Structural dependence of electrosynthesized cobalt phosphide/black phosphorus pre-catalyst for oxygen evolution in alkaline media

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Experimental

Specific activity is a valid descriptor for the density of active sites on the surface of a catalyst, which is calculated by normalizing the original current to the ECSA. ECSA= C_{dl}/C_s C_s is the specific capacitance (0.040 mF/cm^2).

The TOF (s^{-1}) of the best catalyst (CoP/BP-30) is calculated using the following equation:

TOF= j* A/(4F* n)

where j is the measured current density at an overpotential of 300 mV, A is the surface area of the CoP/BP-30 electrode, F is the Faraday constant (96485 C mol^{-1}), and n is the moles of the CoP/BP-30 active materials on the electrode.

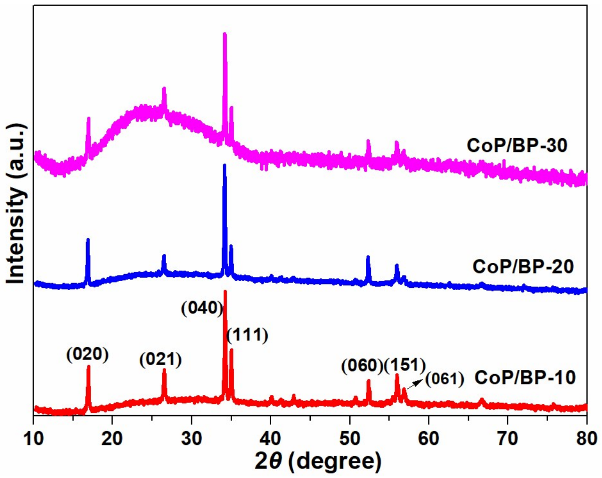

Fig. S1 Normalized XRD spectra based on the (040) peak of BP for CoP/BP-30, CoP/BP-20 and CoP/BP-10.

Table S1 The content of Co with different oxidation states calculated based on the ICP-OES results and XPS results.

Voltage (V)	CoP (XPS)	CoO (XPS)	Co_2O_3(XPS)	**Co (ICP-OES)**	CoP (Cal.)	CoO(Cal.)	Co_2O_3 (Cal.)	CoP + CoO
10	7.61	39.41	52.98	**15.96**	1.21	6.29	8.46	7.50
20	12.04	41.61	46.34	**18.76**	2.25	7.81	8.69	10.06
30	6.96	43.23	49.81	**22.83**	1.59	9.86	11.35	11.45

The electrochemically active surface area (ECSA) of the used catalysts is determined with aid of their electrochemical double-layer capacitances (C_{dl}). For all catalysts, the differences in current density variation ($\Delta J = J_a - J_c$) at an overpotential of 1.27 V plotted against the scan rate fitted to a linear regression enables the estimation of C_{dl}. After extracting the C_{dl} from the fitted linear regressions, we cancalculated the electrochemically active surface area (ECSA) from the equation of ECSA $= C_{dl}/C_s$, where C_s are assumed to be same for all electrodes. Thus, the variation trend of ECSA is in line with that of C_{dl}.

As for Faradaic active sites (FASs), they can be calculated by the following equations[S1].

$$S = \int_{E1}^{E2} i(E)dE \qquad \text{(Eq. S1)}$$

$$q* = \frac{1}{vms}\int_{E1}^{E2} i(E)dE \qquad \text{(Eq. S2)}$$

Table S2 Electrochemical parameters of three CoP/BP heterostructures**

Voltage (V)	*S*	*V* (vs^{-1})	*m* (mg)	*s* (mg cm^{-2})	*q** (mC cm^{-2} mg^{-1})
10	0.263	0.1	0.025	0.07065	1489.0
20	0.296	0.1	0.025	0.07065	1675.9
30	0.428	0.1	0.025	0.07065	2423.2

** *q**, v, *m* and *s* is the voltammetry charge density, scan rate, mass of catalyst loaded on the exposed surface and surface area of glassy carbon electrode, respectively. Their units are mC cm^{-2} mg^{-1}, V s^{-1}, mg and cm^2, respectively. According to the following equations[S1, S2], S and q^* in the potential range of E_1 to E_2 were respectively calculated.

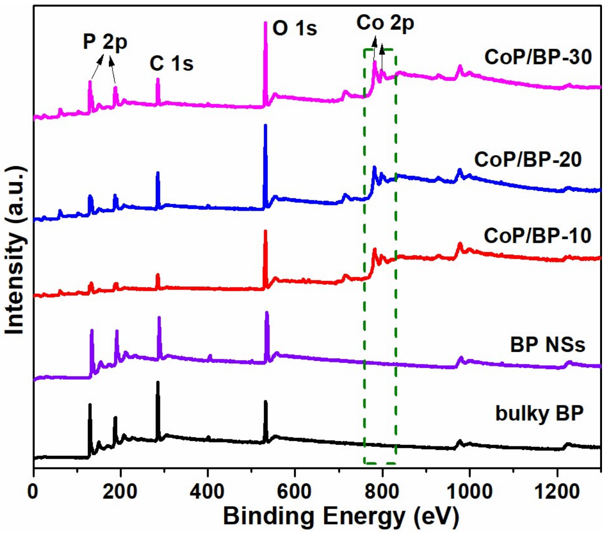

Fig. S2. XPS survey spectra of a bulky BP, BP NSs electrosynthesized at 30 V, the CoP/BP-30 heterojunction, the CoP/BP-20 heterojunction and the CoP/BP-10 heterojunction.

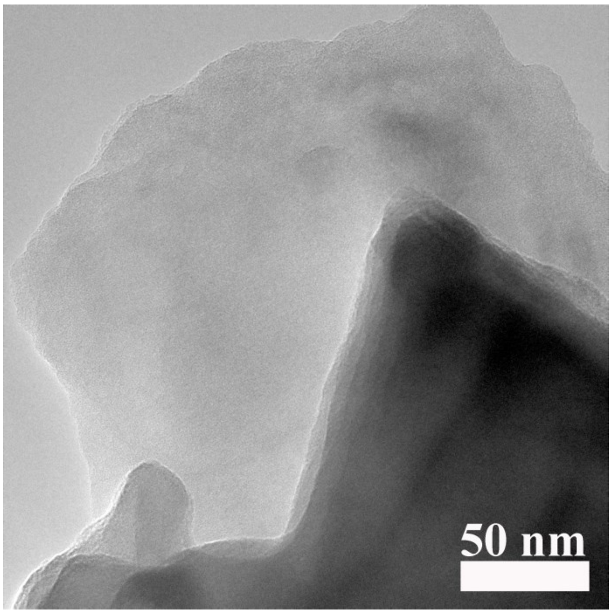

Fig. S3 TEM image of the CoP/BP-30 heterojunction

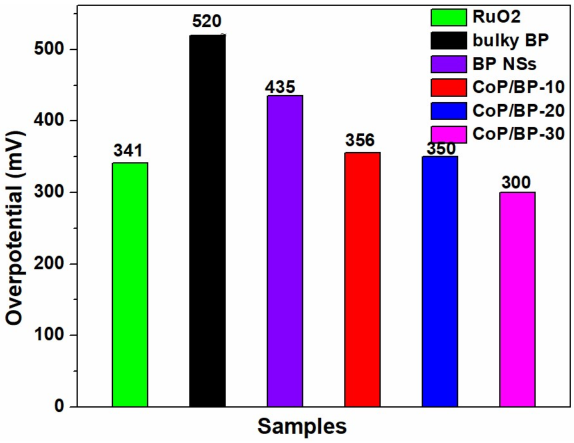

Fig. S4 The overpotential at a current density of 10 mA cm^{-2} in 1 M KOH solutionon over a RuO$_2$ catalyst, a bulky BP, BP NSs electrosynthesized at 30 V, the CoP/BP-30 heterojunction, the CoP/BP-20 heterojunction and the CoP/BP-10 heterojunction.

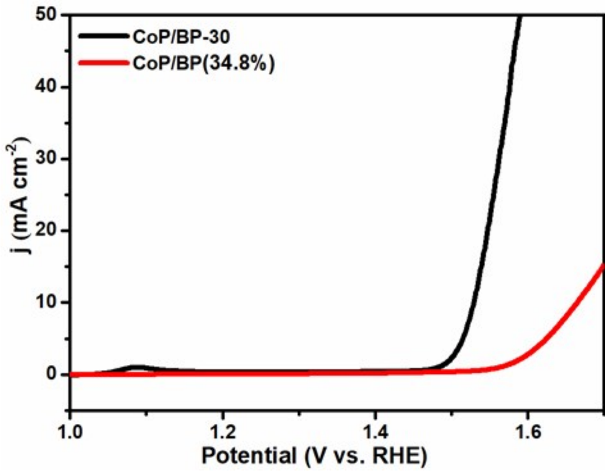

Fig. S5 The compared OER performance between CoP/BP-30 heterostructure and CoP/BP mixture samples (CoP/BP (34.8%)).

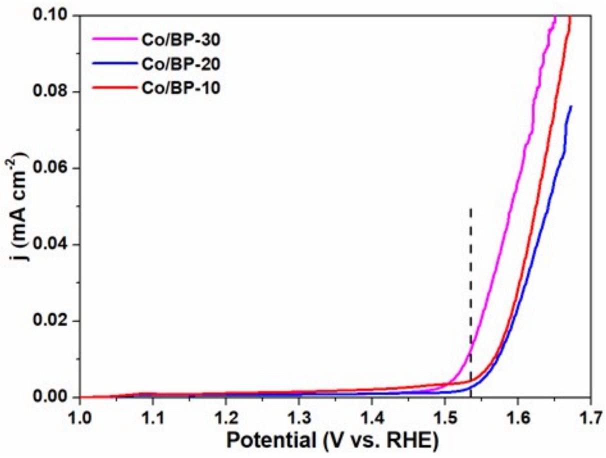

Fig. S6 The OER polarization curves obtained by normalizing the raw current to the electrochemical surface area for the CoP/BP-30 heterojunction, the CoP/BP-20 heterojunction and the CoP/BP-10 heterojunction in 1 M KOH solution.

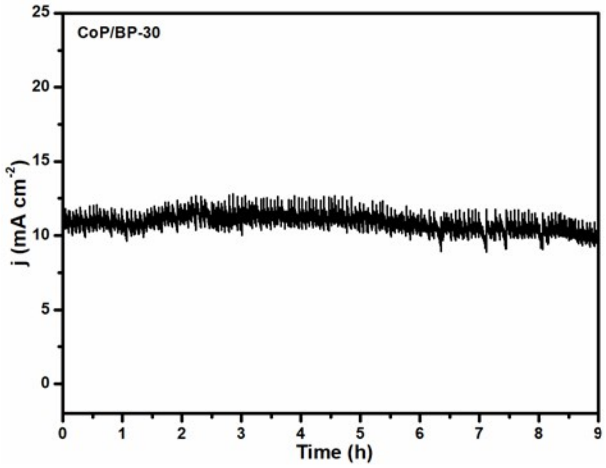

Fig. S7 The chronopotentiometric measurement of CoP/BP-30 precatalyst.

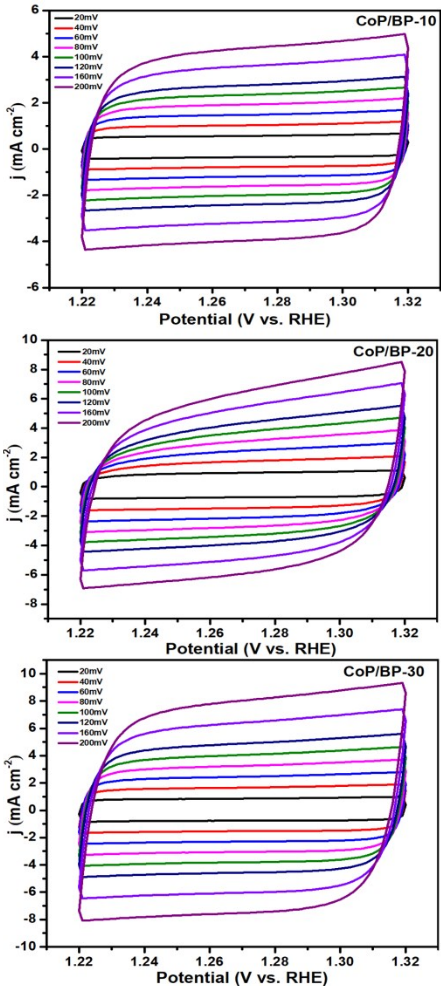

Fig. S8 CVs of the CoP/BP-10, CoP/BP-20 and CoP/BP-30 heterojunctions at different scan rates in 1 M KOH.

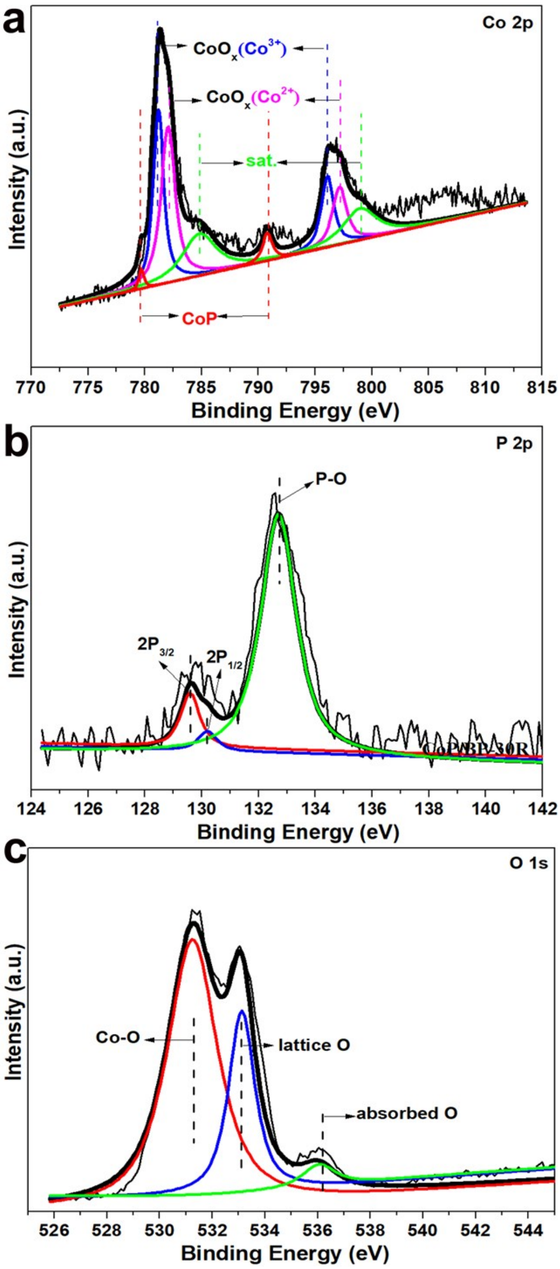

Fig. S9. (a) Co 2p, (b) P 2p and (c) O 1s XPS spectra of the CoP/BP-30R heterojunction after in-situ activation.

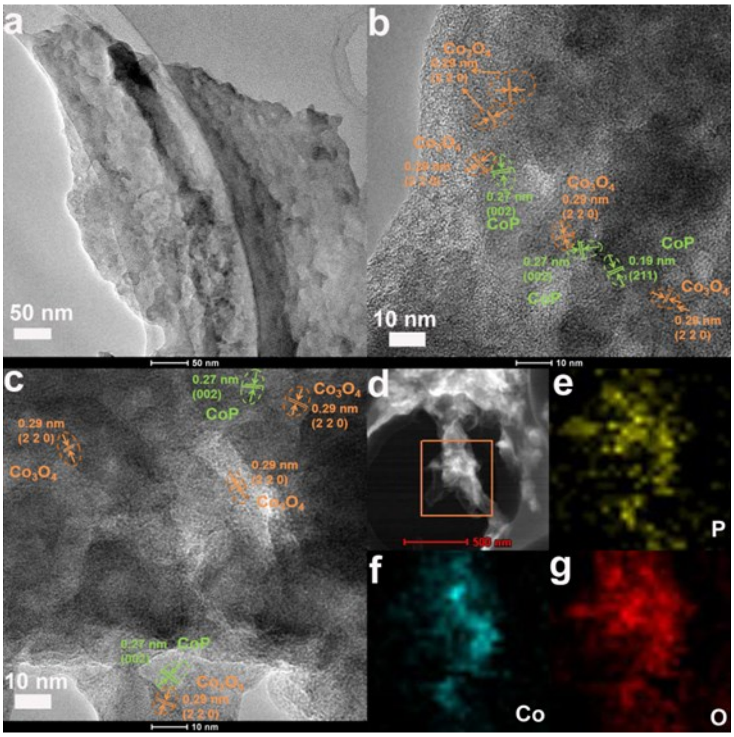

Fig. S10 TEM (a) and HRTEM (b,c), STEM (d) images of the CoP/BP-30 heterojunction after the stability test; EDS mappings of the scanned area (d), the elements of P (e), Co (f) and O (g) in the CoP/BP-30 heterojunction stability test.

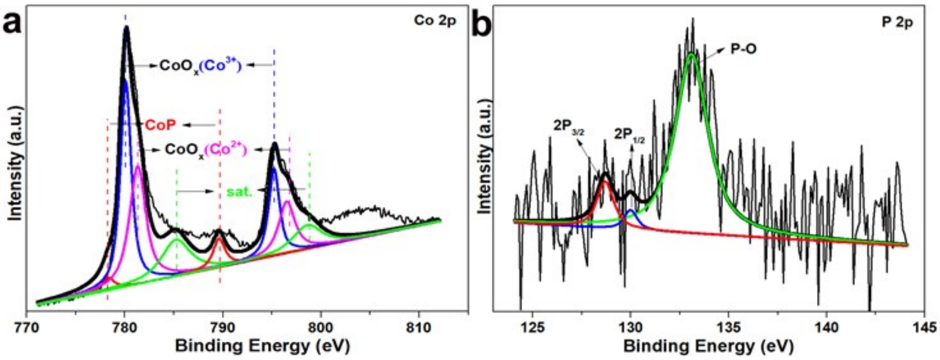

Fig. S11 (a) Co 2p XPS and (b) P 2p XPS spectra of CoP/BP-30 heterojunction after stability test.

Supporting references

[S1] G. Zhang, J. Yang, H. Wang, H. Chen, J. Yang, F. Pan, *ACS Appl. Mater. Interfaces***2017**, *9*, 16159.