

Electronic structure regulation of CoP nanorods by tunable incorporation of oxygen for enhanced electrocatalytic activity toward hydrogen evolution reaction

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Experimental section

1. Reagents and chemicals

Cetyltrimethylammonium bromide (CTAB) and Cyclohexane are supplied by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Urea is purchased from Guangdong Guanghua Sci-Tech Co., Ltd (Guangdong, China). *n*-pentanol is purchased from Shanghai Lingfeng Chemical Reagent Co., Ltd (Shanghai, China). $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China). NaH_2PO_2 is purchased from Aladdin Chemistry Co., Ltd (Shanghai, China). Commercial Pt/C (20 wt%) is purchased from Johnson Matthey Chemicals Ltd (Shanghai, China). All reagents were of analytical reagent grade and used without further purification.

2. Synthesis of *O*-CoP nanorods

In a typical synthesis, two separate solutions with the same volume and composition were prepared by dissolving 0.5 g of CTAB and 0.75 mL of *n*-pentanol into 12.5 mL of cyclohexane. Next, 0.3 mL of 1.67 M $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution and 0.3 mL of 1.67 M urea aqueous solution were added dropwise to the above solutions, respectively, under vigorous stirring. After vigorous stirring of the sample, two transparent solutions were formed. Then, the two solutions were mixed and stirred for another 30 min. Afterwards, the newly formed solution was transferred into a 50 mL stainless Teflon-lined autoclave and heated at 180 °C for 12 h. The resulting pink sample was collected and washed with absolute ethanol and dried under vacuum at 40 °C for 12 h. Subsequently, 20 mg precursor and 400 mg NaH_2PO_2 were

placed in porcelain boat, and NaH_2PO_2 at the upstream side of the furnace. After that, the furnace was heated to 350 °C with a speed 2 °C/min under N_2 atmosphere and kept at this temperature for different time (10 min, 20 min, 30 min, 45 min, 60 min), and then cooled to ambient temperature.

3. *Physicochemical characterizations*

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were acquired using a JEOL JEM-2100F transmission electron microscope operated at a 200 kV accelerating voltage. Scanning electron microscope (SEM) images were taken on a Hitachi S-4800 microscopy. X-ray diffraction (XRD) patterns were carried on a Model D/max-rC X-ray diffractometer using $\text{Cu K}\alpha$ radiation source ($\lambda = 1.5406 \text{ \AA}$) and manipulated at 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS) measurements were executed using a Thermo VG Scientific ESCALAB 250 spectrometer with an $\text{Al K}\alpha$ radiator, and the binding energy was corrected by means of the C 1s peak energy of 284.6 eV.

4. *Electrochemical measurement*

All electrochemical tests were performed on a CHI 760E electrochemical analyzer (Shanghai, Chenhua Co., China). Hydrogen evolution reaction (HER) tests were carried out in 1.0 M KOH solution using a standard three-electrode system in which a glassy carbon electrode modified with O-CoP powders as a working electrode, a graphite rod as the auxiliary electrode, and a saturated calomel reference electrode (SCE) as the reference electrode. Linear sweep voltammetry (LSV) were carried out with a scan rate of 5 mV s^{-1} and manually iR -corrected. All potentials were calibrated

to reversible hydrogen electrode (RHE) by adding a value of $(0.242 + 0.059 \text{ pH})$.

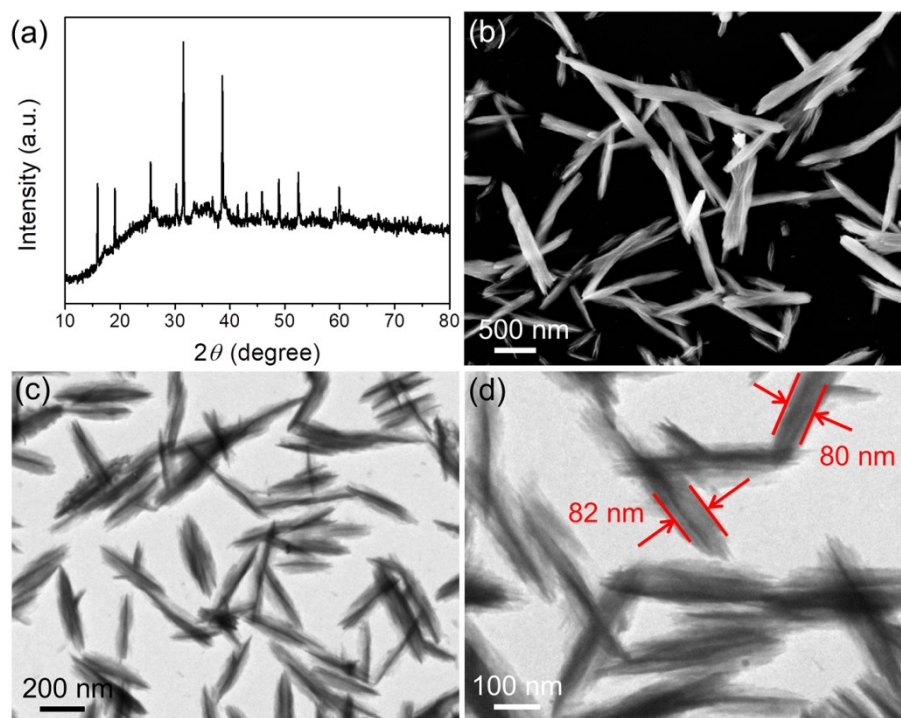


Figure S1. (a) XRD pattern, (b) SEM image, (c-d) TEM images of the Co(OH)_2 nanorods precursors.

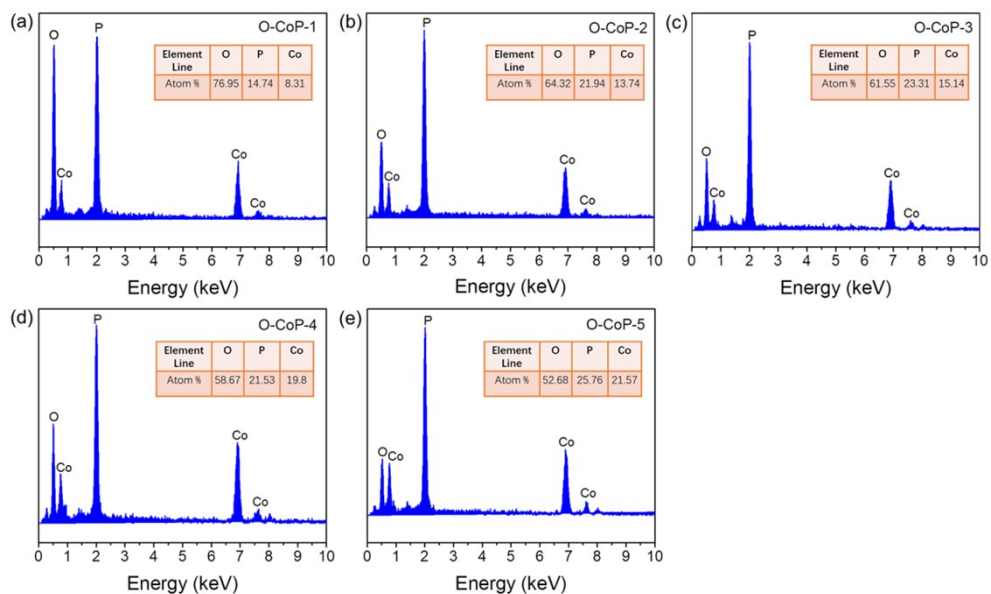


Figure S2. EDX spectra of (a) O-CoP-1, (b) O-CoP-2, (c) O-CoP-3, (d) O-CoP-4 and (e) O-CoP-5 nanorods.

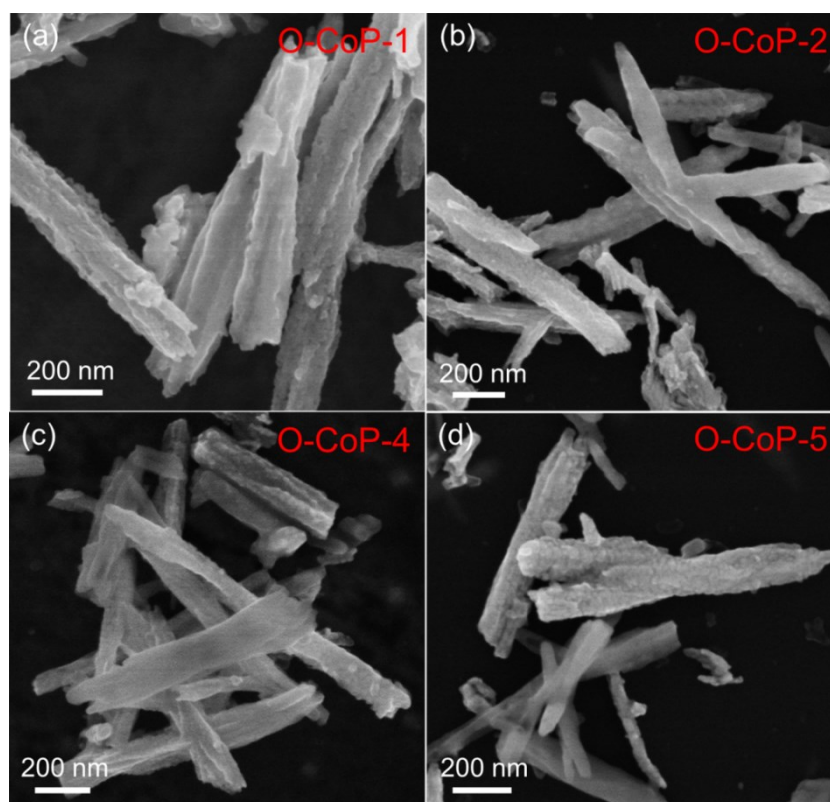


Figure S3. SEM images of (a) O-CoP-1, (b) O-CoP-2, (c) O-CoP-4, and (d) O-CoP-5 nanorods.

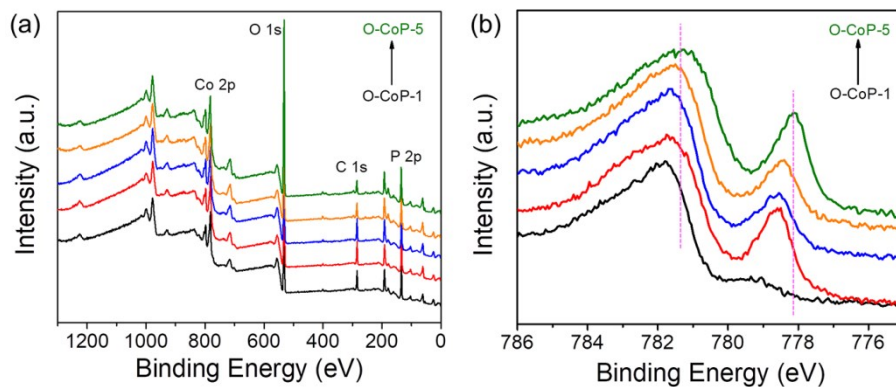


Figure S4. (a) XPS spectrum of all the O-CoP products. (b) High-resolution Co 2p_{3/2} XPS spectrum.

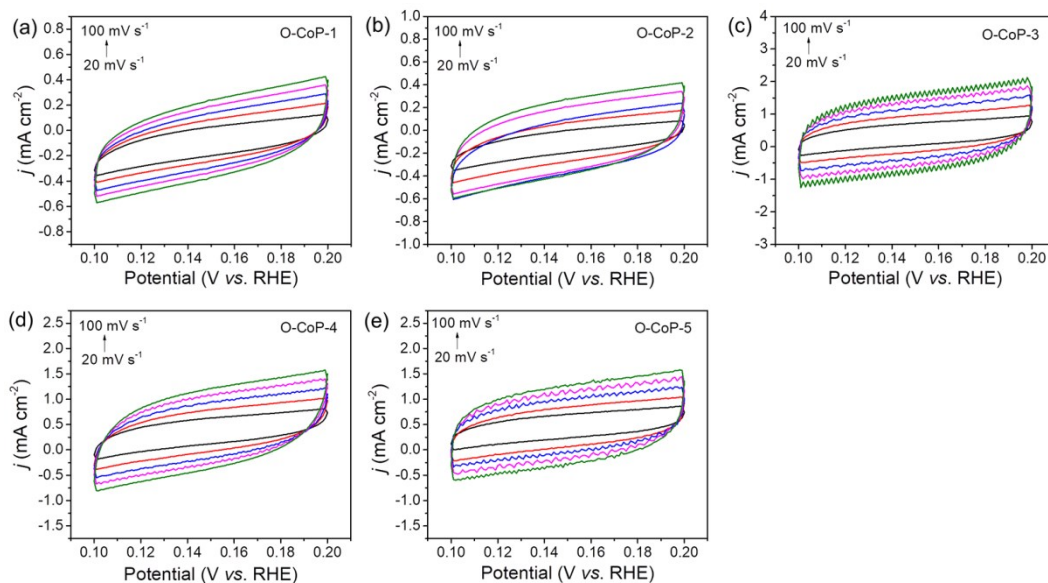


Figure S5. Cyclic voltammetry curves of (a) O-CoP-1, (b) O-CoP-2, (c) O-CoP-3, (d) O-CoP-4, and (e) O-CoP-5 nanorods.

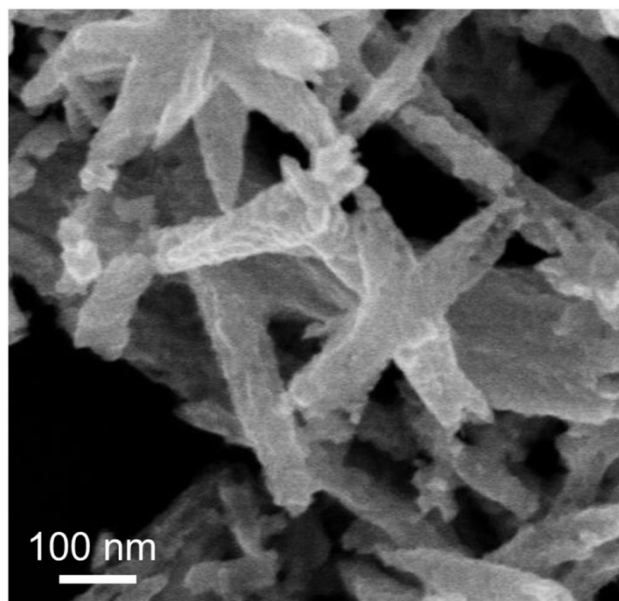


Figure S6. SEM image of the O-CoP-3 nanorods after a continuous 3000 CV test.

Table S1. Contents of O, P, and Co elements obtained from XPS.

Catalysts	O (Atom %)	P (Atom %)	Co (Atom %)
O-CoP-1	69.34	22.24	8.42
O-CoP-2	67.07	23.46	9.47
O-CoP-3	66.54	23.40	10.06
O-CoP-4	64.21	25.54	10.25
O-CoP-5	63.63	26.14	10.23

Table S2. Summary of various non-noble metal catalysts for HER in 1.0 M KOH.

Catalysts	Overpotential at 10 mA cm ⁻² (mV)	Tafel slope (mV dec ⁻¹)	References
O-CoP-3	116	59	This work
CoP@3D-NPC	203	65	<i>Appl. Surf. Sci.</i> , 2019, 476 , 749-756
CoP@NC	129	58	<i>ACS Catal.</i> , 2017, 7 , 3824-3831
CoP/CN@MoS ₂	149	88	<i>ACS Appl. Mater. Interfaces</i> , 2019, 11 , 36649-36657
CoP@NP MG	150	75	<i>Nanoscale</i> , 2018, 10 , 2603-2612
CoP	180	73	<i>ACS Sustainable Chem. Eng.</i> , 2018, 6 , 15162-15169
CoP/NCF	141	84	<i>ACS Sustainable Chem. Eng.</i> , 2019, 7 , 17432-17442
CoP/CC	209	129	<i>J. Am. Chem. Soc.</i> , 2014, 136 , 7587-7590
Cu _{0.3} Co _{2.7} P/NC	220	122	<i>Adv. Energy Mater.</i> , 2017, 7 , 1601555
Co ₂ P@NPG	165	96	<i>Nano Lett.</i> , 2016, 16 , 4691-4698
pure-CoMoP	172	91	<i>Nano Energy</i> , 2020, 68 , 104332-104340
CoP/CN@MoS ₂	149	88	<i>ACS Appl. Mater. Interfaces</i> , 2019, 11 , 36649-36657
CoP/Ti	128	78	<i>Adv. Mater.</i> , 2017, 29 , 1602441
CoP/NiCoP NTs	162	88	<i>Adv. Energy Mater.</i> , 2019, 9 , 1901213
CoP/CP	128	62	<i>Chem. Commun.</i> , 2018, 54 , 1465-1468
CoP/NCP	148	86	<i>J. Am. Chem. Soc.</i> , 2018, 140 , 2610-2618