

Supporting Information

Modulating Geometrical Sites of Cobalt Phosphates by Autologous

Pyrolysis for Electrocatalytic Water Oxidation

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Materials

CoCl₂·6H₂O (Saan Chemical), KOH (Shengao Chemical), H₃PO₄ (Tongjie Chemical) and absolute ethanol were used without further purification. The milli-Q water of 18.2 MΩ·cm was used throughout all experiments.

Synthesis of Co₃(PO₄)₂·8H₂O precursor

1.0 mmol of CoCl₂·6H₂O and 157 μL of H₃PO₄ were dissolved in 30 mL deionized water with continuous stirring. Afterward, 1.0 M KOH solution was added to the above solution until the pH reaches 7.0. The purple mixture changes into pink colour. The resulting materials were collected by centrifugation and washing with deionized water for several times. The as-obtained Co₃(PO₄)₂·8H₂O were drying in a vacuum oven at 60 °C for 12 h.

Synthesis of Co₃(OH)₂(HPO₄)₂

The Co₃(OH)₂(HPO₄)₂ was obtained via a hydrothermal reaction. The Co₃(PO₄)₂·8H₂O precursor (40 mg) was immersed into deionized water (6 mL) and stirred for about 10 min. The obtained pink solution was transferred into a Teflon-lined autoclave (10 mL) and heated at 180 °C for 3 d. The Co₃(OH)₂(HPO₄)₂ was collected and centrifuged, followed by washing with deionized water three times before drying in an oven at 60 °C.

Synthesis of Co₃(PO₄)₂

The architectural-like Co₃(PO₄)₂ were obtained by annealing of the as-synthesized Co₃(OH)₂(HPO₄)₂ at 400 °C for 1 h with a heating rate of 5 °C min⁻¹ in a tube furnace under Ar gas.

Characterization

X-ray diffraction (XRD) patterns of $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and $\text{Co}_3(\text{PO}_4)_2$ were performed using X-ray diffractometer (Rigaku D/Max2550VB+/PC, Cu $\text{K}\alpha$, $\lambda = 1.5406 \text{ \AA}$, 40 kV and 100 mA). The morphologies were observed by scanning electron microscope (SEM) with an accelerating voltage of 5 kV. For surface area measurements, the catalysts were pre-dried under vacuum at $100 \text{ }^\circ\text{C}$ for 12 h and then were measured on a MicroActive ASAP 2460. The X-ray photoelectron spectroscopy (XPS) analyses were performed using a Kratos AXIS ULTRA XPS with monochromatic Al $\text{K}\alpha$ radiation of 1486.6 eV. The binding energy were corrected using C 1s peak at 284.6 eV. Thermogravimetric analysis (TGA) of $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ was carried out by heating the solid at a rate of $5 \text{ }^\circ\text{C min}^{-1}$ with nitrogen flow at 100 mL min^{-1} over $25 \text{ }^\circ\text{C}$ to $800 \text{ }^\circ\text{C}$ in a TA Instruments SDT Q600. Derivative thermogravimetry (DTG) result was obtained based on the TGA data. Ultraviolet-visible diffuse reflectance spectra (UV-vis DRS) of the $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and $\text{Co}_3(\text{PO}_4)_2$ in the range of 300-800 nm were examined under room conditions using a SHIMADZU UV 3600. Raman spectra were obtained using a Renishaw inVia confocal Raman microscope with the excitation laser line at 532 nm. The samples were drop-casted onto the ITO electrode for Raman spectra recording.

Electrochemical studies

4 mg electrocatalyst and 32 μL of 5 wt% Nafion solution were dispersed in 0.774 mL water and 0.194 mL ethanol by sonication for 1 h to form a homogeneous ink. Then, the catalyst ink (5 μL) was dipped onto a glassy carbon electrode (GC, 0.07 cm^2). The electrochemical tests were carried out in 1.0 M KOH solution via a CH Instruments Electrochemical Analyzer (CHI 660E). The electrochemical behavior of $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and $\text{Co}_3(\text{PO}_4)_2$ was measured using a three-electrode electrochemical cell, which includes active materials on the glassy carbon electrode as the working electrode, a Ag/AgCl electrode as the reference electrode, and platinum wire as the counter electrode. All the potentials reported in our work were referred to the reversible hydrogen electrode (RHE) according to $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + E_{\text{Ag/AgCl}}^\theta$

0.059×pH V. The OER activity of the prepared catalysts was measured through cyclic voltammetry (CV) and differential pulse voltammetry (DPV) with 100% compensation of iR drop. Tafel slope was collected from linear scanning voltammetry (LSV) with 5 mV s⁻¹ for both samples. The capacitances of Co₃(OH)₂(HPO₄)₂ and Co₃(PO₄)₂ were obtained by CVs (no iR compensation) in the non-Faradaic potential region at different scan rates (10-200 mV/s). The CV of Co₃(OH)₂(HPO₄)₂ and Co₃(PO₄)₂ at different scan rates (0.5, 1.0, 3 and 4 V s⁻¹) in 1.0 M KOH. The pH-dependence test in KOH with different concentrations (0.1, 0.2, 0.5 and 1.0 M) was tested at 50 mV/s to study the OER process.

TOF values for OER of Co₃(OH)₂(HPO₄)₂ and Co₃(PO₄)₂ in 1.0 M KOH were calculated according to the following formula:

$$\text{TOF} = \frac{j * A}{Z * F * n}$$

where *j* is the measured geometrical current at a given overpotential, *A* is the surface area of the electrode, and *Z* is the number of electrons transferred per mole of O₂. *F* is the Faraday constant, and *n* is the number of moles of Co atom on the electrode. The Co content was calculated from the total charge by integrating the Co²⁺/Co³⁺ redox peak area in the CVs.

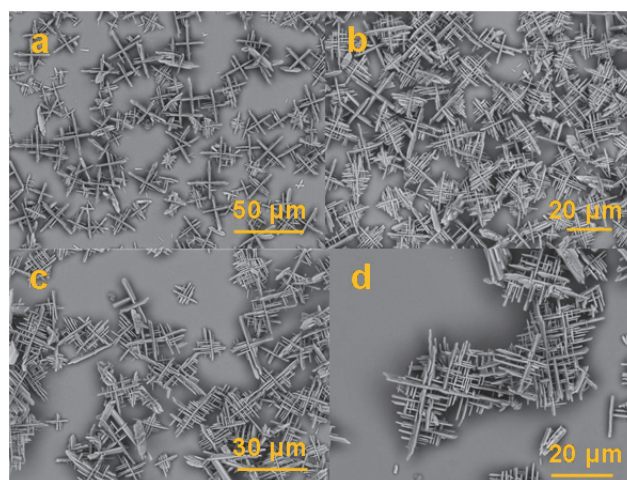


Figure S1. SEM images of $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ after hydrothermal treatment with (a) 0 d, (b) 3 d, (c) 5 d and (d) 7 d at 180 °C.

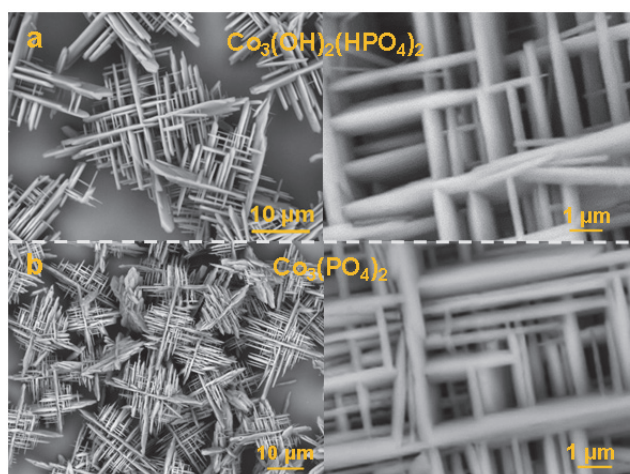


Figure S2. SEM and high-magnification SEM images of (a) $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and (b) $\text{Co}_3(\text{PO}_4)_2$.

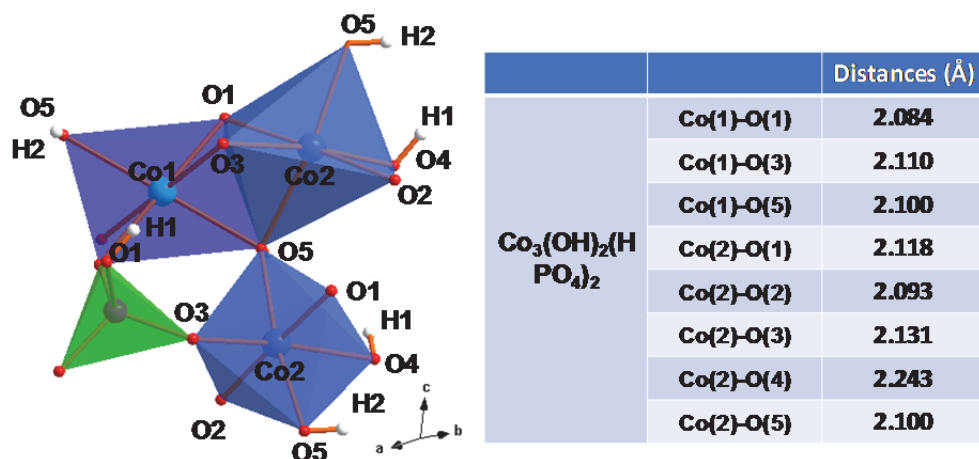


Figure S3. Crystal structure of Co-polyhedrons and bond lengths in $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$.

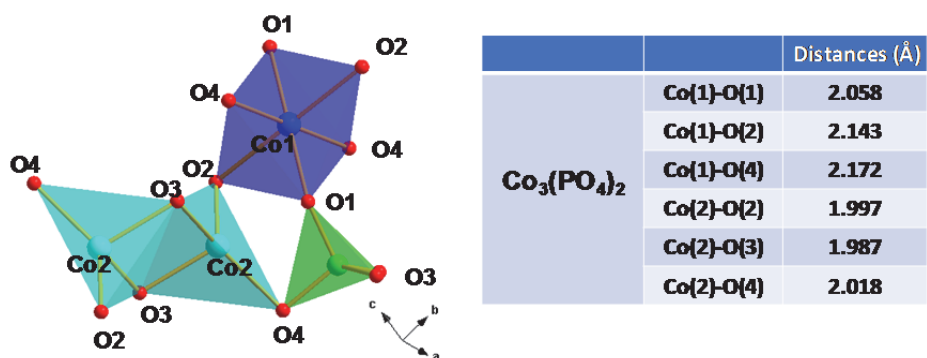


Figure S4. Crystal structure of Co-polyhedrons and bond lengths in $\text{Co}_3(\text{PO}_4)_2$.

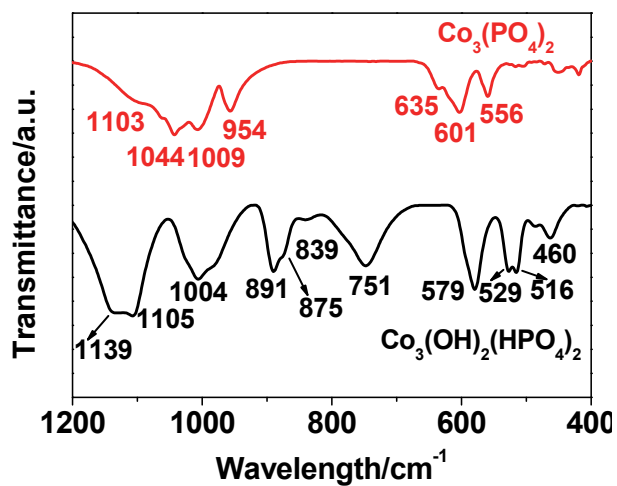


Figure S5. The FTIR spectra of (a) $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and (b) $\text{Co}_3(\text{PO}_4)_2$.

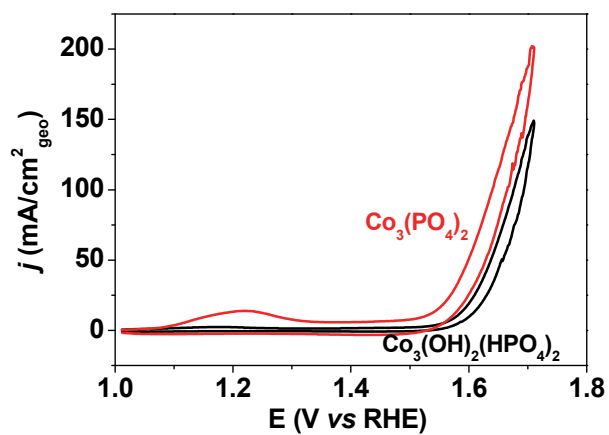


Figure S6. The CV curves of $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and $\text{Co}_3(\text{PO}_4)_2$ normalized by geometric area.

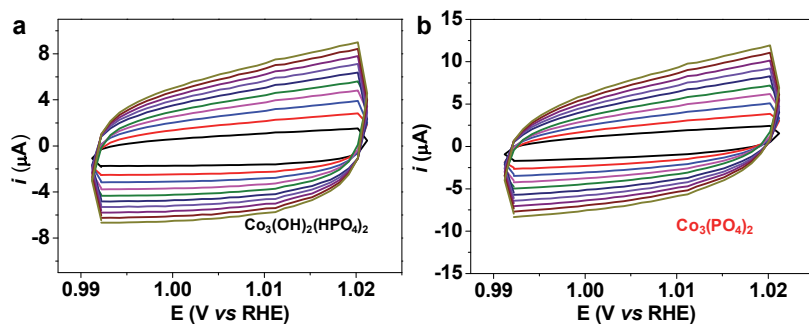


Figure S7. The CVs of (a) $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and (b) $\text{Co}_3(\text{PO}_4)_2$ recorded in the non-Faradaic potential region at different scan rates (black 20, red 40, blue 60, magenta 80, olive 100, navy 120, violet 140, purple 160, wine 180, dark yellow 200 mV/s).

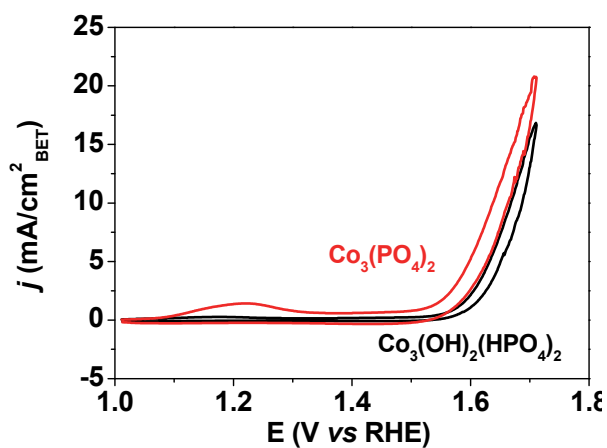


Figure S8. The CV curves of $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and $\text{Co}_3(\text{PO}_4)_2$ normalized by BET surface areas.

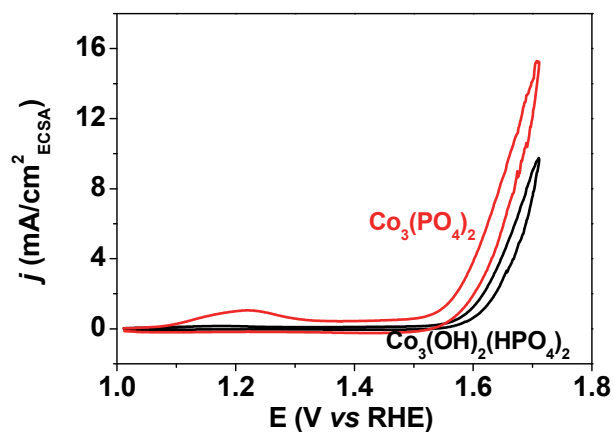


Figure S9. The CV curves of $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and $\text{Co}_3(\text{PO}_4)_2$ normalized by ECSA.

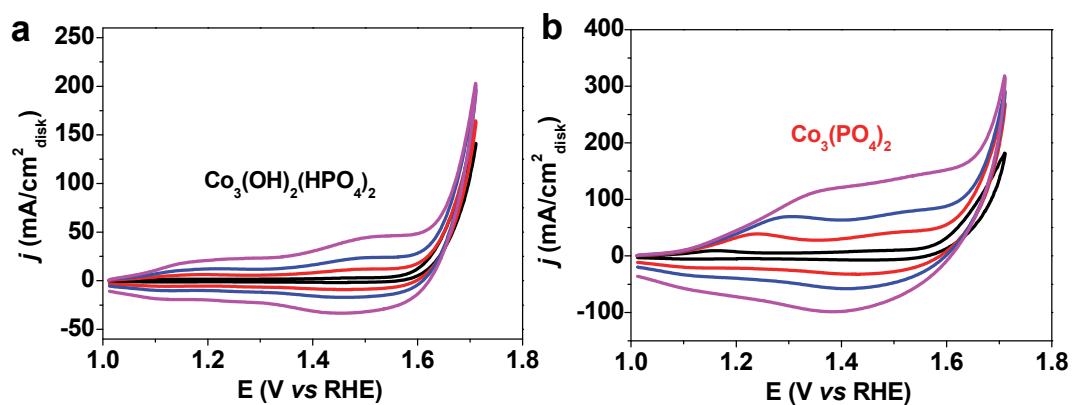


Figure S10. CVs of (a) $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and (b) $\text{Co}_3(\text{PO}_4)_2$ with different scan rates in 1.0 M KOH.

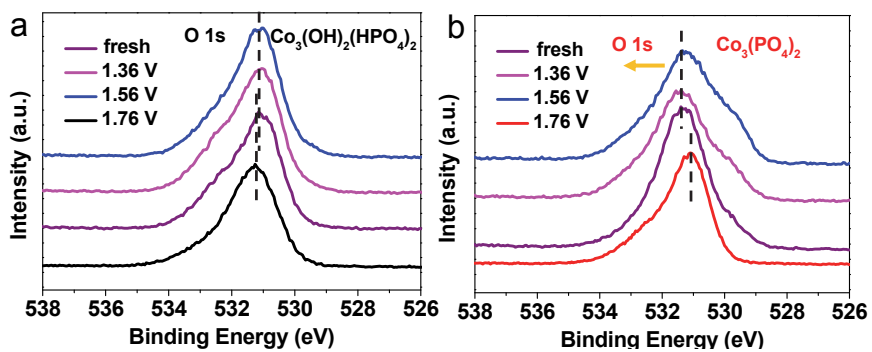


Figure 11. XPS spectra of O 1s in (a) $\text{Co}_3(\text{OH})_2(\text{HPO}_4)_2$ and (b) $\text{Co}_3(\text{PO}_4)_2$ after electrolysis at 1.36, 1.56 and 1.76 V vs RHE for 5 minutes.