

Electronic Supplemental Information for

Noncovalent phosphorylation of CoCr layered double hydroxide nanosheets with improved electrocatalytic activity for oxygen evolution reaction

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S1. Experimental Section

Materials

Co(NO₃)₂·6H₂O, Cr(NO₃)₃·9H₂O, KOH, NaOH, HCl (≈37 wt%), Ni foam, and formamide (CH₃NO) were purchased from China National Pharmaceutical Industry Corporation Ltd. RuO₂ (99.9%) was purchased from Aladdin. Except the Ni foam was washed with diluted hydrochloric acid, water and ethanol successively, other materials were used as received without further treatment.

Synthesis of P-CoCr LDH Nanosheets

Firstly, the CoCr-LDHs with different Co:Cr molar ratios ([Co]²⁺+ [Cr]³⁺=0.05 M, Co:Cr=1:1, 2:1, and 3:1) were synthesized following the procedure reported in literature.^{S1} In brief, aqueous solutions of Co(NO₃)₂·6H₂O and Cr(NO₃)₃·9H₂O were mixed with a specific molar ratio, and the mixed solution was added drop-wise into NaOH aqueous solution with 5 vol%, 10 vol%, 15 vol% or 30 vol% formamide. The product was washed several times with deionized water and dried in oven at 60 °C for 12 h. Then 10 mg CoCr-LDHs was added into 2 mL 0.25, 0.5 or 1.0 mg/mL P₂O₅ isopropanol solution. After ultrasounded for 1 h and dried at room temperature for 48 h, P-CoCr-LDHs was obtained.

Measurements and Characterization.

The morphology characterizations of the samples were performed using a field-emission scanning electron microscope (SEM) (JEOL JSM6335) operating at 20 kV. Transmission electron microscopy (TEM) and element mapping measurements were carried out using a JEOL JEM 2100 system operating at 200 kV. X-ray powder diffraction patterns were characterized on an X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA, λ= 0.154 nm) at a scan rate of 5° min⁻¹. X-ray photoelectron spectra (XPS) were recorded by using a model of ESCALAB 250 and LabRAMAraxis.

Electrochemical Measurements

The electrochemical OER measurements were carried out at room temperature in a three-electrode glass cell connected to an electrochemical workstation (CHI 660e, CH, Shanghai.). 10 mg P-CoCr LDHs, CoCr LDHs or RuO₂ and 60 μL 5 wt% Nafion were added into 2 mL isopropanol and ultrasounded for 2 h. Then 10 μL above solution was dropped in Ni foam, which was used as the work electrode (geometric area is 0.25 cm²). A platinum electrode and a saturated Ag/AgCl were used as counter and reference electrode, respectively. Freshly prepared 1 M KOH aqueous solution (PH=13.9) was used as the electrolyte. Polarization curves were obtained using linear sweep voltammetry (LSV) with a scan rate of 2 mV/s. All polarization curves were corrected for the iR compensation. The electrolysis was carried out at a current density of 20 mA/cm² for 100 min. The amount of O₂ evolution was determined by gas chromatography every 10 min. The EIS was obtained in 1 M KOH solution by applying an AC voltage of 5 mV amplitude at an applied voltage 1.5 V vs. RHE in the frequency range of 0.01 Hz–100 kHz.

S2. Mass spectrum of the as-formed phosphate ester.

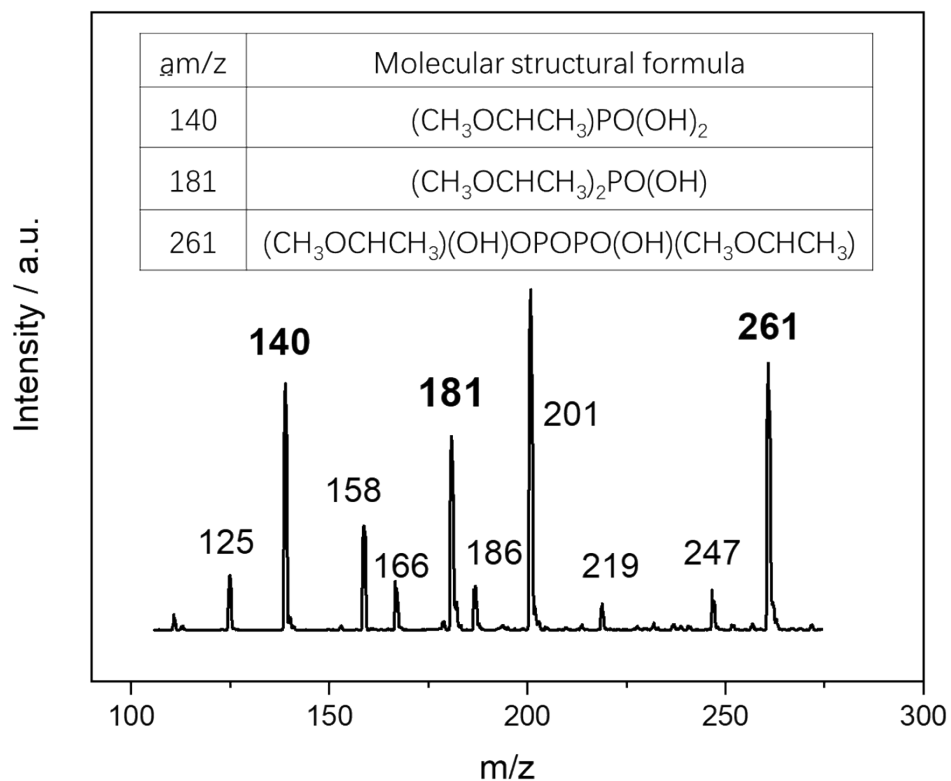


Fig. S1. Mass spectrum of the as-formed phosphate ester and the inset shows the possible molecular structural formula according to the m/z value. The peaks at $m/z=125$ may be the fragments of $(\text{CH}_3\text{CHOCH}_3)\text{PO}(\text{OH})_2$, the peaks at $m/z=158$ and 166 may be the fragments of $(\text{CH}_3\text{CHOCH}_3)_2\text{PO}(\text{OH})$ and the peaks at $m/z=186$, 201 , 219 and 247 may be the fragments of $(\text{CH}_3\text{OCHCH}_3)(\text{OH})\text{OPOPO}(\text{OH})(\text{CH}_3\text{OCHCH}_3)$.

S3. SEM, TEM and element mapping images of Co_2Cr_1 LDHs.

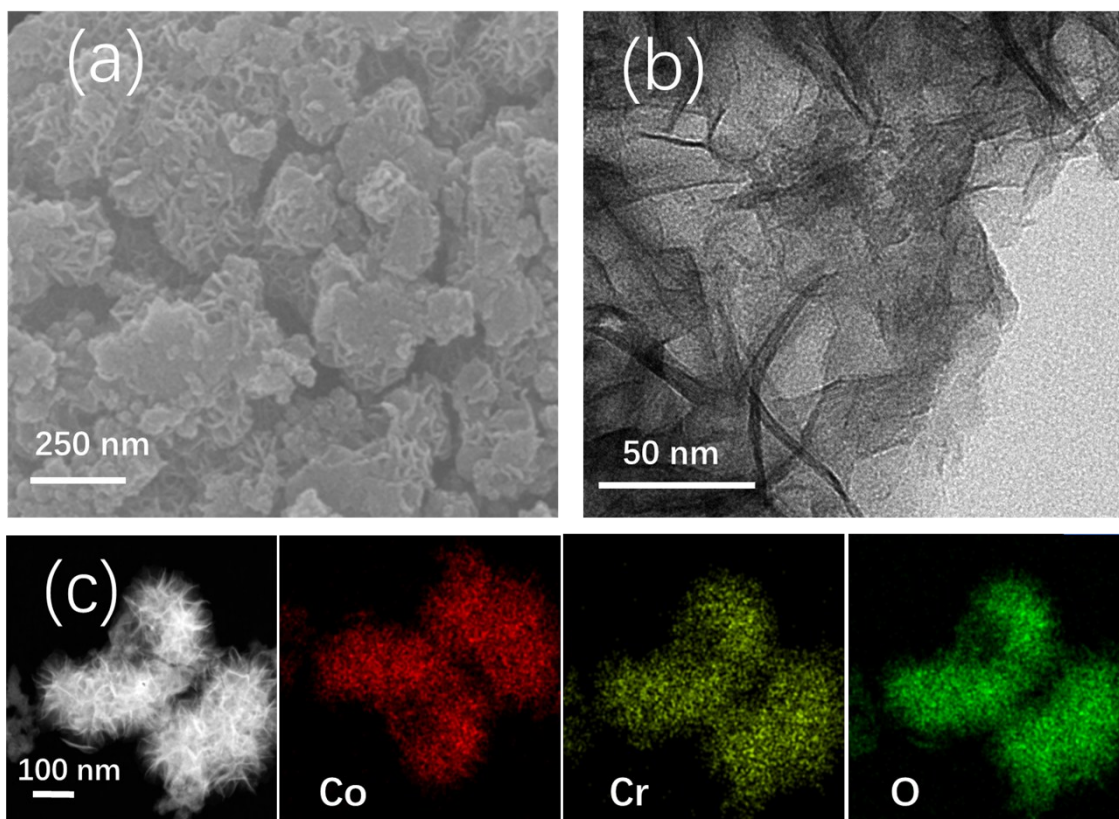


Fig. S2. a) SEM image, b) TEM image and c) Co, Cr, O and P element mapping images of Co_2Cr_1 LDHs.

S4. XPS survey spectra and high-resolution C 1s XPS spectra of P- Co_2Cr_1 LDHs and Co_2Cr_1 LDHs.

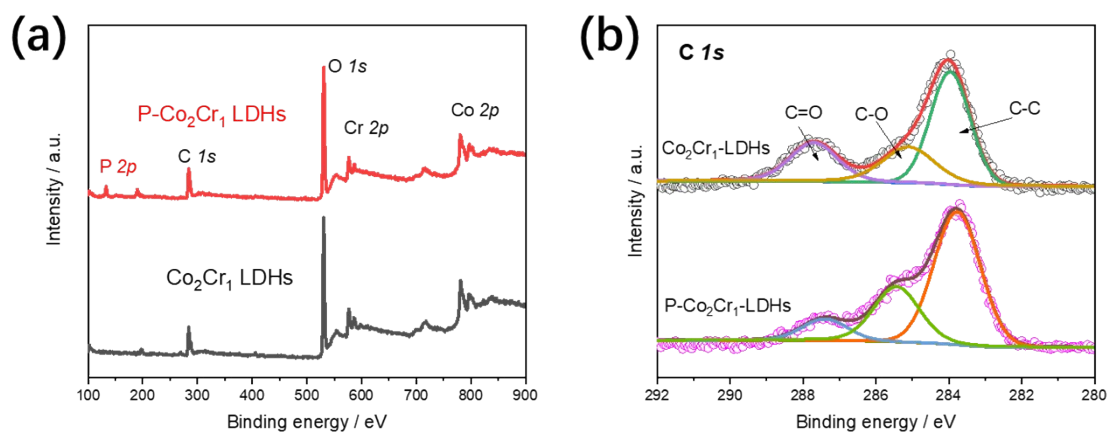


Fig. S3. a) XPS survey spectra and b) high-resolution C 1s XPS spectra of P- Co_2Cr_1 LDHs and Co_2Cr_1 LDHs.

S5. Effect of the atomic ratios of Co:Cr on the performance of CoCr LDHs OER electrocatalytic activity.

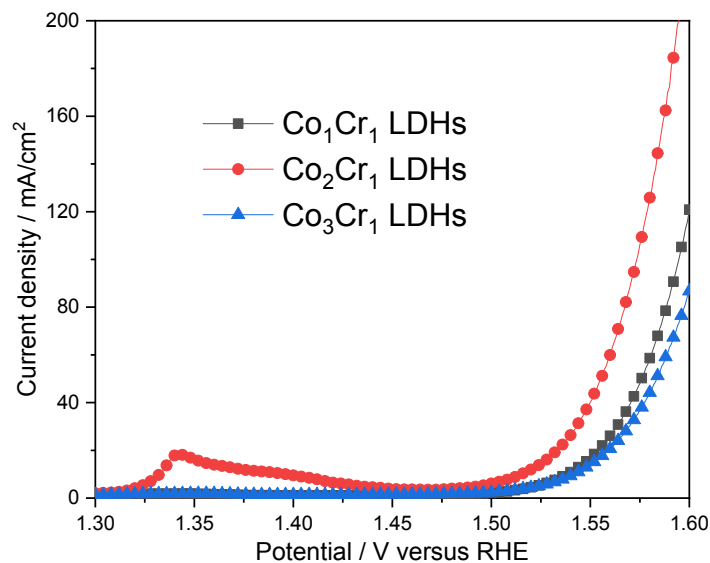


Fig. S4. Polarization curves of CoCr LDHs with different atomic ratios of Co:Cr=1:1, 2:1 and 3:1.

To optimize the electrocatalytic activity of CoCr LDHs, different molar ratios CoCr (Co:Cr=1:1, 1:2 and 1:3) LDHs were prepared and investigated. The linear sweep voltammetry (LSV) curves of CoCr LDH with different molar ratios are showed in ESI Fig. S4, it can be found that the ratio of 2:1 (Co₂Cr₁ LDHs) has the lowest overpotential (285 mV) to obtain a current density of 10 mA/cm², compared with the other samples Co₁Cr₁ LDHs (306 mV) and Co₃Cr₁ LDHs (312 mV), which is consistent with previous study.^{S2}

S6. Effect of the formamide concentration used to prepare CoCr LDHs on the performance of CoCr LDHs OER electrocatalytic activity.

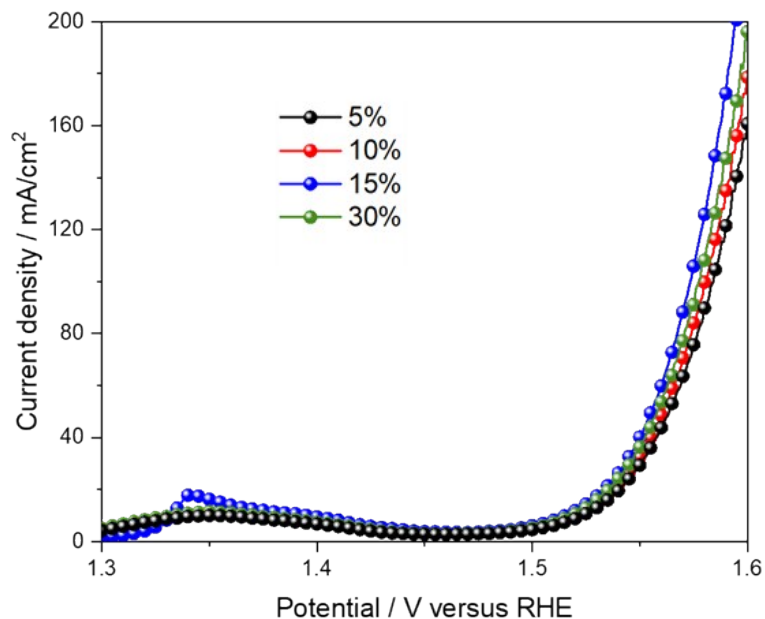


Fig. S5. OER polarization curves of CoCr LDHs synthesized with different volume concentrations of formamide.

The OER catalytical activities of Co_2Cr_1 LDHs prepared with different formamide concentrations are showed in ESI Fig. S5, which displays that the OER catalytical activities of Co_2Cr_1 LDHs synthesized with formamide concentration of 5%, 10.0 vol% and 30.0 vol% are slightly lower than that of 15.0 vol%. Therefore, a formamide concentration of 15.0 vol% is the optimum proportion to achieve high OER performance.

S7. Effect of the initial concentration of P_2O_5 dissolved in isopropanol solution on the performance of P-CoCr LDHs OER electrocatalytic activity.

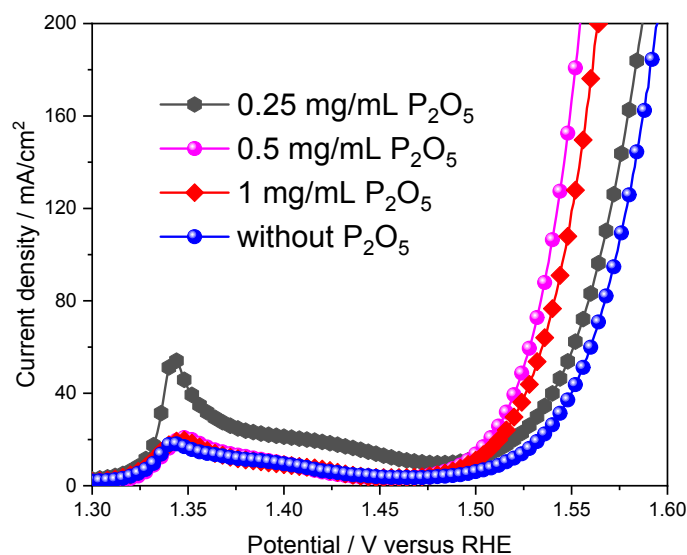


Fig. S6. Polarization curves of CoCr LDHs modified with different concentrations of P_2O_5 dissolved in isopropanol solution.

S8. XRD pattern of P-Co₂Cr₁ LDHs catalyst after galvanostatic stability test.

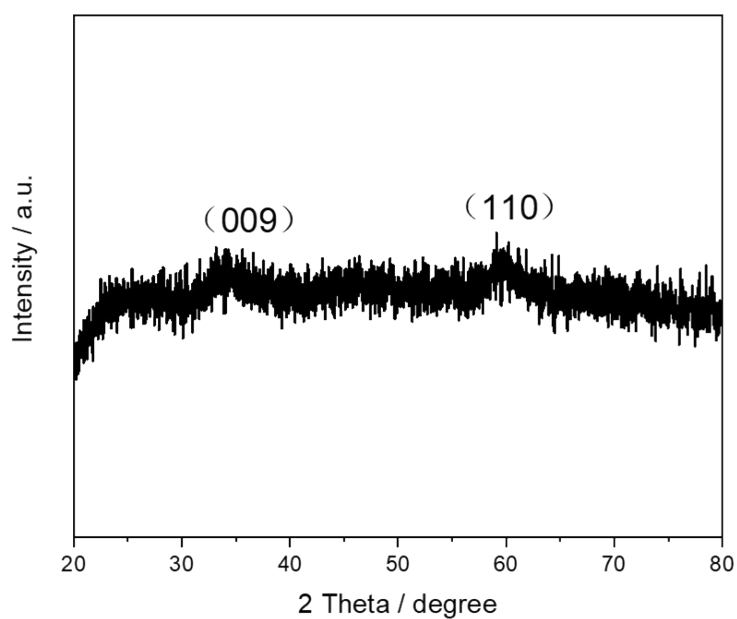


Fig. S7. XRD pattern of P-Co₂Cr₁ LDHs catalyst after galvanostatic stability test.

Compared with the freshly prepared P-Co₂Cr₁ LDH catalyst, there is no phase change in the XRD pattern of P-Co₂Cr₁ LDHs after the galvanostatic stability test as shown in the ESI,† Fig. S7.

S9. XPS spectra of P-Co₂Cr₁ LDHs catalyst after galvanostatic stability test.

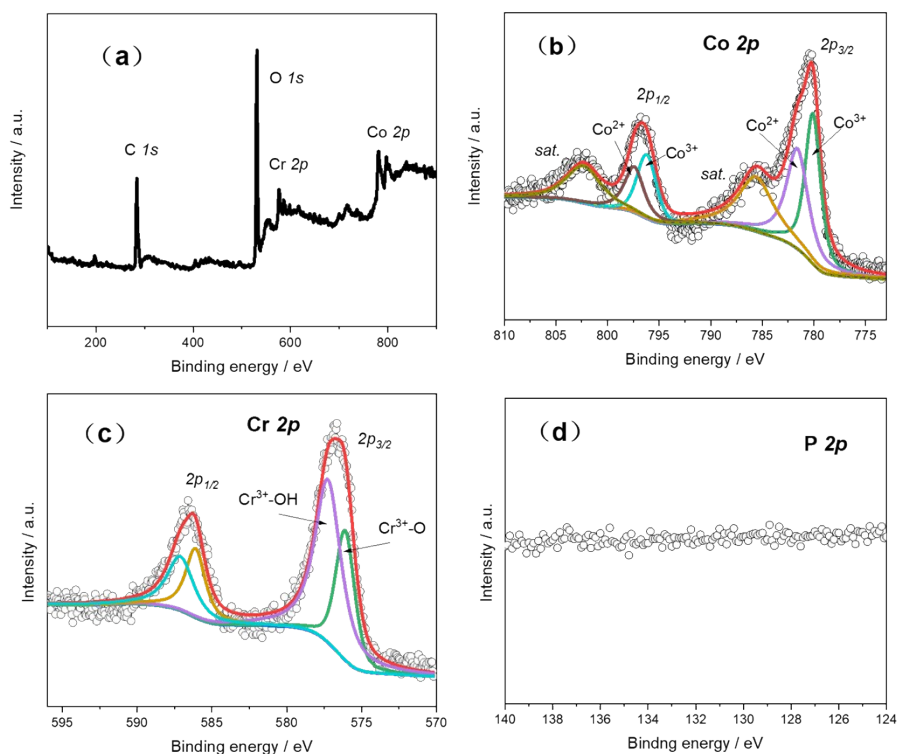


Fig. S8. a) XPS survey spectra, b) high-resolution Co 2p XPS spectra, c) high-resolution Cr 2p XPS spectra and d) high-resolution P 2p XPS of P-Co₂Cr₁ LDHs after galvanostatic stability test.

For the XPS spectra of P-Co₂Cr₁ LDHs (see the ESI,[†] Fig. S8) after 40 hours of the galvanostatic stability test, the high-resolution Co 2p XPS spectra exhibit nearly the same peak locations and contents of Co²⁺ and Co³⁺ as that of the freshly prepared P-Co₂Cr₁ LDH catalyst. But the high-resolution P 2p XPS spectra show no P signal, suggesting that P is unstable during the OER and P almost vanishes after the OER, which is mainly due to the dissolution of phosphate ester. Considering the strong long-term stability for 40 hours of the galvanostatic stability test, therefore, the real OER catalyst is Co₂Cr₁ LDH and the enhanced electrocatalytic activity is attributed to the increase of the content of Co³⁺, which also explains the reason for the maintenance of the high activity after the disappearance of the P element.

S10. Faradaic efficiency of P-Co₂Cr₁ LDHs catalyst for OER.

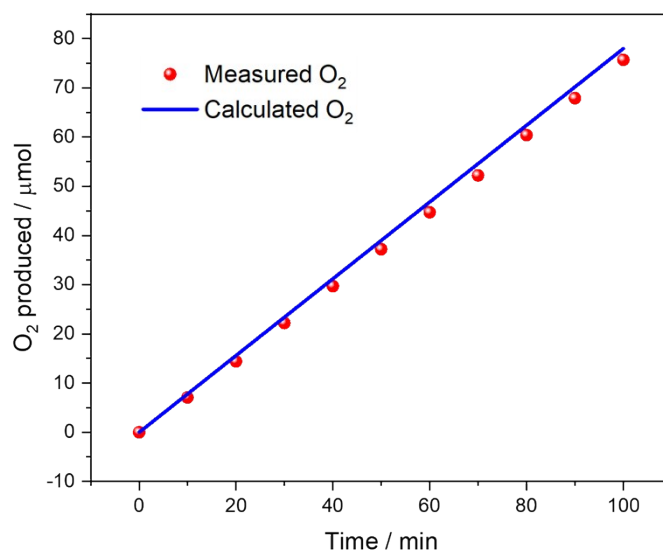


Fig. S9. The measured and theoretical yields of O₂ for 100 min during electrolysis of P-Co₂Cr₁LDHs at the current density of 20 mA/cm².

S11. CV curves of Co₂Cr₁ LDHs and P-Co₂Cr₁ LDHs at different scan rates.

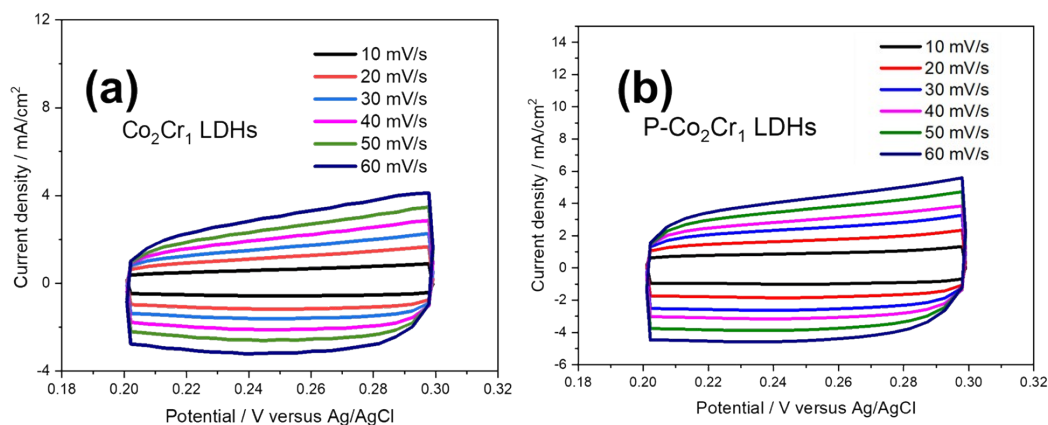


Fig. S10. CV curves of a) Co₂Cr₁ LDHs and b) P-Co₂Cr₁ LDHs in 1.0 M KOH solution at different scan rates.

Supplementary references

S1. J. F. Yu, J. J. Liu, A. Clearfield, J. E. Sims, M. T. Speigle, S. L. Suib and L. Y. Sun, *Inorg. Chem.*, 2016, **55**, 12036.

S2. C. L. Dong, X. T. Yuan, X. Wang, Xi. Y. Liu, W. J. Dong, R. Q. Wang, Y. H. Duan and F. Q. Huang, *J. Mater. Chem. A*, 2016, **4**, 11292.