Experimental Section

Chemicals:

Red phosphorus (RP, 98.5%) and cobalt(III)-oxide (Co_2O_3, 99.5%) were purchased from Tianjin Damao Chemical Reagent Co. Ltd. and Shanghai Fengshun Chemical Technology Co. Ltd., respectively. Nafion® perfluorinated resin (5wt% solution) was obtained from Sigma Aldrich. The rest of the reagents were provided by Sinopharm Chemical Reagent Co. Ltd. at analytical grade. All chemicals were used without further purification.

Synthesis of BP:

Stainless steel balls (d = 1 cm) and 5 g RP powder were put into a sealable stainless steel ball milling tank (V = 50 mL) with a ball to powder weight ratio of 20:1. The milling process was carried out in an argon atmosphere with a rotation rate of 1200 rpm and two hours at room temperatures 25 °C using the High Energy Ball Mill Emax (Retsch GmbH).

Synthesis of Co_xP:

Stainless steel balls (d = 1 cm) and 5 g of a BP/Co_2O_3 powder mixture were put into a sealable stainless steel ball milling tank (V = 50 mL) with a ball to powder weight ratio of 20:1. The milling process was again carried out in an argon atmosphere with a rotation rate of 1200 rpm and a molar ratio of 1:1, 2:1, 3:1 and 4:1 at room temperatures 25 °C using the High Energy Ball Mill Emax (Retsch GmbH) for two hours.

Material characterization:

The crystallinity and purity of the materials was evaluated qualitatively by thin film powder x-ray diffraction (XRD) using the Shimadzu XRD-6000 X-ray diffractometer with Cu-Kα (λ= 1.5406 Å) irradiation source. The morphology and chemical composition of the materials were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy

(EDX) using the JEOL JSM-6. The Hitachi H-8100 transmission electron microscope (TEM) was employed to obtain and analyze structural information in greater detail. Furthermore, to confirm the chemical composition of the materials and learn about the bonding states of the species involved X-ray Photoelectron Spectroscopy (XPS) was performed using the Thermo ESCALAB 250Xi device with an Al-Kα (hν = 1486.6 eV) excitation source. In addition, Raman spectra were conducted on a Renishaw RM2000 confocal Raman spectrometer with a 532 nm excitation laser.

Electrochemical measurements:

Firstly, 10 mg of as-prepared catalyst powder were dispersed in a mixture of 450 µL isopropanol and 50 µL Nafion$^{\circ;R}$ resin solution by sonication for 1 hour. Subsequently, 5 µL of this catalyst ink were deposited on a polished glassy carbon rotating disk electrode (GC-RDE, d = 3 mm, PINE Research Instrumentation) and dried at room temperature for 1 h to obtain the working electrode.

The electrochemical measurements were performed on a CHI760E electrochemical workstation (Shanghai Chenhua, China) with a three-electrode setup at a rotation speed of 1600 rpm in N_2-saturated 1.0 M KOH electrolyte (pH = 14). A graphite rod and an Ag/AgCl electrode were employed as counter and reference electrode, respectively. Linear sweep voltammograms (LSV) were recorded for HER and OER after 10 scans at a scan rate of 5mVs^{-1} with 90% iR compensation. The measured potentials vs. Ag/AgCl electrode $V_{Ag/AgCl}$ were corrected to obtain the potentials vs. standard hydrogen electrode V_{SHE} using the linear relation $V_{RHE} = V_{Ag/AgCl} + 0.059pH + 0.197$. Tafel slopes were calculated by linear regression using the equation $\eta = b \cdot lg(j) + a$, where η [V] is the overpotential, j [mA cm^{-2}] is the corresponding current density and a,b are the y-intercept and Tafel-slope [mV dec^{-1}], respectively. The compensated resistances of all samples were measured by electrochemical impedance spectroscopy (EIS) with a test frequency

scope from 0.01 Hz to 100 kHz at the corresponding open circuit voltages. The electrode durability was tested by cyclic voltammetry (CV) and chronopotentiometry measurements.

1. J. Wu, D. Wang, S. Wan, H. Liu, C. Wang, X. Wang, *Small,* **2019**, e1900550.
2. L. Yao, N. Zhang, Y. Wang, Y. Ni, D. Yan, C. Hu, *Journal of Power Sources,* **2018**, *374*, 142.
3. L. Su, X. Cui, T. He, L. Zeng, H. Tian, Y. Song, K. Qi, B. Y. Xia, *Chemical science,* **2019**, *10*, 2019.
4. X. Yu, S. Zhang, C. Li, C. Zhu, Y. Chen, P. Gao, L. Qi, X. Zhang, *Nanoscale,* **2016**, *8*, 10902.
5. C. Tang, R. Zhang, W. Lu, L. He, X. Jiang, A. M. Asiri, X. Sun, *Advanced materials (Deerfield Beach, Fla.),* **2017**, *29*.
6. B. You, N. Jiang, M. Sheng, S. Gul, J. Yano, Y. Sun, *Chem. Mater.* **2015**, *27*, 7636.
7. T. Wu. M. Pi, D. Zhang, S. Chen. *J. Mater. Chem. A,* **2016**, *4*, 14539.
8. L. Zhang, C. Chang, C.-W. Hsu, C.-W. Chang, S.-Y. Lu, *J. Mater. Chem. A,* **2017**, *5*, 19656.
9. S. H. Yu, D. H. C. Chua, *ACS applied materials & interfaces,* **2018**, *10*, 14777.
10. C. Zhang, Z. Pu, I. S. Amiinu, Y. Zhao, J. Zhu, Y. Tang, S. Mu, *Nanoscale,* **2018**, *10*, 2902.
11. N. Jiang, B. You, M. Sheng, Y. Sun, *Angewandte Chemie (International ed. in English),* **2015**, *54*, 6251.
12. Y. Hou, M. Qiu, G. Nam, M. G. Kim, T. Zhang, K. Liu, X. Zhuang, J. Cho, C. Yuan, X. Feng, *Nano letters,* **2017**, *17*, 4202.
13. Y. Ge, H. Chu, J. Chen, P. Zhuang, Q. Feng, W. R. Smith, P. Dong, M. Ye, J. Shen, *ACS Sustainable Chem. Eng.* **2019**.
14. L. Jiao, Y.-X. Zhou, H.-L. Jiang, *Chemical science,* **2016**, *7*, 1690.
15. P. Wang, F. Song, R. Amal, Y. H. Ng, X. Hu, *ChemSusChem,* **2016**, *9*, 472.
16. Y. Bai, H. Zhang, Y. Feng, L. Fang, Y. Wang, *J. Mater. Chem. A,* **2016**, *4*, 9072.
17. Y.-P. Zhu, Y.-P. Liu, T.-Z. Ren, Z.-Y. Yuan, *Adv. Funct. Mater.* **2015**, *25*, 7337.
18. H. Li, Q. Li, P. Wen, T. B. Williams, S. Adhikari, C. Dun, C. Lu, D. Itanze, L. Jiang, D. L. Carroll et al., *Advanced materials (Deerfield Beach, Fla.),* **2018**, *30*.
19. M. Jiang, J. Li, J. Li, Y. Zhao, L. Pan, Q. Cao, D. Wang, Y. Du, *Nanoscale,* **2019**, *11*, 9654.

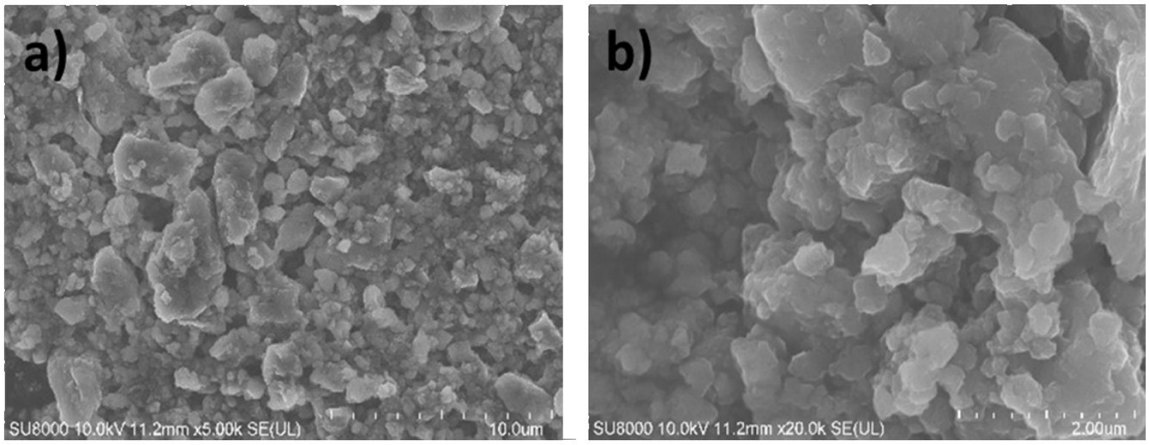

Figure S1 SEM images of black phosphorous at different scales

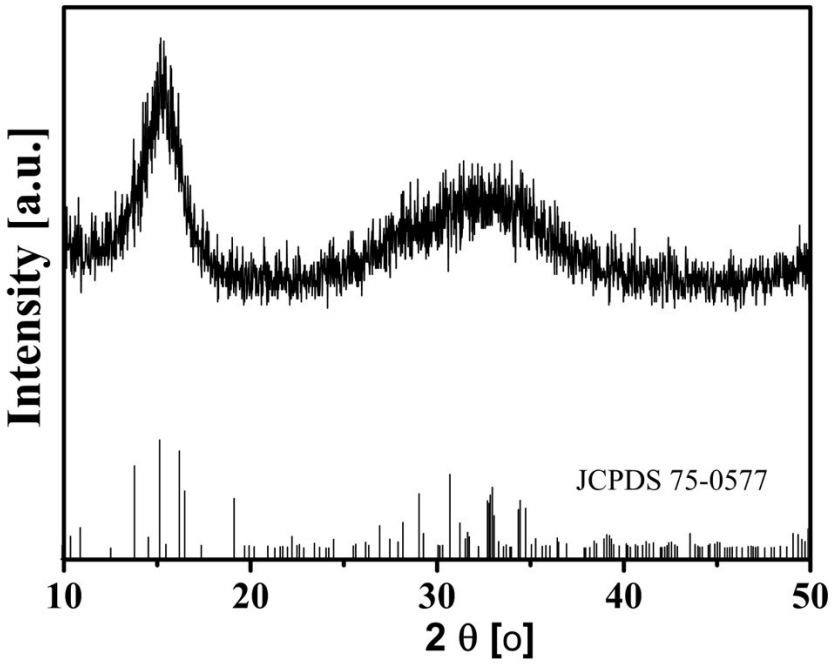

Figure S2 XRD pattern of red phosphorous

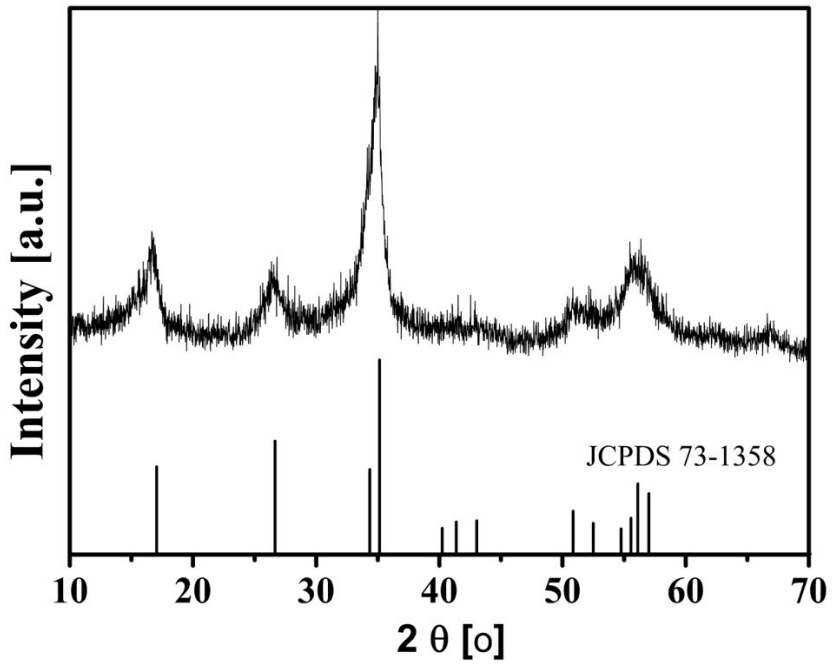

Figure S3 XRD Pattern for as synthesized black phosphorous

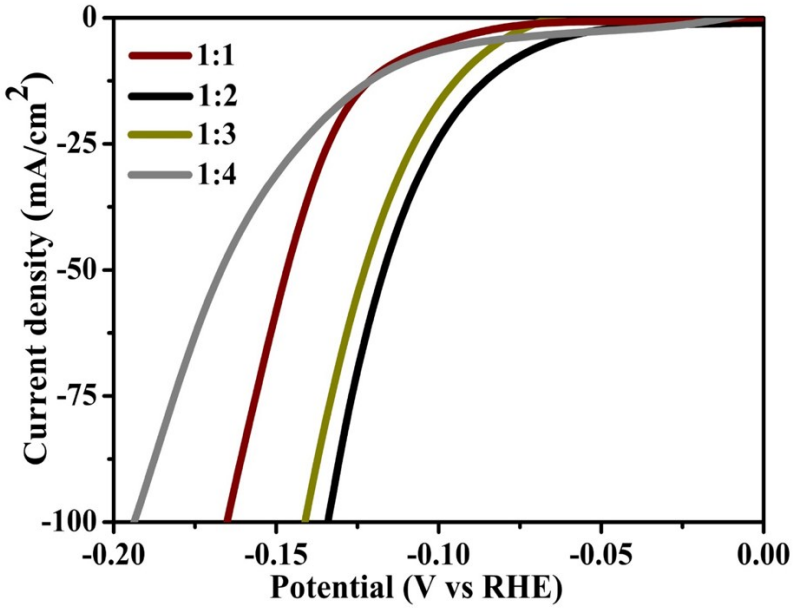

Figure S4 LSV measurements of Co_xP with different BP/Co_2O_3 molar ratios for HER

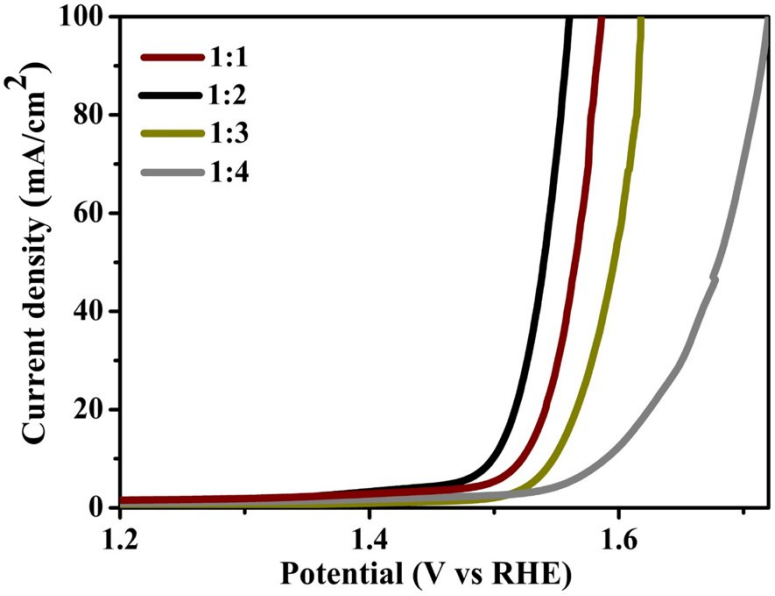

Figure S5 LSV measurements of Co_xP with different BP/Co_2O_3 molar ratios for OER

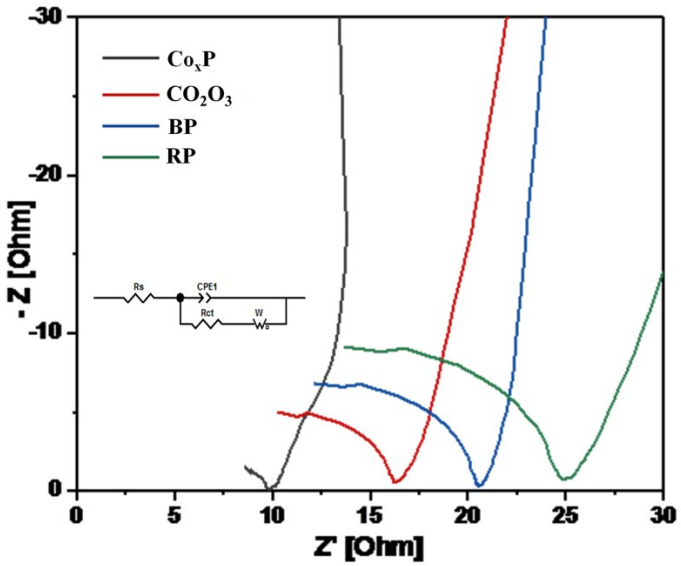

Figure S6 Electrochemical impedance spectroscopy of Co_xP, Co_2O_3, BP and RP

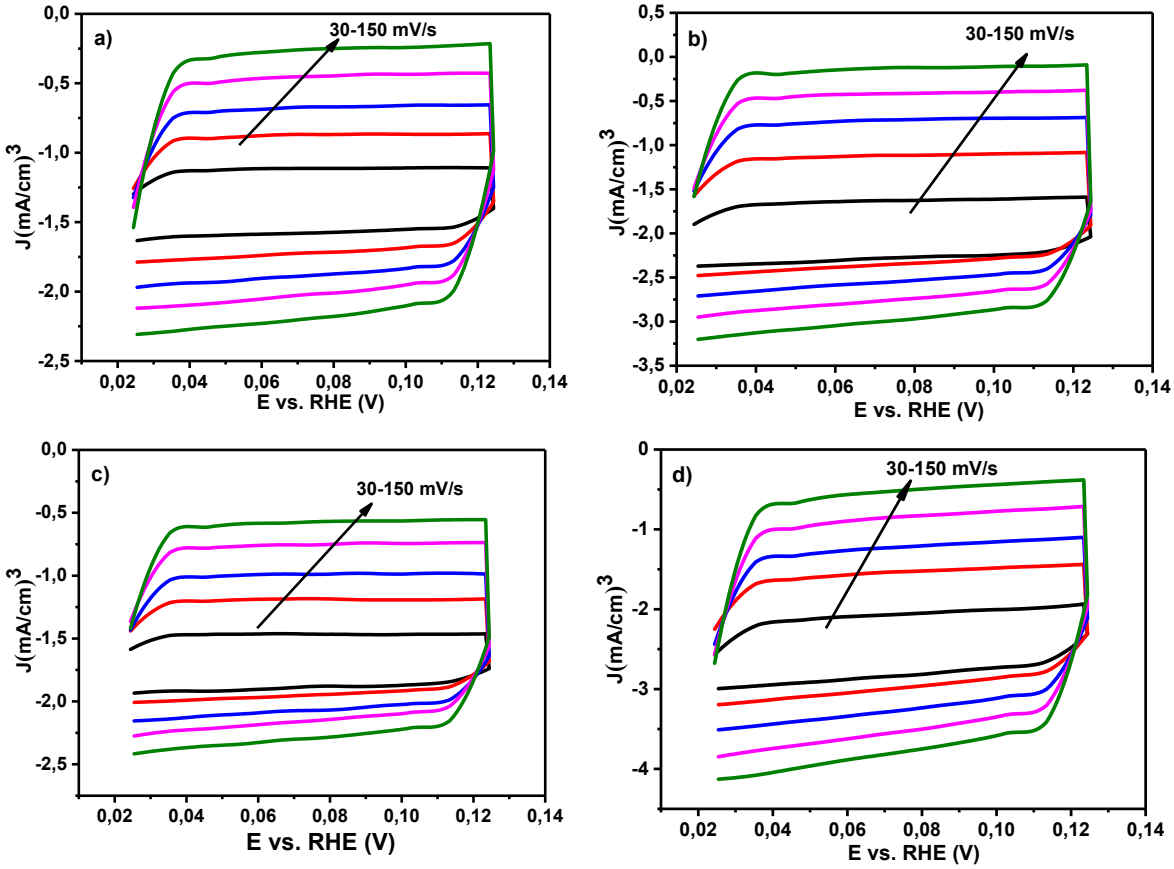

Figure S7 Cyclometametric measurements of a) red phosphorous, b) black phosphorous, c) Co_2O_3 and d) Co_xP

Table S1: Catalytic HER activity in alkaline solution (1M KOH) of different cobaltphosphide based catalysts

Catalyst	**Overpotential** $\eta[mV]$ **(@ j = 10 mA cm^{-2})**	**Tafel slope** $[mV\ dec^{-1}]$	**Stability**	**Reference**
Co_xP	**69**	**50.6**	**24 h**	**This research**
CoP@C	76	52	20 h	Small **2019**,e1900550[1]
2D Co_2P@Co_3O_4	159	78	8 h	*Journal of Power Sources* **2018**, *374*, 142[2]
CoP-A	100	76	10 h	*Chemical science* **2019**, *10*, 2019[3]
CoP NPs@graphene	83	54	1000 cycles	*Nanoscale* **2016**, *8*, 10902[4]
CoP/Ti	128	78	20 h	*Advanced materials* **2017**, *29*[5]
Co-P/NC	191	51	24 h	*Chem. Mater.* **2015**, *27*, 7636[6]
Co/NC	250	152		
CoP_3 nanoneedle arrays/carbon fiber paper (CFP)	119	91	3000 cycles	*J. Mater. Chem. A* **2016**, *4*, 14539[7]
CoP Nanosheet/carbon	111	85.9	24 h	*J. Mater. Chem. A* **2017**, *5*, 19656[8]
CoP/CFP-E	128	49.7	2000 cycles	*ACS applied materials & interfaces* **2018**, *10*, 14777[9]
Co_2P@NPC-800	129	93	20 h	*Nanoscale* **2018**, *10*, 2902[10]
Co-P film	343	47	24 h	*Angewandte Chemie* **2015**, *54*, 6251[11]
Co_xP/Cu-Co_9S_8	118	66.75	24 h	*Nano letters* **2017**, *17*, 4202[12]
MCPS	77	58	10 h	*ACS Sustainable Chem. Eng.* **2019**[13]

Table S2: Catalytic OER activity in alkaline solution (1 m KOH) on different cobaldphosphide based catalysts

Catalyst	**Overpotential** $\eta[mV]$ **(@ j = 10 mA cm^{-2})**	**Tafel slope** $[mV\ dec^{-1}]$	**Stability**	**Reference**
Co_xP	**266**	**62.1**	**24 h**	**This study**
CoP@C	283	53	20 h	Small **2019**,e1900550[1]
2D Co_2P@Co_3O_4	335	60	8 h	*Journal of Power Sources* **2018**, *374*, 142[2]
CoP nanosheet/carbon	277	85.6	24 h	*J. Mater. Chem. A* **2017**, *5*, 19656[8]
CoP/rGO	340	66	22 h	*Chemical science* **2016**, *7*, 1690[14]
CoP nanoneedles/carbon cloth	281	62	17 h	*ChemSusChem* **2016**, *9*, 472[15]
CoP/C	330	53	25 h	*J. Mater. Chem. A* **2016**, *4*, 9072[16]
CoP mesoporous nanorod arrays	310	65	32 h	*Adv. Funct. Mater.* **2015**, *25*, 7337[17]
Co_2P NCs	280	60.4	30 h	*Advanced materials* **2018**, *30*[18]
Co-P film	340	47	24 h	*Angewandte Chemie* **2015**, *54*, 6251[11]
$Co_{0.8}Fe_{0.2}P$	270	50	1000 cycles	*Nanoscale* **2019**, *11*, 9654[19]

Table S3: Catalytic HER and OER activity of measured materials in this study

	HER		**OER**	
	η_{10} $[mV]$	**b** $[mV\ dec^{-1}]$	η_{10} $[mV]$	**b** $[mV\ dec^{-1}]$
Co_xP	69	50.6	266	62.1
Pt/C	45	72.4	-	-
RuO_2	-	-	287	124.8
Co_2O_3	338	70.2	481	104.7
BP	322	220.9	298	154.4
RP	467	159.2	690	363.7