Electronic Supplementary Information

Metal-Organic Framework-Based CoP/Reduced Graphene Oxide: High-Performance Bifunctional Electrocatalyst for Overall Water Splitting

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Experimental Section

Preparation of graphene oxide (GO): The GO was prepared using a modified Hummers and Offeman's method.[1] Briefly, graphite powder (5 g), $NaNO_3$ (5 g), and concentrated sulfuric acid (169 mL) were stirred in an ice bath for 15-20 min. Next, $KMnO_4$ (22.5 g) was slowly added. The solution was heated to 20±5 °C in a water bath and stirred for about 2 h and a thick green viscous solid was formed during this step. After the removal of the ice bath, the mixture was stirred at room temperature for 5 days. Then, H_2SO_4 solution (0.5%, 500 mL) was added very slowly followed by stirring for 1 h while the temperature was controlled below 98 °C. Finally, the solution of H_2O_2 (30%) was added and the solution color turned from dark brown to pale golden yellow. The mixture was left overnight. The GO particles, settled at the bottom, were separated from the excess liquid by decantation followed by centrifugation. The solution was then washed with 500 mL water for several times to adjust its pH at 7. Then the wet form of GO was centrifuged and freeze-dried. A fine brown powder of the initial GO was obtained.

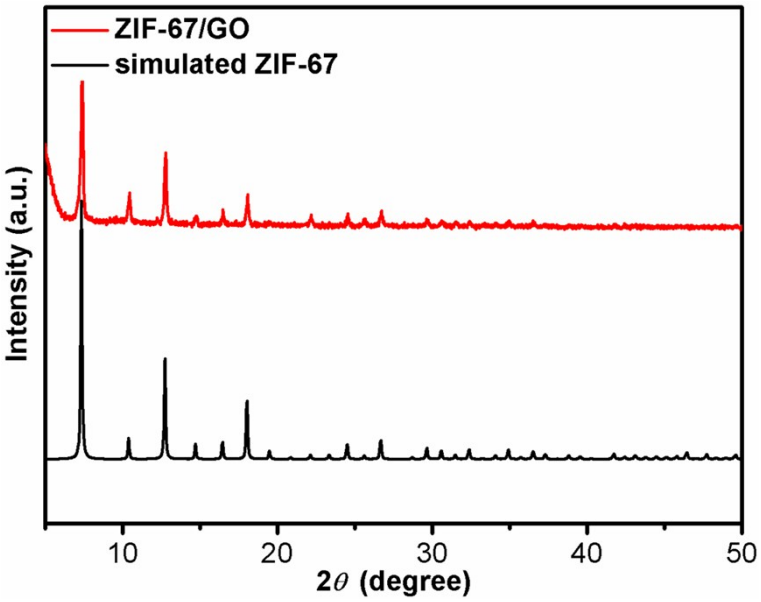

Fig. S1 Powder XRD patterns of ZIF-67/GO and simulated ZIF-67.

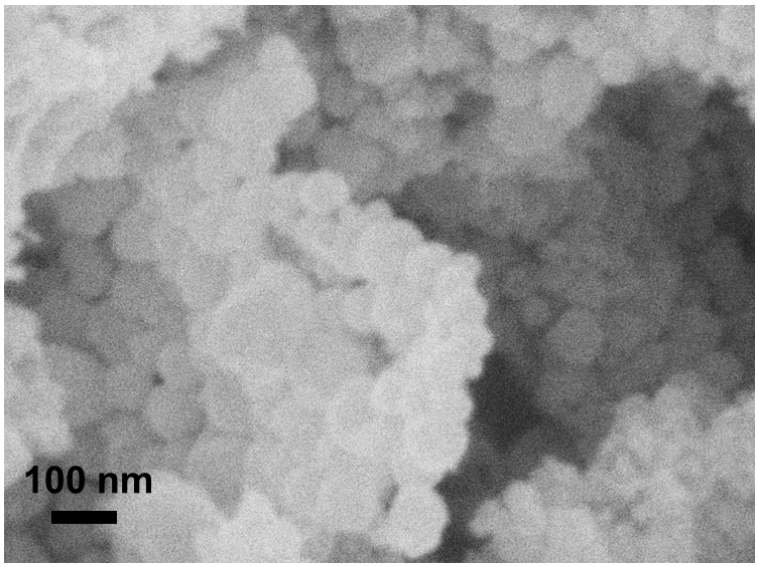

Fig. S2 SEM image of Co_3O_4/rGO-400, showing the layered structure.

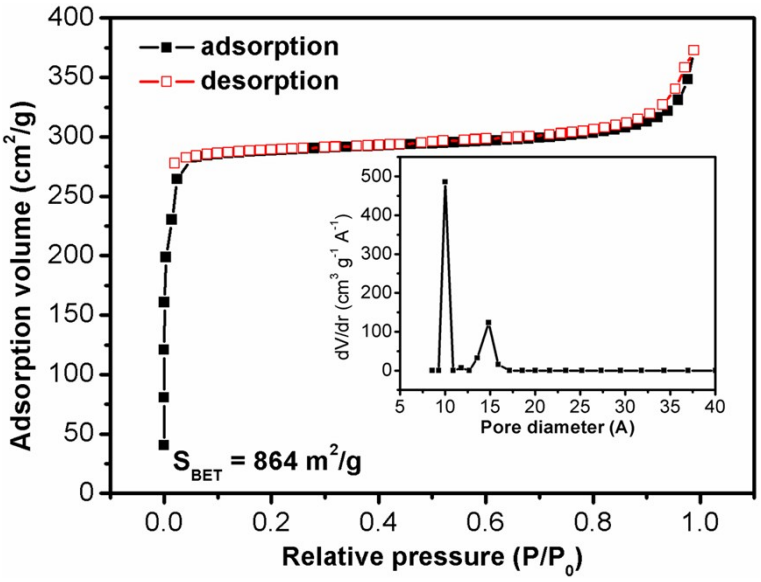

Fig. S3 N_2 adsorption/desorption isotherms of ZIF-67/GO (inset: pore size distribution analysis based on the DFT model).

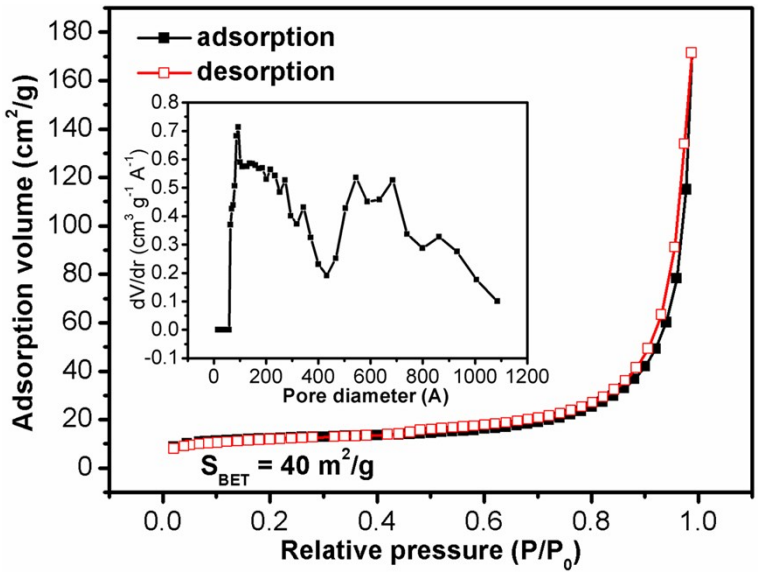

Fig. S4 N_2 adsorption/desorption isotherms of Co_3O_4/rGO-400 (inset: pore size distribution analysis based on the DFT model).

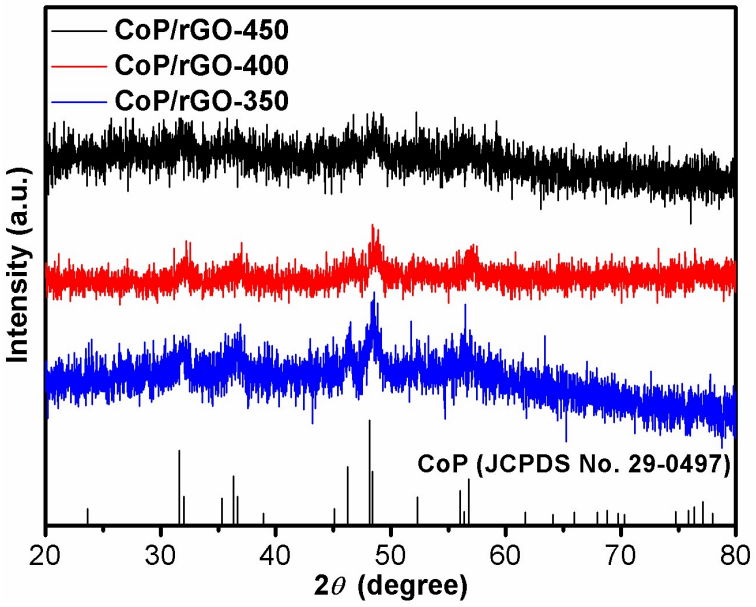

Fig. S5 Powder XRD patterns of CoP/rGO-T (T = 350, 400 and 450).

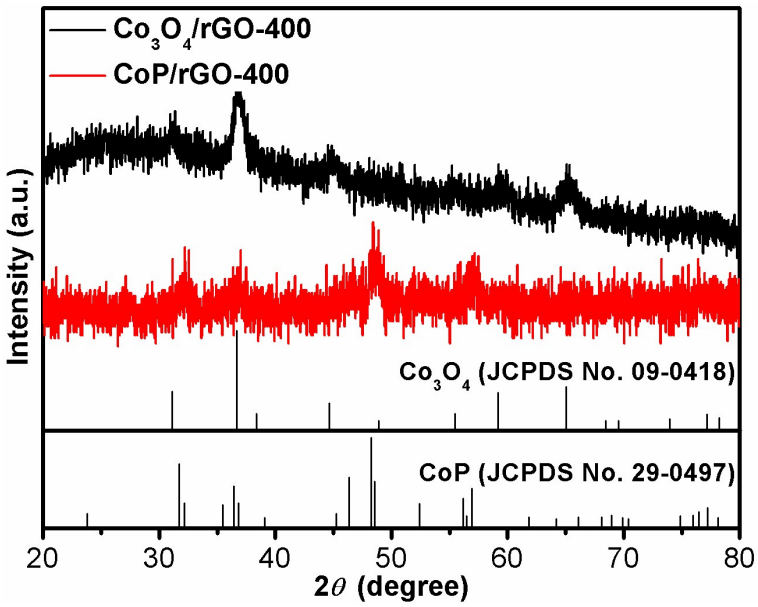

Fig. S6 Powder XRD patterns of Co_3O_4/rGO-400 and CoP/rGO-400.

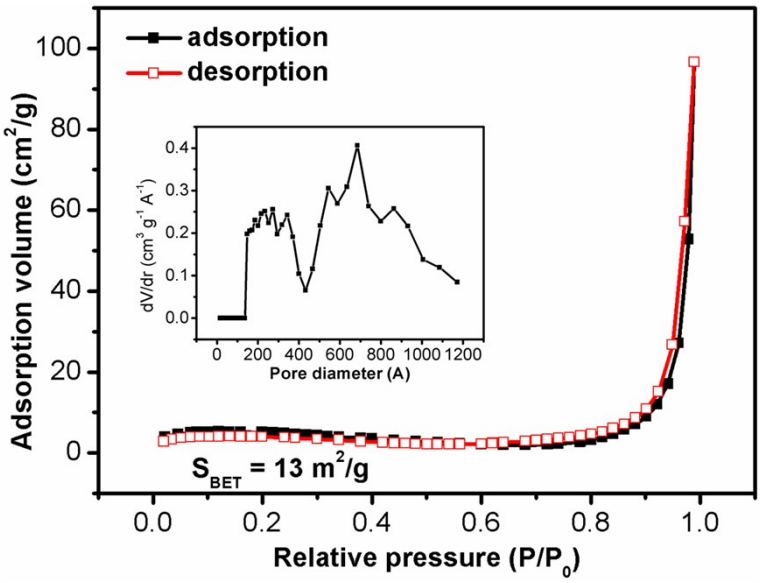

Fig. S7 N_2 adsorption/desorption isotherms of CoP/rGO-400 (inset: pore size distribution analysis based on the DFT model).

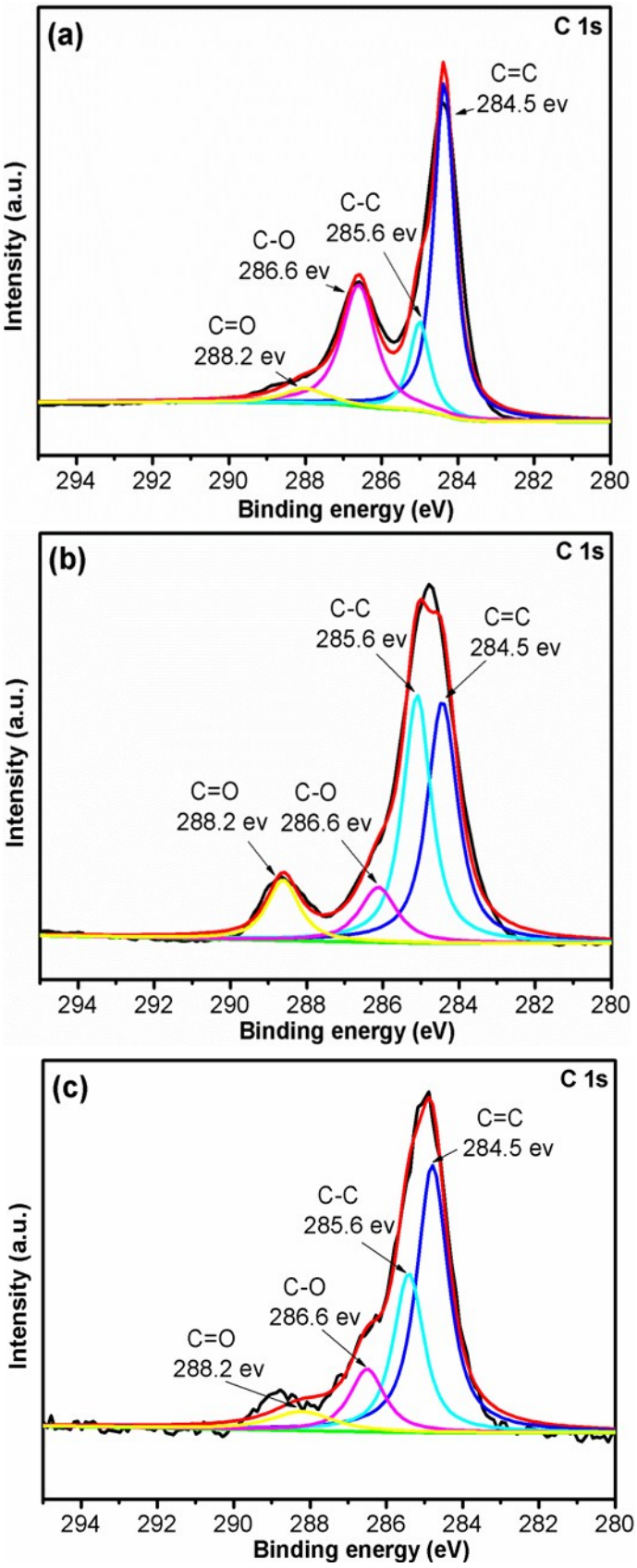

Fig. S8 The XPS spectra of high-resolution C 1s for (a) GO, (b) Co_3O_4/rGO, and (c) CoP/rGO.

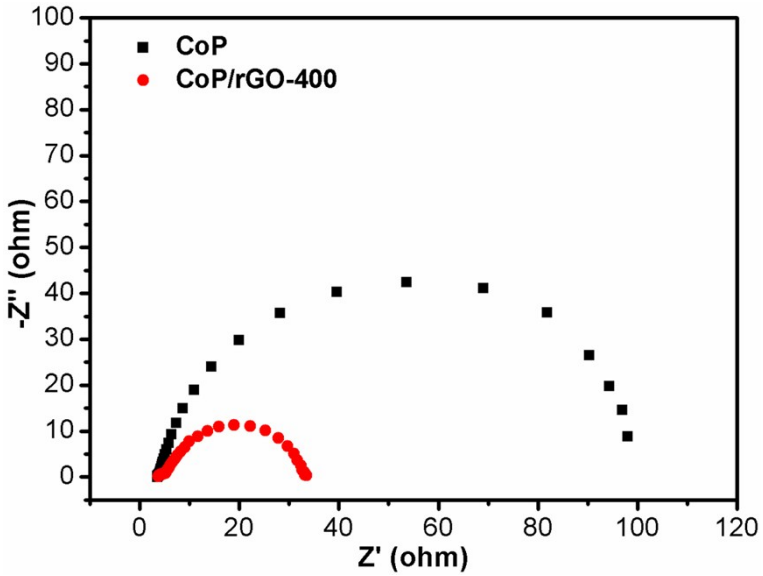

Fig. S9 Nyquist plots of electrochemical impedance spectra of CoP/rGO-400 and CoP at -100 mV vs RHE in 1M KOH.

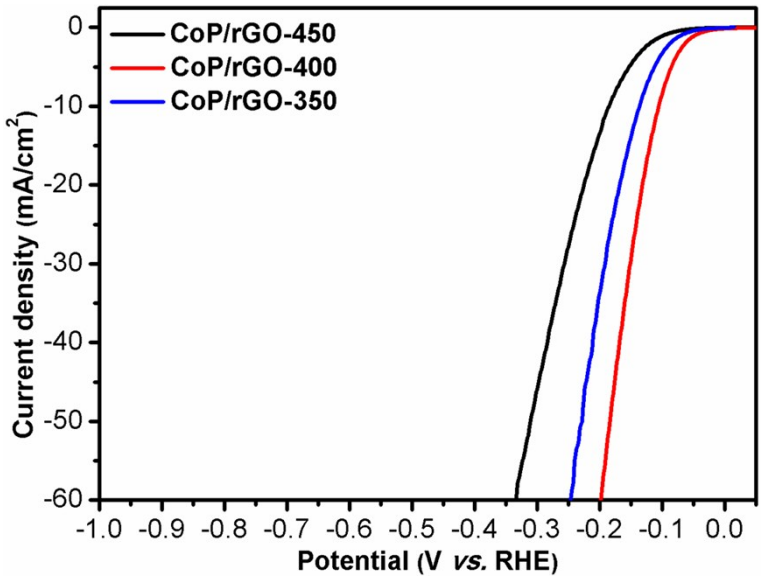

Fig. S10 Electrochemical hydrogen evolution reaction (HER) activity for CoP/rGO-T (T = 350, 400, and 450) in 0.5M H_2SO_4 with a scan rate of 5 mV/s.

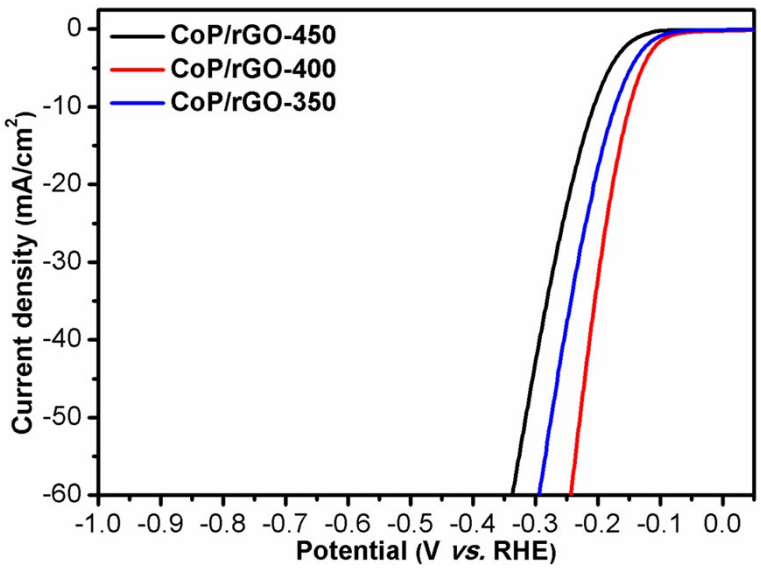

Fig. S11 Electrochemical hydrogen evolution reaction (HER) activity of CoP/rGO-T (T = 350, 400, and 450) in 1M KOH with a scan rate of 5 mV/s.

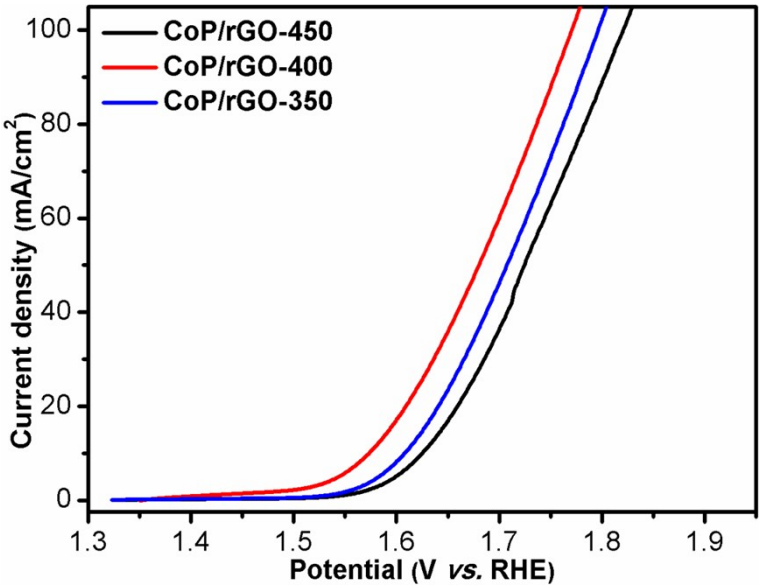

Fig. S12 Electrochemical oxygen evolution reaction (OER) activity of CoP/rGO-T (T = 350, 400, and 450) in 1M KOH with a scan rate of 5 mV/s.

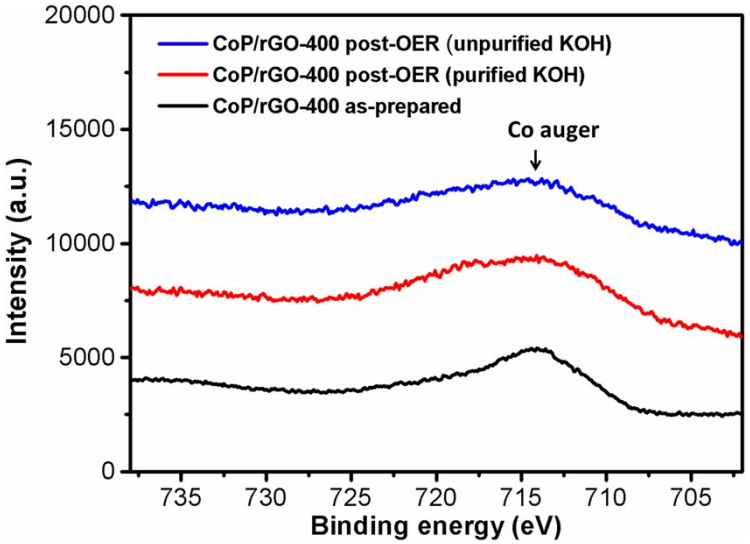

Fig. S13 High-resolution XPS survey spectra of Fe 2p for CoP/rGO-400.

The 1 M KOH was purified as follows: $Co(OH)_2$ was precipitated from the mixture of $Co(NO_3)_2$ (1 g) and 0.1M KOH (200 mL), and was washed three times. The triple-washed $Co(OH)_2$ was added to the 1M KOH and stirred for 10 min to absorb Fe impurities. The resultant brown suspension was centrifuged, and the obtained Fe-free KOH solution was used as electrolyte for OER.

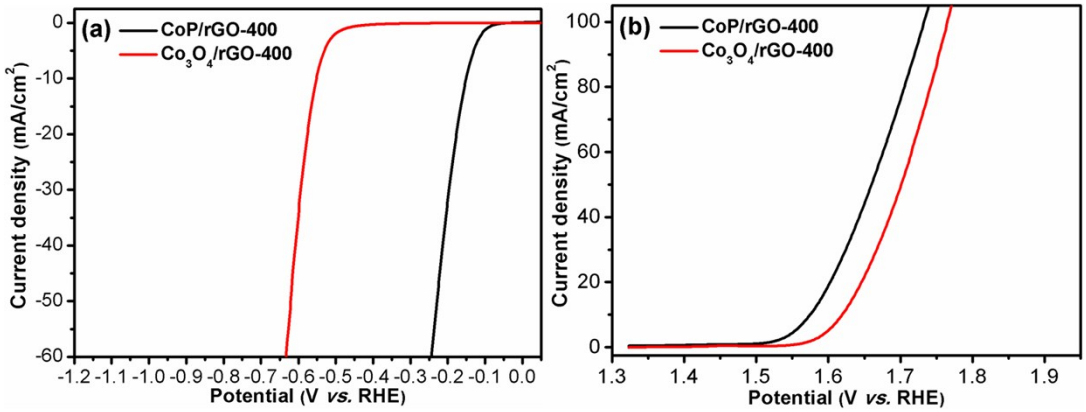

Fig. S14 Activity comparison of electrochemical (a) hydrogen evolution reaction (HER) and (b) oxygen evolution reaction (OER) over CoP/rGO-400 and Co_3O_4/rGO-400 catalysts, respectively, in 1M KOH with a scan rate of 5 mV/s.

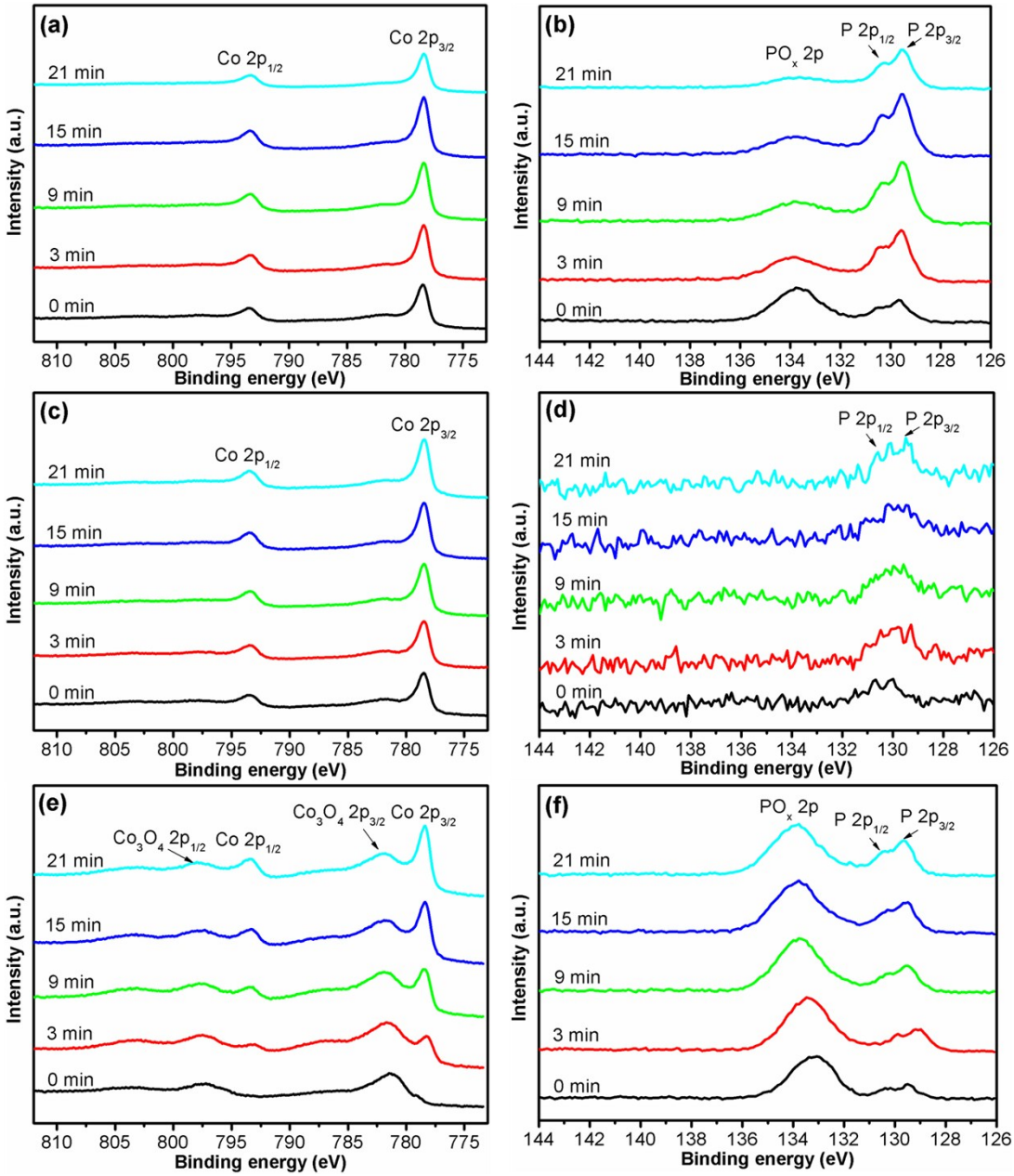

Fig. S15 High-resolution XPS survey spectra of Co 2p for (a) as-prepared, (c) post-HER, and (e) post-OER CoP/rGO-400 catalyst, and P 2p for (b) as-prepared, (d) post-HER, and (f) post-OER CoP/rGO-400 catalyst, respectively, during Ar^+ sputtering for different time.

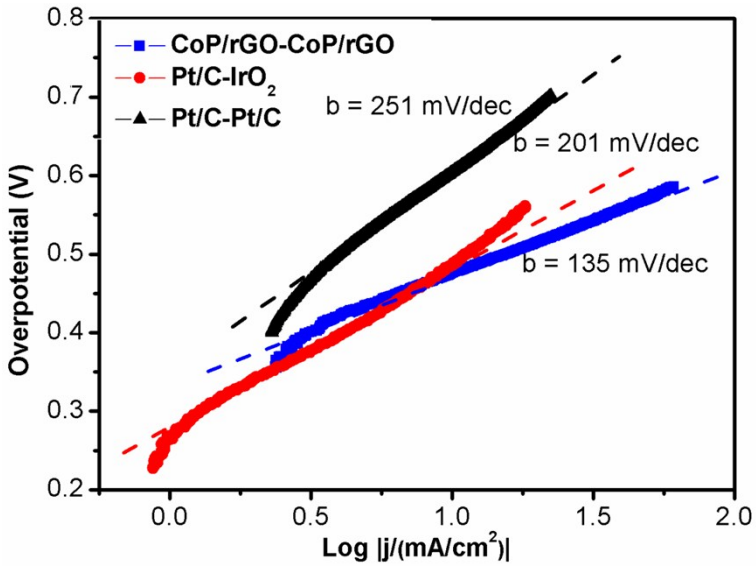

Fig. S16 Tafel plots of integrated CoP/rGO-CoP/rGO, Pt/C-IrO_2 and Pt/C-Pt/C couples for overall water splitting.

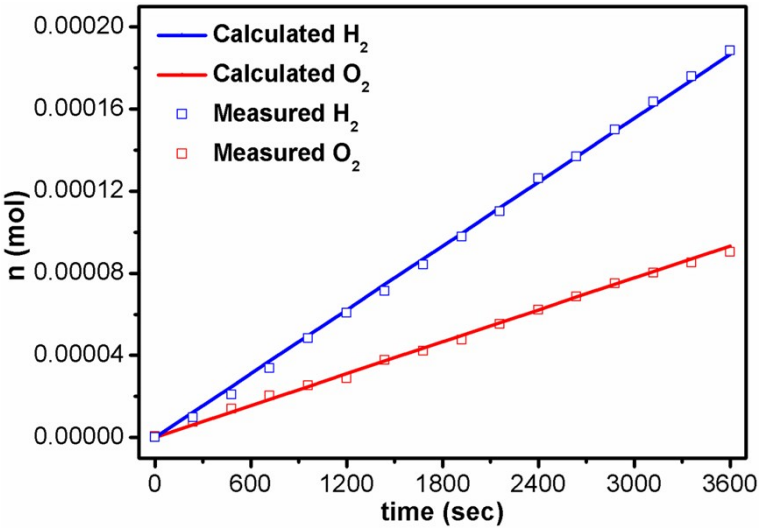

Fig. S17 The measured and theoretical (assuming a 100% faradaic efficiency) yields of H_2 and O_2 over time during water splitting over CoP/rGO-400 catalyst in 1M KOH at a current density of 10 mA/cm^2.

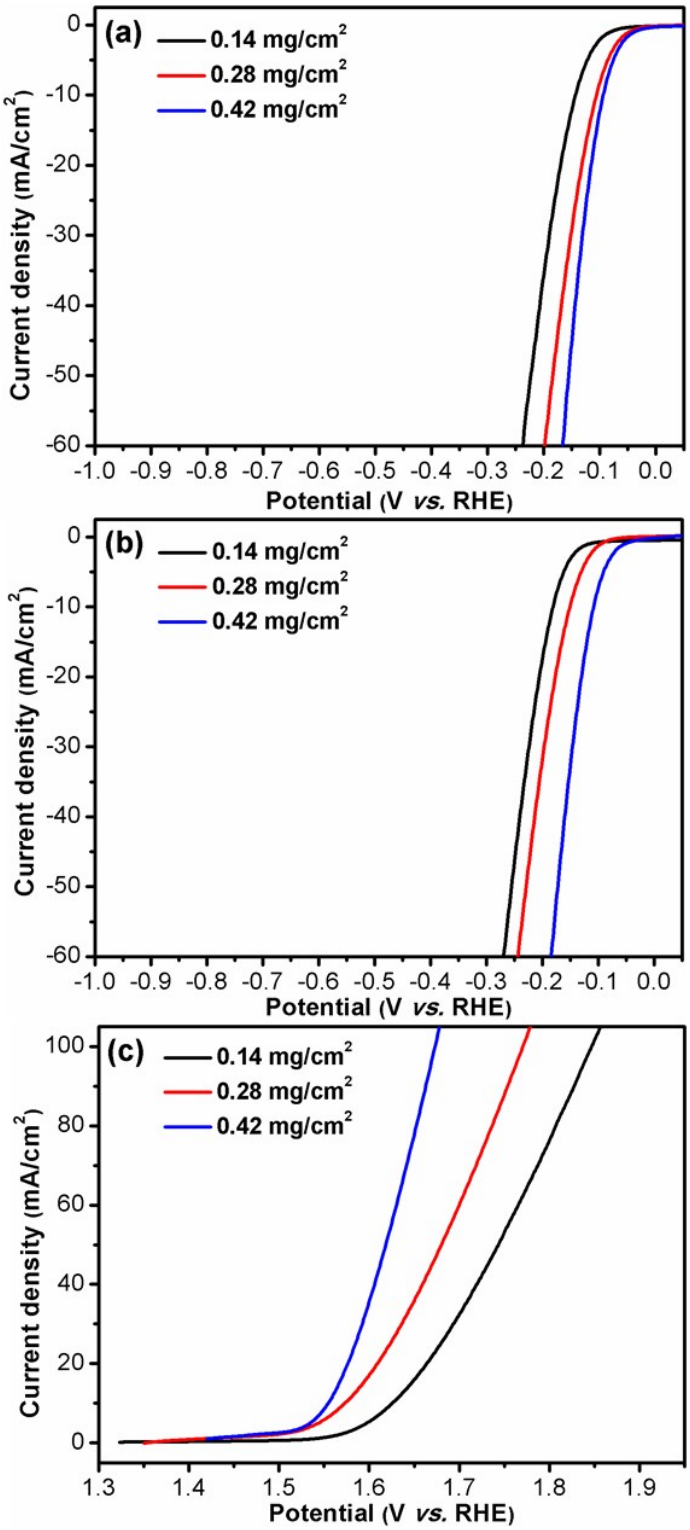

Fig. S18 Electrochemical hydrogen evolution reaction (HER) activity in (a) 0.5M H_2SO_4 (b) 1M KOH and (c) Electrochemical oxygen evolution reaction (OER) activity over CoP/rGO-400 at different mass loadings in 1M KOH with a scan rate of 5 mV/s.

Table S1 Comparison of HER performance in 0.5M H_2SO_4 solution for CoP/rGO-400 with other non-noble metal electrocatalysts.

material	Current density (j, mA/cm^2)	η at the correspondi ng j (mV)	Catalyst loading (mg/cm^2)	Tafel slopes(m V/dec)	Ref
CoP/rGO-400	**10**	**105**	**~0.28**	**50**	**This work**
	20	**130**			
CoP/CNT	2	70	0.285	54	*Angew. Chem., Int. Ed.* **2014**, *53*, 6710
	10	122			
CoP/CC	10	67	0.92	51	*J. Am. Chem. Soc.* **2014**, *136*, 7587
	20	100			
Co_2P nanorods	10	134	1	71	*Nano Energy* **2014**, *9*, 373
	20	167			
CoP/RGO-0.36	10	~250	0.29	104.8	*J. Mater. Chem. A* **2015**, *3*, 5337
CoP@C	10	170	0.353	61	*J. Power Source* **2015**, *286*, 464
$Ni_{12}P_5$/Ti	10	137	1	63	*ACS nano* **2014**, *8*, 8121
Cu_3P NW/CF	10	143	15.2	67	*Angew. Chem., Int. Ed.* **2014**, *53*, 9577
MoCx	10	142	0.8	53	*Nat. Commun.* **2015**, *6*, 6512
CoNi@NC	10	142	1.6	104	*Angew. Chem., Int. Ed.* **2015**, *54*, 2100

Table S2 Comparison of HER performance in 1M KOH solution for CoP/rGO-400 with other non-noble metal electrocatalysts.

material	Current density (j, mA/cm^2)	η at the correspondin g j (mV)	Catalyst loading (mg/cm^2)	Tafel slopes (mV/dec)	Ref
CoP/rGO-400	**10**	**150**	**~0.28**	**38**	**This work**
	20	**175**			
MoB	10	225	2.3	59	*Angew. Chem., Int. Ed.* **2012**, *51*, 12703
Ni	10	400	1	-	*ACS Catal.* **2013**, *3*, 166
CoP/CC	10	209	0.92	129	*J. Am. Chem. Soc.* **2014**, *136*, 7587
Co_2P nanorods	20	171	1	-	*Nano Energy* **2014**, *9*, 373
MoC_x	10	151	0.8	59	*Nat. Commun.* **2015**, *6*, 6512
Co-embedded N-rich CNTs	10	370	0.28	-	*Angew. Chem., Int. Ed.* **2014**, *53*, 4372

Table S3 Comparison of OER performance in 1M KOH solution for CoP/rGO-400 with other non-noble metal electrocatalysts.

material	Current density (j, mA/cm^2)	η at the corresponding j (mV)	Catalyst loading (mg/cm^2)	Tafel slopes (mV/dec)	Ref
CoP/rGO-400	**10**	**340**	**~0.28**	**66**	**This work**
	20	**379**			
CoP Nanoparticles (0.1M KOH)	10	360	0.05	66	*ACS Catal.* **2015**, *5*, 4066
N-doped graphene-CoO	10	340	0.7	71	*Energy Environ. Sci.* **2014**, *7*, 609
$Zn_xCo_{3-x}O_4$ nanowire array	10	320	~1	51	*Chem. Mater.* **2014**, *26*, 1889
NiCo LDH nanosheets	10	367	0.17	40	*Nano Lett.* **2015**, *15*, 1421

Table S4 Comparison of OER and HER performance in 1M KOH solution for CoP/rGO-400 with other non-noble metal bifunctional electrocatalysts.

material	η_{HER}@10mA/cm^2 (mV)	η_{OER}@10mA/cm^2 (mV)	E (V) [a]	Ref
CoP/GO-400	**150**	**340**	**1.70**	**This work**
Ni_5P_4	150	290	~1.7	*Angew. Chem., Int. Ed.* **2015**, 54, 12361
NiFe LDH/Ni foam	210	240	1.7	*Science* **2014**, *345*, 1593
PCPTF	~380	~310	-	*Adv. Mater.* **2015**, *27*, 3175
Co-P film	94	345	~1.64	*Angew. Chem., Int. Ed.* **2015**, *54*, 6251
NiSe/Ni foam	96	-	1.63	*Angew. Chem., Int. Ed.* **2015**, *54*, 9351

Note: [a]represents the overall water splitting overpotential at 10 mA/cm^2.

References

1. M. Jahan, Z. Liu and K. P. Loh, *Adv. Funct. Mater.,* 2013, **23**, 5363.