Electronic Supplementary Information

Experimental Section

Materials: Natural graphite powders with an average diameter of 300 µm were supplied from Qingdao Graphite Company. Sulfuric acid (98%, AR), phosphorus pentoxide (98%, AR), potassium permanganate (AR), hydrogen peroxide (30%, AR), KOH (AR), NaH₂PO₂ (AR) and ethanol (AR) were purchased from Shanghai Jinlu Chemical Co., Ltd. CoCl₂•6H₂O were purchased from Beijing Chemical Corp. Nafion (5 wt%) was purchased from Sigma-Aldrich. Pt/C (10 wt% Pt) was purchased from Alfa Aesar (China) Chemicals Co. Ltd. RuCl₃•3H₂O was purchased from Alladin Ltd (China). Graphite oxide was prepared from natural flake graphite using a modified Hummers method.¹ All the reagents were used as received. The ultrapure water used throughout all experiments was made by the Flom ultrapure water system.

Synthesis of CoP₂/RGO catalyst: To prepare the CoP₂/RGO catalyst, a precursor solution was first prepared by sonicating GO and CoCl₂•6H₂O (weight ratio GO/Co=1:1) in water to form a uniform suspension. The well-mixed precursor suspension was then freeze-dried to minimize re-stacking of the GO sheets. 0.1 g of the resulting product was ground to powder followed by putting into two separate positions in a porcelain boat with 1 g of NaH₂PO₂ at the upstream side of the furnace. Subsequently, the samples were heated at 600 °C for 120 min with a heating peed of 2 °C min⁻¹ in Ar atmosphere, then naturally cooled to ambient temperature. The pure CoP₂ nanoparticles and RGO were prepared by the same procedure without introduction of GO and CoCl₂•6H₂O, respectively for comparison.

Preparation of RuO₂: RuO₂ was prepared following the previous publication.² Briefly, 1 mL KOH (1.0 M) was added to a solution of 0.01 M RuCl₃•3H₂O in 100 mL deionized water and stirred for 45 min at 100 °C. Then the resulting precipitate was washed with deionized water three times and dried in the oven at 60 °C. Finally, the obtained product was calcined in air at 300 °C for 3 h to afford RuO₂ for further use.

Preparation of the working electrode: Glass carbon electrodes (GCE, 3 mm diameter) were first polished with 0.5, 0.1 and 0.03 mm alumina slurries, followed by rinsing with copious amounts of water. Then the electrodes were further cleaned via brief sonication with ethanol and water. To prepare the working electrode, 5 mg of the catalyst and 10 μ L 5 wt% Nafion solution were dispersed in 990 μ L water/ethanol (V:V = 1:1) followed by 40 min sonication to form a catalyst ink. 4 μ L of the catalyst suspension was loaded onto a GCE (mass loading 0.285 mg cm⁻²) and dried at room temperature.

Characterization: X-ray diffraction (XRD) patterns were recorded on a RigakuD/MAX 2550 diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). The X-ray photoelectron spectroscopy (XPS) measurements were collected on an ESCALABMK II X-ray photoelectron spectrometer with an Mg KX-ray source. Scanning electron microscopy (SEM) images were taken on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. X-ray spectrometry (EDS) was recorded with an energy dispersive spectrometer attached to the SEM. Transmission electron microscopy (TEM) measurements were made on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo) with an accelerating voltage of 200 kV. Raman spectra were obtained on a Jobin-Yvon HR800 Raman spectrometer with 633 nm wavelength incident laser.

Electrochemical Measurements: A conventional three-electrode system was used throughout the electrochemical experiment with a CHI-760D electrochemical workstation (CHI Instruments, Shanghai, China) at room temperature. Glass carbon electrode (GCE) was served as the working electrode. A platinum foil and a saturated calomel electrode (SCE) were used as the auxiliary and reference electrodes. In all measurements, the SCE reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). In 1.0 M KOH, E (RHE) = E (SCE) + 1.068 V and in 0.5 M H₂SO₄, E (RHE) = E (SCE) + 0.281 V. Since the as-measured reaction currents cannot directly reflect the intrinsic behavior of electrocatalysts due to the effect of ohmic resistance,³ *iR* compensation was applied for all the electrochemical

measurements by impedance measurements.

Determination of Faradic efficiency: The generated gas was confirmed by gas chromatography (GC) analysis and measured quantitatively using a calibrated pressure sensor to monitor the pressure change in the cathode compartment of an H-type electrolytic cell.⁴ The Faradic efficiency was calculated by comparing the amount of measured hydrogen generated by galvanostatic electrolysis with calculated hydrogen (assuming 100% FE). The rough agreement of both values (Fig. S6 and Fig. S7) suggests nearly 100% FE for HER and OER in 1.0 M KOH. GC analysis was carried out on GC–2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second.

Active sites calculation: According to previous report the number of active sites (n) was determined using cyclic voltammetry (CV) data collected between -0.2 V and +0.6 V vs. RHE in 1.0 M PBS solution (pH 7) with a scan rate of 50 mV s^{-1.4} While it is difficult to assign the observed peaks to a given redox couple, n should be proportional to the integrated charge over the whole potential range. Assuming a one-electron process for both reduction and oxidation, the upper limit of n could be calculated with the following equation:

n = Q/2F

Where Q is the voltammetric charge, F is Faraday constant (96500 C mol⁻¹). For CoP_2/RGO , Q is 1.188×10^{-4} , n (mol) = $1.188 \times 10^{-4}/(2 \times 96500)$ mol = 6.155×10^{-10} mol. **TON calculation:** The turnover number was calculated following equation: TON = moles of amount of gas/moles of catalytic sites



Fig. S1. EDX spectrum for CoP₂/RGO composite.



Fig. S2. EDX spectrum for bulk CoP₂.



Fig. S3. Raman spectra of CoP₂/RGO, RGO and GO.



Fig. S4. (a) Polarization curves recorded for CoP_2/RGO , bulk CoP_2 , Pt/C and RGO before and after 1000 CV with a scan rate of 2 mV s⁻¹. (b) Polarization curves for CoP_2/RGO , bulk CoP_2 and Pt/C with enlarged region from 0 to -10 mA cm⁻². (c) Tafel plots for CoP_2/RGO , bulk CoP_2 and Pt/C. (d) Time-dependent current density curves for CoP_2/RGO and bulk CoP_2 under static overpotentials of 75 mV and 100 mV, respectively. The electrolyte is 0.5 M H₂SO₄.



Fig. S5. CVs of CoP_2/RGO and blank GCE in 1.0 M PBS (pH 7) between -0.2 V and +0.6 V vs. RHE in 1.0 M PBS solution with a scan rate of 50 mV s⁻¹.



Fig. S6. The amount of H_2 theoretically calculated and experimentally measured versus time for HER of CoP₂/RGO composite at a static overpotential of 80 mV and the corresponding TON.



Fig. S7. The amount of O_2 theoretically calculated and experimentally measured versus time for OER of CoP₂/RGO composite at a static overpotential of 290 mV and the corresponding TON.

Catalyst	Loading mass	Electrolyte	Overpotential (mV)	Ref.
_	(mg cm ⁻²)			
Co ₂ P nanorods	0.285	1.0 M KOH	$\eta_{20 \text{ mA cm}}^{-2} = 171$	5
NiP ₂ nanosheet	4.3	1.0 M KOH	$\eta_{10 \text{ mA cm}}^{-2} = 102$	6
Ni–P/CF ^a	5	1.0 M KOH	$\eta_{10 \text{ mA cm}}^{-2} = 98$	7
FeP NAs/CC ^b	1.5	1.0 M KOH	$\eta_{20 \text{ mA cm}}^{-2} = 250$	8
Co _{0.59} Fe _{0.41} P	0.35	1.0 M KOH	$\eta_{10 \text{ mA cm}}^{-2} = 92$	9
Co-P film	~	1.0 M KOH	$\eta_{10 \text{ mA cm}}^{-2} = 94$	10
	$0.285 m_{\pi} cm^{2}$		$\eta_{10 \text{ mA cm}}^{-2} = 88$	this work
Cor ₂ /KGO	0.265 mg cm ²	1.0 IVI KOH	$\eta_{20 \text{ mA cm}}^{-2} = 106$	uns work

Table S1. Comparison of HER performance in alkaline electrolytes for CoP₂/RGO and some reported high-efficient non-noble metal phosphides based HER electrocatalysts.

a: Nickel-phosphorus nanoparticles film on copper foam

b: FeP nanorod arrays on carbon cloth

Catalyst	Loading mass	Electrolyte	Overpotential (mV)	Ref.
	(mg cm ⁻²)			
Co ₂ P nanoparticles	1	0.5 M H ₂ SO ₄	$\eta_{10 \text{ mA cm}}^{-2} = 95$	11
CoP nanoparticles	2	$0.5 \text{ M} \text{H}_2 \text{SO}_4$	$\eta_{10 \text{ mA cm}}^{-2} = 70$	12
Branched CoP	1		$\eta_{20 \text{ mA cm}}^{-2} = 117$	13
nanostructures	1	$0.5 \text{ M H}_2 \text{SO}_4$		
CoP film	~	$0.5 \text{ M H}_2 \text{SO}_4$	$\eta_{10 \text{ mA cm}}^{-2} = 85$	14
CoP nanowire arrays	0.92	0.5 M H ₂ SO ₄	$\eta_{10 \text{ mA cm}}^{-2} = 67$	4
CoP/Carbon nanotubes	0.285	0.5 M H ₂ SO ₄	$\eta_{10 \text{ mA cm}}^{-2} = 122$	15
Nanoporous CoP nanowires	0.8	$0.5 \text{ M H}_2\text{SO}_4$	$\eta_{20 \text{ mA cm}}^{-2} = 95$	16
Urchin like CoP nanocrystals	0.28	0.5 M H ₂ SO ₄	$\eta_{20 \text{ mA cm}}^{-2} = 130$	17
	0.005	0.5 M H ₂ SO ₄	$\eta_{10 \text{ mA cm}}^{-2} = 70$.1. 1
CoP ₂ /RGO	0.285		$\eta_{20 \text{ mA cm}}^{-2} = 88$	uns work

Table S2. Comparison of HER performance for CoP₂/RGO composite and some other Co-P electrodes under the same measurement condition.

Catalyst	Loading mass	Electrolyte	Overpotential (mV)	Ref.
	(mg cm ⁻²)			
СоР	0.05			10
nanoparticles	0.05	0.1 M KOH	$\eta_{10 \text{ mA cm}}^2 = 360$	18
NiOOH/Ni ₅ P ₄	~	1.0 M KOH	$\eta_{10 \text{ mA cm}}^{-2} = 290$	19
CoP nanorod	0.71	1.0 M KOH	$\eta_{10 \text{ mA cm}}^{-2} = 320$	20
Co-P film	~	1.0 M KOH	$\eta_{10 \text{ mA cm}}^{-2} = 345$	10
Ni-P/CF	5	1.0 M KOH	$\eta_{10 \text{ mA cm}}^{-2} = 325$	7
	0.285		$\eta_{10 \text{ mA cm}}^{-2} = 300$	this work
Cor ₂ /KGO	0.285	1.0 WI KOH	$\eta_{20 \text{ mA cm}}^{-2} = 330$	

Table S3. Comparison of OER performance in alkaline electrolytes for CoP₂/RGO and some reported high-efficient non-noble metal phosphides based OER electrocatalysts.

Catalyst	Loading mass	Electrolyte	Voltage@10 mA cm ⁻²	Ref.
	(mg cm ⁻²)		(V)	
NiSe nanowire film	2.8	1.0 M KOH	1.63	21
CoP nanorod	5	1.0 M KOH	1.587	20
CoSe film	3.8	1.0 M KOH	1.65	22
Ni ₅ P ₄ film	~	1.0 M KOH	1.7	19
Co-P film	~	1.0 M KOH	~1.64	10
Ni–P/CF	5	1.0 M KOH	1.68	7
CoP ₂ /RGO	0.285	1.0 M KOH	1.56	this work

Table S4. Comparison of full water splitting performance in alkaline electrolytes for CoP_2/RGO and some reported high-efficient non-noble metal based electrolyzers.

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