(G\) = Δ\(G\)\(_{\text{OH}}\) and Δ\(G\)\(_{\text{OOH}}\) for various compositions (i: Fe\(_3\)Co(PO\(_4\))\(_4\) (010), ii: FeCo\(_3\)PO\(_4\)\(_4\) (010), iii: Fe\(_3\)Co(PO\(_4\))\(_4\) cluster, iv: FeCo\(_3\)PO\(_4\)\(_4\) cluster, v: Fe\(_6\)Co\(_2\)O\(_{12}\) cluster, vi: Fe\(_2\)Co\(_6\)O\(_{12}\) cluster) at Fe (gray circle) and Co (dark gray triangle) active sites. b Optimized geometries of the *O, *OH, and *OOH intermediates on the Fe sites of Fe\(_3\)Co(PO\(_4\))\(_4\) (010) (Supplementary Table 1). c Free-energy profiles of OER at zero and equilibrium (1.23 V) potentials for Fe and Co sites of Fe\(_3\)Co(PO\(_4\))\(_4\) (010). OER typically undergoes a four-electron step process in alkali media.
they are not a significant issue, because all experimental results are well explained by our theoretical models.

We conducted FT X-ray absorption fine structure (FT–EXAFS) analysis, which provided the chemical state and coordination environments\textsuperscript{22–25}. The energies of both XANES Fe K-edges and Co K-edges of \textsuperscript{1} and FeCo(PO\textsubscript{4})\textsubscript{4}@rGO (\textsuperscript{2}) are positively shifted compared with those of Fe/Co foils (Fig. 3a, d), suggesting the oxidized states of Fe/Co. The FT–EXAFS data of Fe and Co in \textsuperscript{1} and \textsuperscript{2} exhibit similar peak patterns, but the peak intensities and positions are slightly changed due to their different compositions. Meanwhile, Fe and Co foils show different peak positions for Fe–Fe and Co–Co bonds (Fig. 3b, e). We analyzed the EXAFS curve of \textsuperscript{1} using least-square fit for first and second shells. Figure 3c (and Supplementary Fig. 7a) show that the major peaks at 2.0 Å (coordination number (CN): 4.1) and 2.2 Å (CN: 1.9) reflect Fe–O and Fe–O bond distances, while the minor peak reflects the overlapped peaks at Fe··P distances (via O) of 2.9/3.1/3.3 Å (CN: 1.6/1.2/4.1) respectively (Supplementary Table 3). Similarly, Fig. 3f and Supplementary Fig. 7b show peaks at 2.0 Å (CN: 2.4 Å (CN: 4) for Co = O and Co–O bond distances, while a major peak at 2.8 Å (CN: 5) for the Co··P distance via O (Supplementary Table 4).

We calculated theoretical Fe and Co K-edge EXAFS of Fe\textsubscript{3}Co(PO\textsubscript{4})\textsubscript{4} using the FDMX package\textsuperscript{26,27}. These theoretical FT–EXAFS spectra of the Co and Fe atoms are similar to the experimental FT–EXAFS spectra of \textsuperscript{1} in r-space (Supplementary Fig. 8 and Fig. 3c, f). It seems that the difference between Fe and Co K-edge EXAFS of \textsuperscript{1} arises from different Fe-P distances at each Fe sites in the crystal (Supplementary Tables 3 and 4). To confirm this, we calculated EXAFS of pure Fe\textsubscript{3}(PO\textsubscript{4})\textsubscript{4} and Co\textsubscript{4}(PO\textsubscript{4})\textsubscript{4}, where the Co K-edge FT–EXAFS spectra of Co\textsubscript{4}(PO\textsubscript{4})\textsubscript{4} are similar to the Fe K-edge FT–EXAFS in r-space. This indicates that Co atoms well replace Fe sites in the Fe\textsubscript{3}Co(PO\textsubscript{4})\textsubscript{4} lattice.

The core level P-2p X-ray photoelectron spectroscopy (XPS) shows two major peaks at binding energies of 133.2 ± 0.1 and 134.1 ± 0.1 eV, corresponding to the 2p\textsubscript{3/2} and 2p\textsubscript{1/2} core levels of central phosphorus atoms in phosphate species\textsuperscript{28}, respectively, which is characteristic of the tetrahedral (PO\textsubscript{4})\textsubscript{3−} group (Supplementary Fig. 9a). Furthermore, the O-1s XPS spectra show two peaks at 531.4 and 532.5 eV, assigned to phosphate species\textsuperscript{30} (Supplementary Fig. 9b). The atomic ratio of Fe/Co are 3/1 or 3/1, as measured by inductively coupled plasma atomic-emission spectrometry (ICP-AES) (Supplementary Table 5). In addition, XPS analysis provides the atomic percentage near the sample surface. As compared with ICP-AES bulk sample analysis, the XPS surface analysis increases the Fe(PO\textsubscript{4})\textsubscript{3−} content, whereas the atomic content of P (or PO\textsubscript{4}) is almost the sum of Co and Fe.

![Fig. 2 Preparation route, structural, and compositional characterizations of Fe\textsubscript{3}Co(PO\textsubscript{4})\textsubscript{4}@rGO (1). a Synthesis procedure: first, mix the sample of graphene oxide, red phosphorus, FeCl\textsubscript{3} and Co(ClO\textsubscript{4})\textsubscript{2}·6H\textsubscript{2}O, and then heat. Second, leach with acid, wash with DI water, and dry in the oven. b Scanning (left) and transmission (right) electron micrographs. Scale bars, 200 nm. c Representative high-resolution transmission electron microscopy (HRTEM) images for different positions of single-particle (yellow dots denote atomic dislocations). Fast Fourier transform (FFT) image is on right-bottom panel. Scale bars, 2 nm. d High-angle annular-dark field scanning transmission electron microscope (HAADF-STEM) image with the corresponding individual element maps of C, Fe, Co, P, and O in a part of 1. e HAADF-STEM image with the overlapping image showing the corresponding EDS line-scan profiles. Scale bars, 50 nm. f X-ray diffraction pattern, which confirms the formation of Fe\textsubscript{3}Co(PO\textsubscript{4})\textsubscript{4} in 1. The peak marked by black diamond denotes the rGO peak. Additional small unmatched peaks may be resulted from the byproduct adduct of Fe\textsubscript{3}Co\textsubscript{2.9}(PO\textsubscript{4})\textsubscript{6} and mono-metallic iron or cobalt phosphate (Supplementary Fig. 6). Source data for e and f are provided as a Source Data file.](image-url)
atomic contents, indicating the charges of Co and Fe are +3 (Supplementary Table 6). The content of O is slightly larger than four times of the content of P due to environmental oxygen. An extra content of Fe(PO4), as noted from XPS over ICP-AES, could be present on the surface more than in bulk. However, the XPS data are not so reliable for accurate composition analysis as compared with ICP-AES. The Fe/Co metals composition ratio from ICP-AES is more reliable. Overall, the elemental composition turns out to be 1: Fe2Co(PO4)3@rGO (Fe/Co = 1–1.33), and 3: Fe3Co(PO4)4@rGO (or Fe3Co2(PO4)@rGO) (Fe/Co = 1.5–2).

To facilitate our discussion, 2 and 3 will be simply denoted as 2: Fe2Co(PO4)3@rGO and 3: Fe3Co(PO4)4@rGO in consideration with the experimental component analysis.

**Electrochemical performance.** We performed electrochemical measurements to check the catalytic activities of catalysts 1–9 and commercial 20 wt% Ir/C for OER in 1 M KOH electrolyte (Fig. 4a and Supplementary Figs. 10–12). The OER activity of these electrocatalysts are influenced by the amount of Fe or Co in the presence of phosphate and the best activity is achieved for 1. Compound 1 exhibits very small overpotential of ~237 mV to afford a current density of 100 mA cm−2, lower than catalysts 2–9 and Ir/C (Fig. 4a and Supplementary Figs. 10–12), and other catalysts with a carbon-supporting substrate including the benchmark Ir/C catalyst (303 mV). This activity is found to be among the best OER-active catalysts (Supplementary Table 8) among which some catalysts of pure metals without the carbon-supporting substrate31–33 do not show high stability (<10 h at 10 mA cm−2), except for the special case of core-shell FeNiCu, which shows a promising result with high stability at low overpotential34. Nevertheless, in most cases the industrial application still requires carbon substrates.

The TOF35,36 is calculated to be 0.54 s−1 at an overpotential of 237 mV, indicating a highly active catalyst, 7.6 times that of Ir/C 0.071 s−1 (details in Methods), which further confirms the

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**Fig. 3** X-ray absorption spectra. a–f Co K-edge. a, d XANES spectra for Fe K- and Co K-edges. b, e Fourier transform (FT) of the EXAFS spectra in real space at Fe K- and Co K-edges. c, f FT-EXAFS spectra in r-space and the corresponding least-squares fit (black rectangular line) for first and second shells. 1: Fe3Co(PO4)4@rGO; 2: FeCo(PO4)2@rGO. Source data for a–f are provided as a Source Data file.

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**Fig. 4** Electrochemical performance of electrocatalysts toward OER and whole-cell water splitting. a Linear sweep voltammograms (LSVs) curves measured in 1 M KOH at a scan rate of 5 mV s−1. b Tafel slope. c LSVs recorded at a scan rate of 5 mV s−1 during the OER before and after continuous polarization of the electrode in 1 M KOH for 5000 cycles. d Chronoamperometry curves recorded in 1 M KOH for 70 h. e Current density of Pt/C-Ir/C for overall water splitting in 1 M KOH. 1: Fe3Co(PO4)4@rGO; 2: Fe3Co2(PO4)@rGO; 3: (CoFe2O4)(Fe2O3)@rGO. Source data for a–e are provided as a Source Data file.
outstanding OER performance of 1. The Tafel slope is 57 mV per decade (Fig. 4b), smaller than that of Ir/C (117 mV per decade). The small overpotential at Fe sites of 1 is the key factor for the superior OER activity of 1. For achieving this optimal overpotential, other environmental factors have also been utilized as follows. The large BET surface area (238 m²/g) (Supplementary Fig. 13) with an average pore size 4.3 nm promotes the contact between 1 and an electrolyte, thereby helping in the optimal OER activity. The very low charge-transfer resistance (0.29 Ω) on a nickel foam (NF) substrate, 7.5 Ω on glassy carbon electrode (GCE) substrate promotes electron transport, thereby leading to faster kinetics (Supplementary Fig. 14a, b). The electrochemical double-layer capacitance (Cdl = 0.0162 F), which is directly correlated to the catalyst’s active surface area, is very large, 8.1-fold the Cdl of Ir/C (0.002 F) (Supplementary Fig. 15). The defects/dislocations (strain effect) 37–39 of Fe and Co atoms in crystal help in improving the performance of active sites.

After initial and 5000 cyclic voltammmograms (CV) cycles, accelerated degradation test of 1 indicates the excellent durability as demonstrated by the near overlay of OER-curves (Fig. 4c). No significant changes in TEM, EDX (energy-dispersive X-ray spectroscopy), HRTEM, hard/soft XAS, XPS, and Raman spectra (except for minor increase in FeO4−/FeOOH and CoO4−/CoOOH 40–42, which would not be so active such as Fe sites of 1, Supplementary Fig. 16) were observed before and after the test, indicating that 1 is quite durable (Supplementary Figs. 17–23). The stability of this catalyst was further assessed by chronoamperometry (CA). Compound 1 exhibited outstanding stability with no changes in current density of ~10–11 mA cm⁻² (70 h on NF and 55 h on GCE) and ~210 mA cm⁻² (for 45 h on NF) (Fig. 4d and Supplementary Fig. 24). The high stability and durability of nanocrystal in 1 is ascribed to the graphene support (which is very stable in alkaline and acid media) and the strong coordination between Fe/Co and PO₄. Initially and 54 h after the stability test, the Faradic efficiency (after 1 h test) is ~98 and ~96% in alkaline electrolyte, respectively (Methods).

To evaluate the real application, an overall water-splitting cell was fabricated in which 1 M/6 M KOH was used as electrolyte and benchmark Ir/C. The remarkable performance is attributed to the Fe/Co sites of 1 for 5000 CV cycles in the potential range of 1.1–1.7 V vs. reversible hydrogen electrode (RHE). The linear sweep voltammograms test were performed at a scan rate of 5 mV s⁻¹ with 100% iR compensation, which was automatically derived from the electrochemical workstation. The cycling durability test was carried out at a scan rate of 100 mV s⁻¹ for 5000 CV cycles in the potential range of 1.2–1.7 V vs. RHE. CA response were performed on both GC (for 55 h) and NF (for 70 h) substrates at potentials on which the current densities reached to the range of 10 mA cm⁻². To evaluate the durability of 1 for high current density generation, the CA response were performed on NF substrate at a
The number of moles oxygen gas produced in water displacement before the stability:

\[
\text{number of moles} = \left( \frac{0.975 \text{ atm}}{0.00048 \text{ L atm/mol K}} \right) \times 0.00048 \text{ L atm/mol K} \\
= 0.0821 \text{ L atm/mole} \times 0.00048 \text{ L atm/mol K} = 19.1 \mu \text{mol}
\]

The number of mol oxygen gas produced in water displacement after the stability:

\[
\text{number of moles} = \left( \frac{0.975 \text{ atm}}{0.00048 \text{ L atm/mol K}} \right) \times 0.00048 \text{ L atm/mol K} \\
= 0.0821 \text{ L atm/mole} \times 0.00048 \text{ L atm/mol K} = 18.3 \mu \text{mol}
\]

Faradaic efficiency before stability.

Faradaic efficiency: 19.10/18.3 * 100

Faradaic efficiency after stability.

Faradaic efficiency: \( \frac{19.10}{19.32} \times 100 \)

The Faradaic efficiency after stability was 98%, whereas it was 96% after the 54 h of chronoamperometric stability test.

Computation method: Spin-polarized calculations were performed to obtain ground DFT energies of Fe\( \text{Co}_{6}\)O\(_{6}\)\( \text{O}_{4}\) (\( n = 2,4,6,8 \)) clusters, Fe\( \text{Co}_{6}\)(PO\(_{4}\))\(_{4}\), (\( n = 4 \)) clusters, and Fe\( \text{Co}_{6}\)(PO\(_{4}\))\(_{4}\) (010) surfaces using Vienna ab initio simulation package\(^{44,45,46} \) with projected augmented wave function\(^{45,46} \). The exchange-correlation potential was corrected by Perdew, Burke, and Ernzerhof (PBE)\(^{47} \) for generalized gradient approximation with Tkatchenko-Scheffler\(^{48} \) (TS) dispersion correction (PBE + TS). For structure optimization, a 2 × 2 × 2 grid for clusters was used to sample the first Brillouin zone and the cut-off energy was set to 500 eV. Self-consistent field calculations were used to optimize electronic and ionic steps until the energy difference between two successive steps becomes 0.01 meV and the force constant on each ion reaches to 0.02 eV Å\(^{-1} \). Calculations were optimized with spin-polarized method, resulting in the high-spin ferromagnetic configuration for Fe\( \text{Co}_{6}\)(PO\(_{4}\))\(_{4}\) (010) surfaces (Supplementary Table 9) and the most stable magnetic configuration was also considered for cluster models. These ferromagnetic configurations are in agreement with the experimentally verified ferromagnetic magnetic materials of catalysts 1–3.

The Gibbs free-energy changes (\( \Delta G \)) for OER mechanism in alkaline environment are as follows (equations 8–11):

\[
\begin{align*}
&\text{O} + \text{OH}^- \rightarrow \text{OH} + \text{e}^-: \Delta G_{1} = \Delta G_{\text{OH}} - eU + k_{\text{B}} \text{ln} (n_{\text{OH}^-}) \\
&\text{O} + \text{OH}^- \rightarrow \text{O} + \text{H}_2\text{O} + \text{e}^-: \Delta G_{2} = \Delta G_{\text{OH}^-} - eU + k_{\text{B}} \text{ln} (n_{\text{OH}^-}) \\
&\text{O} + \text{OH}^- \rightarrow \text{OOH} + \text{e}^-: \Delta G_{3} = \Delta G_{\text{OH}^-} - \Delta G_{\text{O}} - eU + k_{\text{B}} \text{ln} (n_{\text{OH}^-}) \\
&\text{OOH} + \text{OH}^- \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{e}^-: \Delta G_{4} = 4.92 [\text{V}] - \Delta G_{\text{OOH}} - eU + k_{\text{B}} \text{ln} (n_{\text{OH}^-}) \\
\end{align*}
\]

where \( \Delta G_{\text{O}} \), \( \Delta G_{\text{OH}} \), and \( \Delta G_{\text{OOH}} \) are the Gibbs free energies of \( \text{O} \), \( \text{OH}^- \), and \( \text{OOH} \) intermediate reactions, respectively. Corrections to the Gibbs free energies were adopted from ref. \(^{13}\). Theoretical overpotentials of all considered structures were calculated at the given pH by the following equation\(^{49,50} \):

\[
\text{overpotential} = \text{max} (\Delta G_{1}, \Delta G_{2}, \Delta G_{3}, \Delta G_{4})/e - 1.23 [\text{V}], \text{whereas the pH effect is canceled out in evaluating the overpotential.}
\]

Data availability

The data that support the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request. The source data underlying Figs. 1a, c, 2e, f, 3a, e, and 4a, c, e, and Supplementary Figs. 6a, b, 7a, b, 9a, b, 10, 11a, 12a, b, 13a, b, 19a, 20a-c, 21a-d, 22a-a, 23, 24a, b, 29, and 30–37 are provided as a Source Data file.

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