

Electronic Supplementary Information

Modulation of crystal water in cobalt phosphate for promoted water oxidation

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1. Experimental Section

1.1 Materials

The chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd. and used as received without further purification.

1.2 Preparation of the β -Co(OH)₂ nanosheet precursor

The synthesis of β -Co(OH)₂ nanosheets were performed in a three-neck flask. Typically, 2 mmol CoCl₂·6H₂O and 36 mmol hexamethylenetetramine (HMT) were added directly into 300 mL N₂-purged deionized water under vigorous stirring. The reaction system was heated to 92 °C and maintained for 4 hours. Then, pink powdery product can be obtained. The product was then vacuum-filtrated over a cellulose acetate membrane with 0.22 μ m pore size, washed by deionized water for several times, and finally dried under vacuum at 40 °C for 24 hours.

1.3 Synthesis of cobalt phosphate with tunable contents of crystal water

Cobalt phosphate (Co-Pi) catalysts with tunable contents of crystal water were synthesized via a one-step hydrothermal method. In detail, 4 mmol KH₂PO₄ and 0.4 mmol β -Co(OH)₂ were dispersed in 40 mL deionized water and stirred for 10 min. After sonicating for 2 min, the homogeneous dispersion was transferred into a 50 mL Teflon-lined stainless-steel autoclave, sealed and heated at 160 °C for 9 hours. Then, the as-obtained violet Co-Pi tetrahydrate (Co-Pi-4W; JCPDS card No. 34-0844) powdery product was collected by centrifugation and washed with deionized water for several times. By simply altering the synthetic conditions, Co-Pi octahydrate and Co-Pi dihydrate can be prepared. For the synthesis of Co-Pi octahydrate, lower temperature is essential, for which a hydrothermal procedure at 120 °C for 9 hours is conducted with the other experimental parameters unchanged. The as-obtained pink powdery Co-Pi octahydrate (Co-Pi-8W; JCPDS card No. 33-0432) can be collected by centrifugation and decontamination. For preparing Co-Pi dihydrate, a higher reaction temperature with longer reaction period is demanded. In brief, the reaction was proceeded at 200 °C for 10 hours. After that, fuchsia-colored Co-Pi dihydrate

(Co-Pi-2W; JCPDS card No. 80-1996) can be formed. The product was collected by centrifugation and decontamination similarly, and dried at 40 °C under vacuum for 24 hours. For the synthesis of anhydrous $\text{Co}_3(\text{PO}_4)_2$ (Co-Pi; JCPDS card No. 77-0225), the as-obtained Co-Pi-4W was calcined in Ar atmosphere at 600 °C for 2 hours with heating/cooling rate of 5 °C/min.

1.4 Structural characterizations

X-ray diffraction (XRD) was performed on a Philips X'Pert Pro Super diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The Fourier transform infrared (FT-IR) spectra were measured on a MAGNA-IR 750 (Nicolet Instrument Co., USA). The scanning electron microscopy (SEM) images were taken on a JEOL JSM-6700F SEM. The transmission electron microscopy (TEM) was carried out on a JEM-2100F equipment at an acceleration voltage of 200 kV. The high-resolution TEM (HRTEM) was performed on a JEOL-2010 TEM at an acceleration voltage of 200 kV. The X-ray photoelectron spectroscopy (XPS) analyses were performed on a VGESCALAB MKII X-ray photoelectron spectrometer with an excitation source of Mg $K\alpha = 1253.6 \text{ eV}$, and the resolution was lower than 1 atom%.

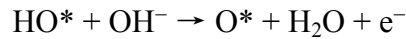
1.5 Electrocatalytic study

All the electrochemical measurements were performed in a three-electrode system linked with an electrochemical workstation (CHI660E) at room temperature. All potentials were calibrated to a reversible hydrogen electrode (RHE) and the data are presented without iR correction. Typically, 4 mg of catalyst and 40 μL Nafion solution (Sigma Aldrich, 5 wt%) were dispersed in 1 mL water-isopropanol mixed solution (volume ratio of 3:1) by sonicating for at least 30 min to form a homogeneous ink. Then 5 μL of the dispersion (containing 20 μg of catalyst) was loaded onto a glassy carbon electrode with 3 mm diameter, leading to a catalyst loading of 0.285 mg cm^{-2} . The as-prepared catalyst film was allowed to be dried at room temperature. The cyclic voltammetry (CV) and linear sweep voltammetry (LSV) with a scan rate of 5 mV s^{-1} were conducted in O_2 -purged 1 M KOH solution. A Hg/HgO electrode was used as the reference electrode, a platinum gauze electrode (2

cm × 2 cm, 60 mesh) was used as the counter electrode, and the glassy carbon electrodes loaded with various catalysts were served as the working electrodes. For the chronoamperometry test, a static potential of 1.7 V vs. RHE was applied. The electrochemical impedance spectroscopy (EIS) measurements were operated in the same configuration at 1.55 V vs. RHE from 10⁻²-10⁵ Hz.

2. Possible mechanism for alkaline OER

As well accepted, four steps are involved in alkaline OER, which could be described as follows:



where the label * represents the active surface sites which are usually the high-valence metal sites in transition metal compounds. For Co-based catalysts, a pre-oxidation process could occur on the surface, leading to the generation of in-situ formed high-valence Co sites as the active surface sites for alkaline OER.¹

3. Additional physical and electrochemical characterizations

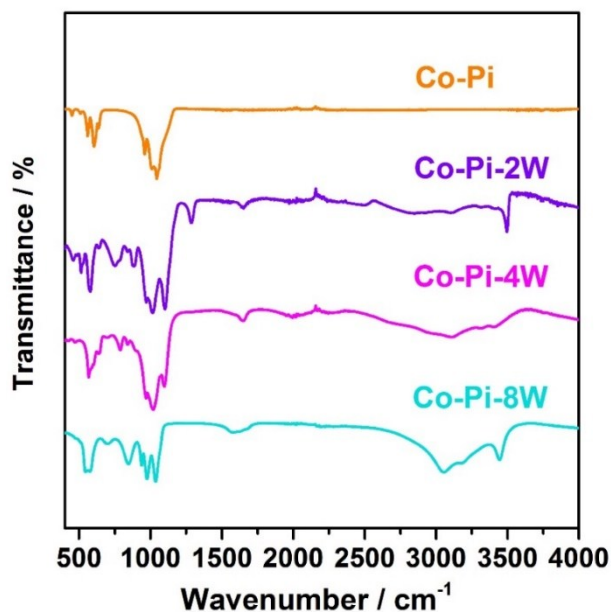


Fig. S1 FT-IR spectra of the catalysts reveal the presence of PO_4^{3-} and crystal water in hydrated Co-Pi.

In detail, all the samples possess characteristic peaks corresponding to the cobalt phosphates with the symmetric stretching vibration of the P-O ($900\text{-}1200\text{ cm}^{-1}$) and the finger peaks of the lattice vibration modes of Co-O ($400\text{-}900\text{ cm}^{-1}$). For the hydrated Co-Pi samples (Co-Pi-2W, Co-Pi-4W and Co-Pi-8W), additional peaks from crystal water can be identified with the stretching vibration of O-H in the crystal water (generally appearing at $3300\text{-}3540\text{ cm}^{-1}$) and the bending vibration of O-H in the crystal water ($1600\text{-}1700\text{ cm}^{-1}$).² No signal of water can be detected for the anhydrous Co-Pi.

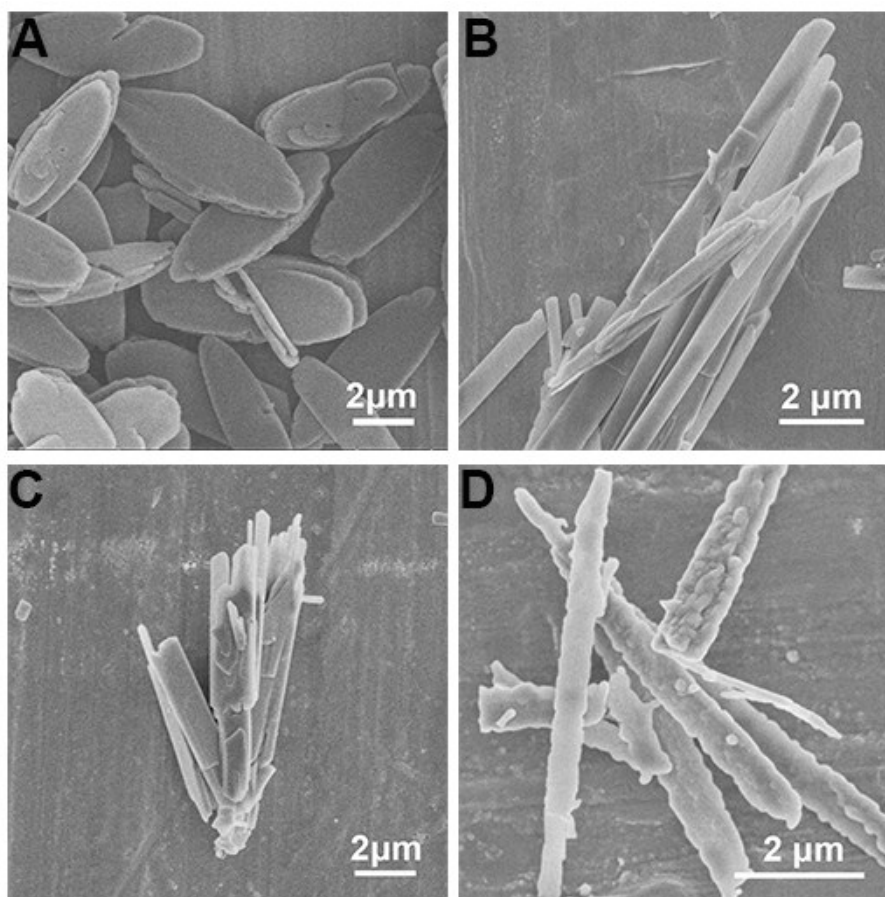


Fig. S2 (A-D) SEM images of (A) Co-Pi-8W, (B) Co-Pi-4W, (C) Co-Pi-2W and (D) anhydrous Co-Pi.

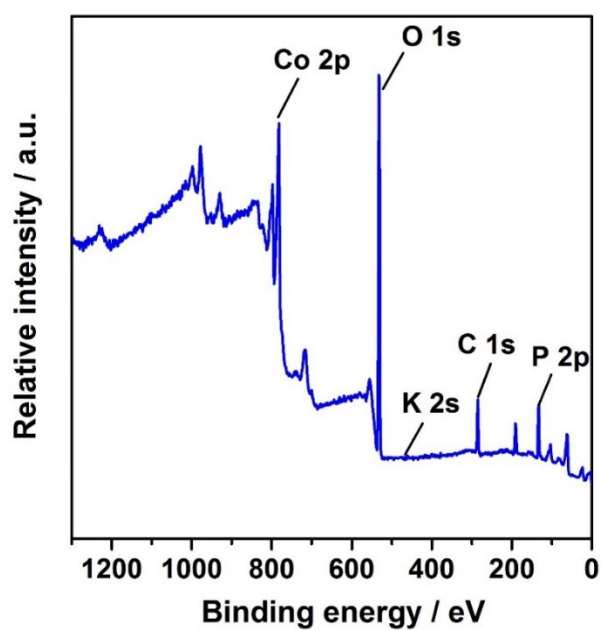


Fig. S3 XPS survey spectrum of Co-Pi-4W.

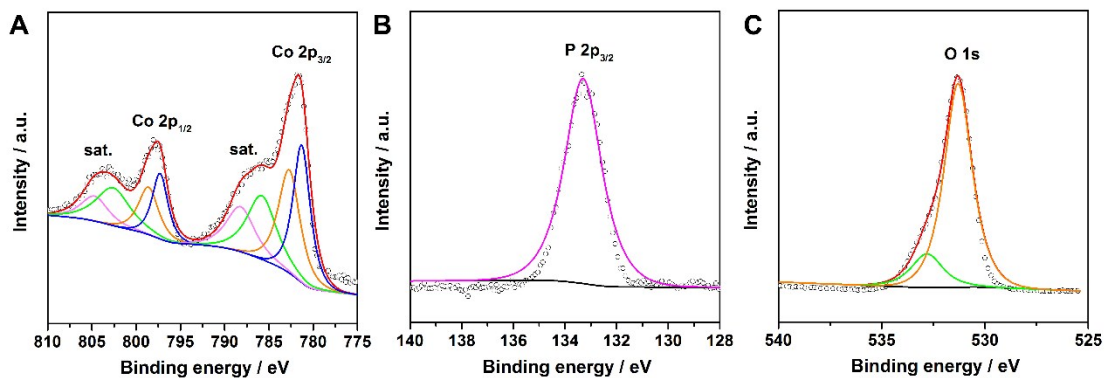


Fig. S4 XPS spectra of (A) Co, (B) P and (C) O in Co-Pi-8W.

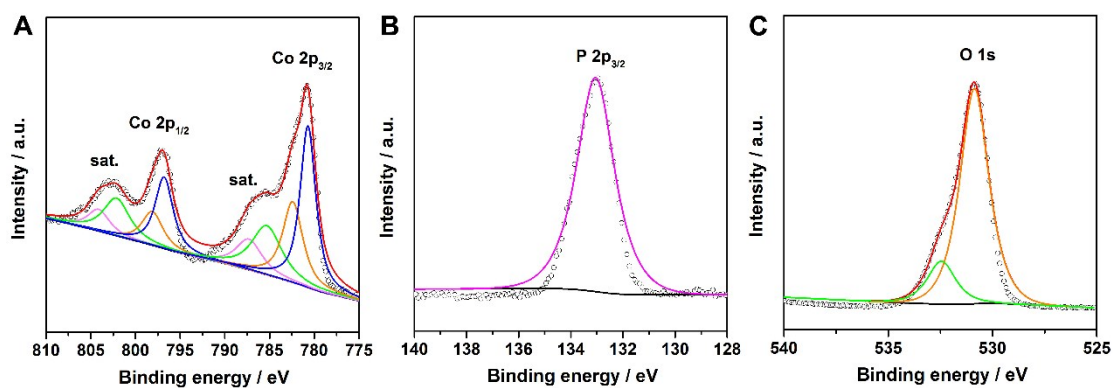


Fig. S5 XPS spectra of (A) Co, (B) P and (C) O in Co-Pi-2W.

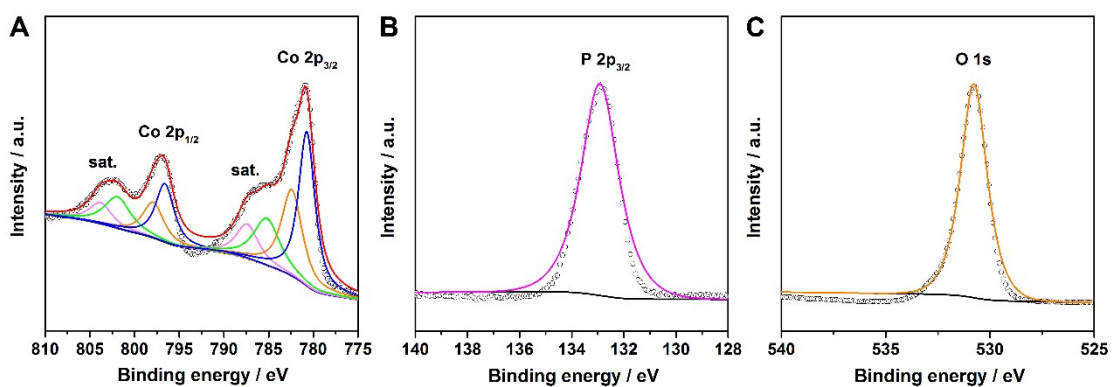


Fig. S6 XPS spectra of (A) Co, (B) P and (C) O in anhydrous Co-Pi.

Table S1 Summary of the binding energies of Co^(II) and Co^(III) species for the as-obtained Co-Pi-based catalysts.

	BE for Co ^(III) [eV]	BE for Co ^(II) [eV]	Average Co-O bond length [Å]
Co-Pi-8W	781.2 / 797.3	782.8 / 798.6	2.11
Co-Pi-4W	781.5 / 797.5	783.0 / 798.8	1.95
Co-Pi-2W	780.7 / 796.8	782.4 / 798.2	2.10
Co-Pi	780.8 / 796.7	782.5 / 798.0	2.05

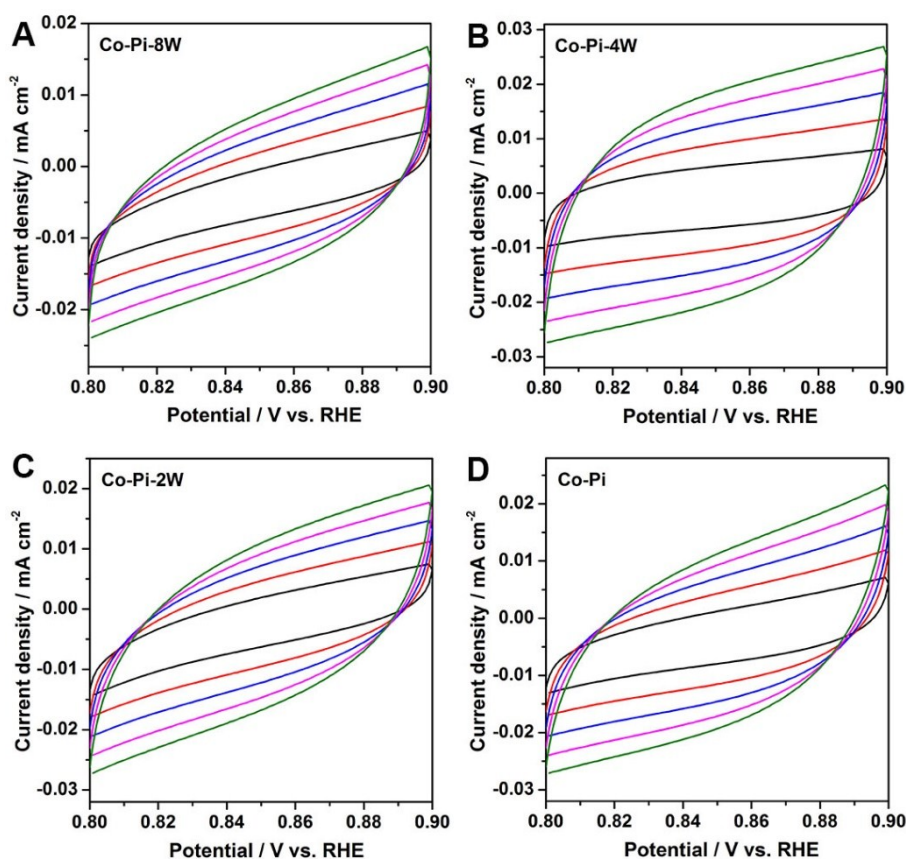


Fig. S7 CV curves in the non-redox region for the estimation of C_{dl} .

The estimation of the effective active surface area of the samples was carried out according to literature.^{3,4} Cyclic voltammetry (CV) were conducted at various scan rates (2, 4, 6, 8, 10 mV s^{-1}) in the region of 0.80-0.90 V vs. RHE where no redox reaction occurs, which can be considered as the double-layer capacitive behavior. The electrochemical double-layer capacitance (C_{dl}) of various catalysts can be identified from the cyclic voltammograms, which is expected to be linearly proportional to the

electrochemically active surface area. The C_{dl} value is estimated by plotting the Δj ($j_a - j_c$) at 0.85 V vs. RHE against the scan rate, where the slope is twice C_{dl} . The calculated C_{dl} values were listed in Table 1. Of note, Co-Pi-4W possesses the highest C_{dl} value among the tested samples, or equivalently, the largest ECSA, which could offer more surface sites for electrocatalysis.

Reference

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