

Table S1. Compositions of sandwich-like CoP/C, CoO/C and macroporous CoP materials, determined by ICP-AES.

Composites	Targeted element ratio	Experimental (ICP-AES) element ratio
Sandwich-like CoP/C	Co:P=1.00:1.00	Co:P=1.008:0.992
Sandwich-like CoO/C	Co:O=1.00:1.00	Co:O=1.003:0.997
Macroporous CoP	Co:P=1.00:1.00	Co:P=0.991:1.009

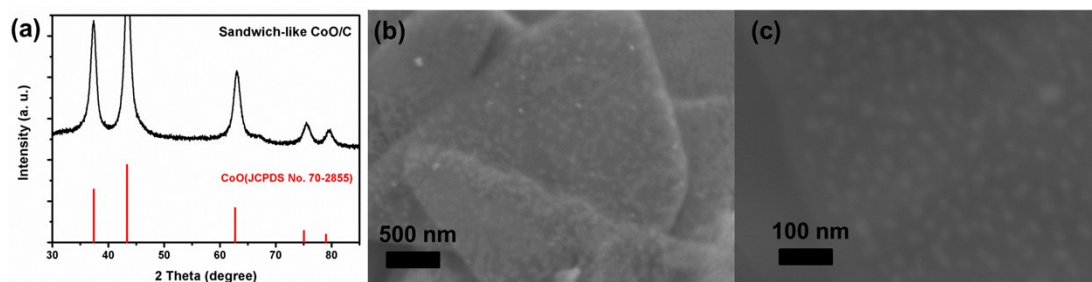


Figure S1. Sandwich-like CoO/C nanocomposites: (a) X-ray diffraction patterns; (b) and (c) SEM images.

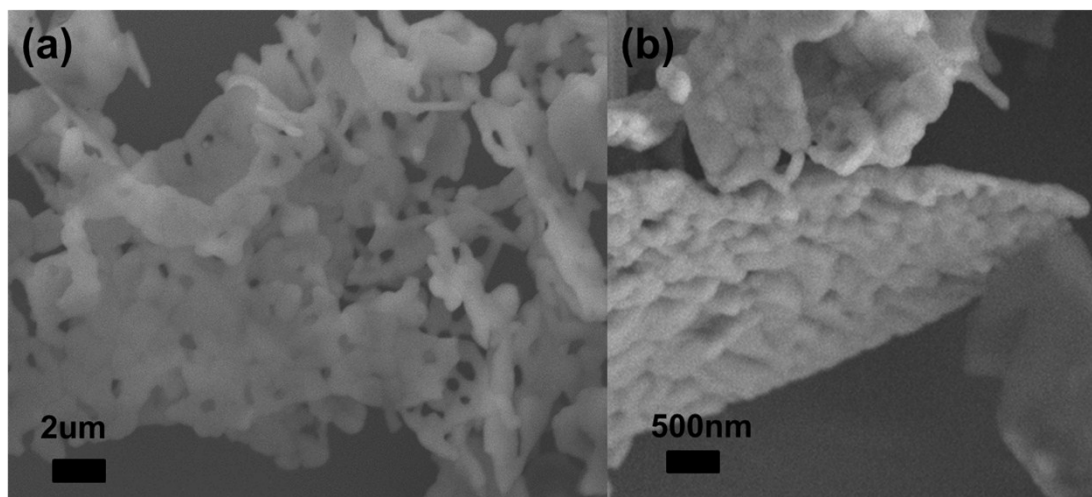


Figure S2. SEM images of macroporous CoP materials.

Table S2. Comparison of the OER activity for several recently reported highly active Co-based electrocatalysts in alkaline media.

Catalysts	Electrolyte	Mass loading (mg/cm ²)	E _{J=10} (V vs. RHE)	Tafel slop (mV dec ⁻¹)	Reference
Sandwich-like CoP/C	1.0 M KOH	0.36	1.56	53	This work
Commercial IrO ₂ /C	1.0 M KOH	0.36	1.63	69	This work
CoP NR/C	1.0 M KOH	0.71	1.58	71	ACS Catal. 2015 , 5, 6874
CoP/C	0.1 M KOH	0.4	1.59	66	ACS Catal. 2015 , 5, 4066
Co-P film	1.0 M KOH	1.0	1.56	47	Angew. Chem. Int. Ed. 2015 , 54, 6251
CoP	0.1M NaOH	0.285	1.63	80	ACA Appl. Mater. Interfaces. 2015 , 7, 28412
Co ₃ O ₄ /N-rmGO	1.0 M KOH	1.0	1.54	67	Nature Materials. 2011 , 10, 780
CoO _x @CN	1.0 M KOH	1.0	1.5	N. A	J. Am. Chem. Soc. 2015 , 137, 2688
Co _x O _y /NC	0.1 M KOH	0.21	1.69	N. A	Angew. Chem. Int. Ed. 2014 , 53, 8508
Co ₃ O ₄			1.68		
NCG-CoO	1.0 M KOH	NA	1.57	71	Energy Environ. Sci. 2014 , 7, 609
Co ₃ O ₄ C-NA	0.1 M KOH	0.2	1.52	70	J. Am. Chem. Soc. 2014 , 136, 13925
Co ₃ O ₄ -NA			1.63	123	
NiCo LDH	1.0 M KOH	0.17	1.6	40	Nano Lett. 2015 , 15, 1421.
CoCo LDH	1.0 M KOH	0.07	1.61	59	Nat. Commun. 2014 , 5, 4477
CoSe ₂	0.1 M KOH	0.2	1.71	66	ACS Nano, 2014 , 4, 3970
Zn _x Co _{3-x} O ₄ nanowire array (Ti foil substrate)	1.0 M KOH	~1.0	1.56	51	Chem. Mater. 2014 , 26, 1889
Ni _x Co _{3-x} O ₄ nanowire array (Ti foil substrate)	1.0 M KOH	2.3~2.7	~1.6	59~64	Adv. Mater. 2010 , 22, 1926

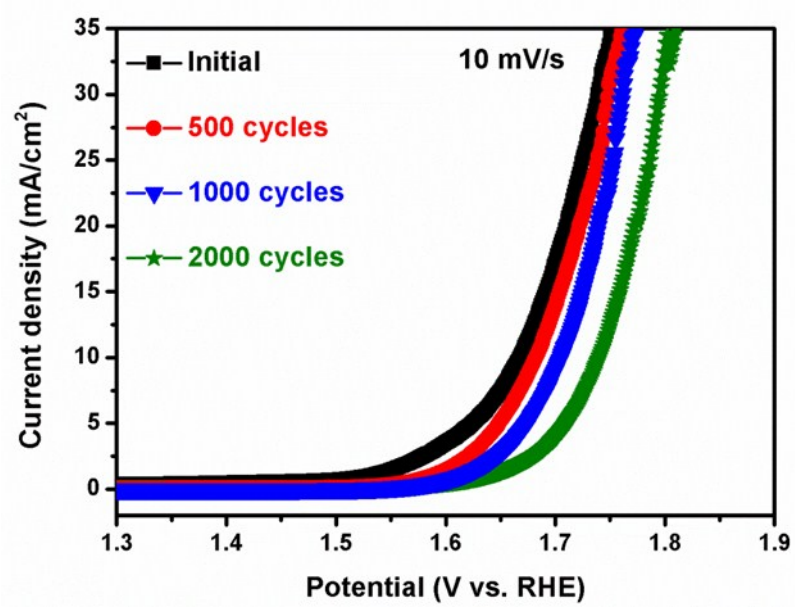


Figure S3. Polarization curves for sandwich-like CoO/C in KOH solution (1.0 M) at a scan rate of 10 mV/s.

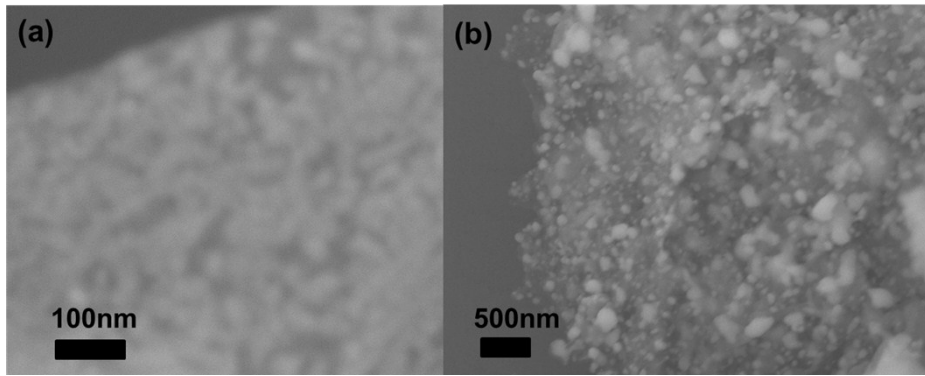


Figure S4. SEM images of CoP/C (a) and CoO/C (b) after 2000 cycling tests.

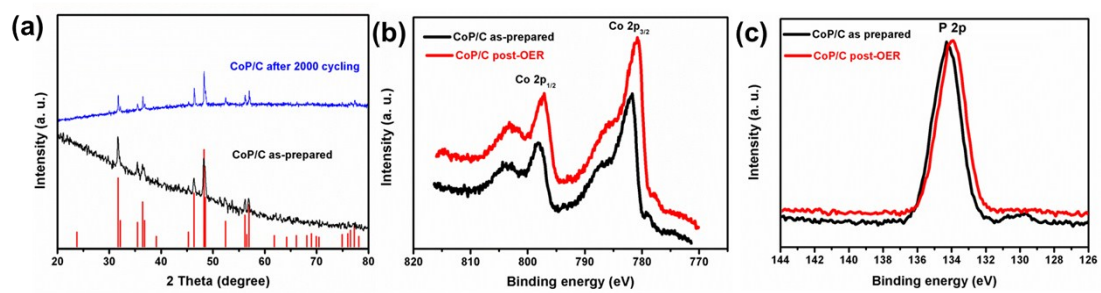


Figure S5. a) XRD data and b-c) XPS spectrum of sandwich-like CoP/C after 2000 cycling tests.

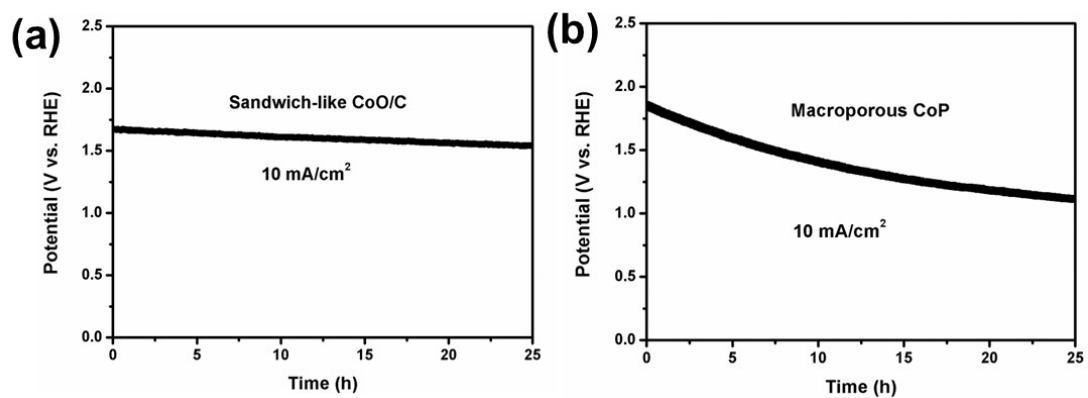


Figure S6. Chronoamperometric technology at a constant current density of 10 mA/cm² of (a) sandwich-like CoO/C and (b) macroporous CoP

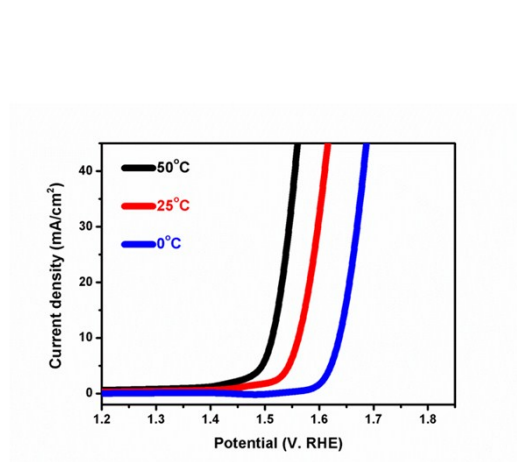


Figure S7. Polarization curves of sandwich-like CoP/C at different temperature.