Electronic supplementary information

Three dimensional metal-organic framework derived porous CoP_3 concave polyhedrons as superior bifunctional electrocatalysts for the evolution of hydrogen and oxygen

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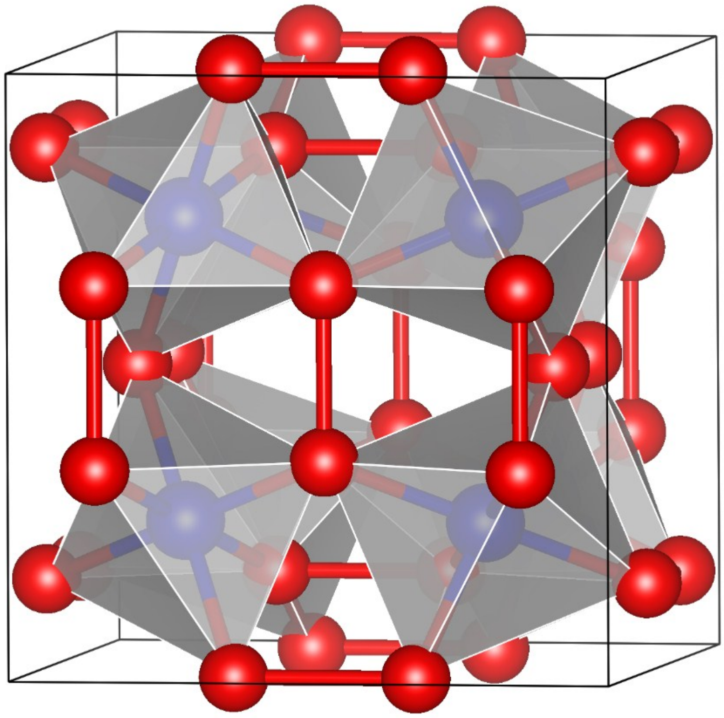

Fig. S1 Crystal structure of CoP_3. The cobalt and phosphorus atoms are represented by blue and red, respectively.

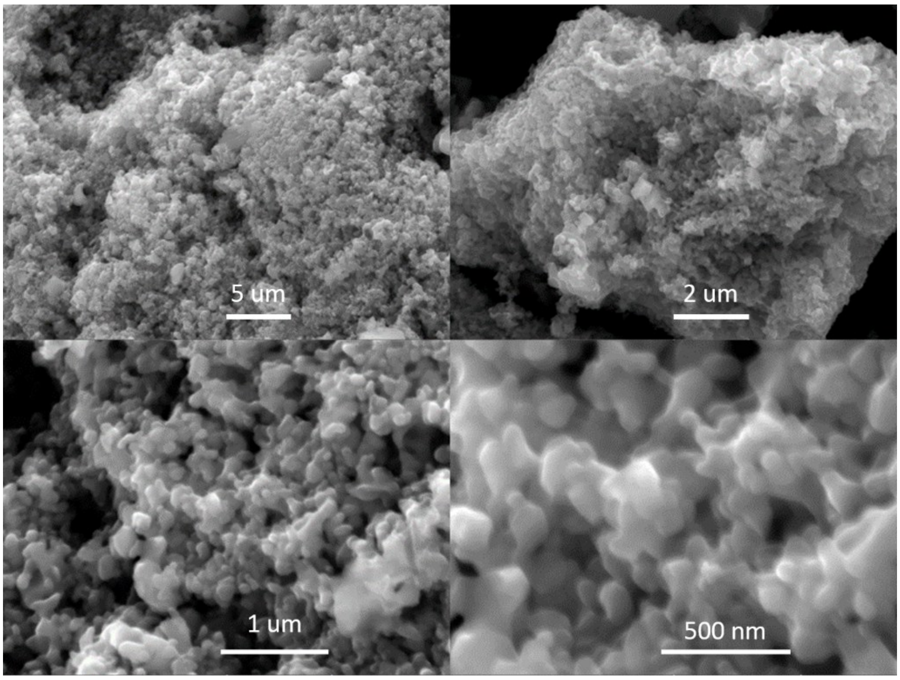

Fig. S2 Low- and high- magnification SEM images of CoP_3 NPs.

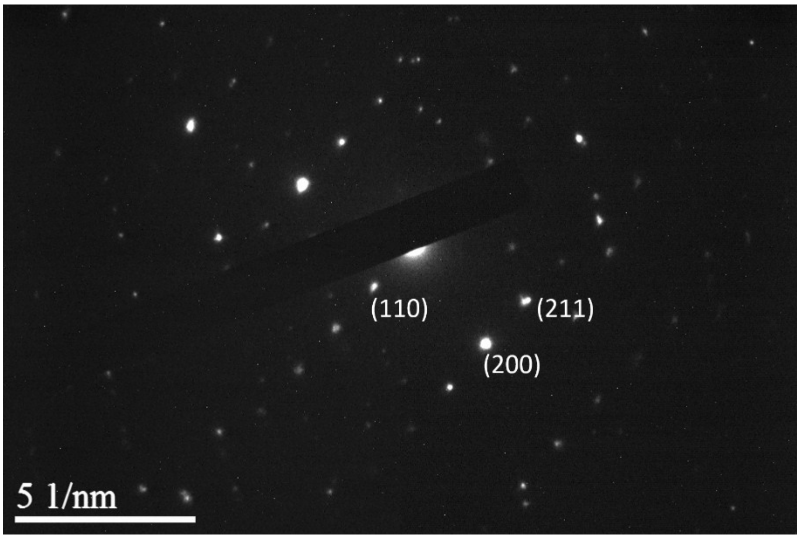

Fig. S3 SAED pattern of CoP_3 CPs.

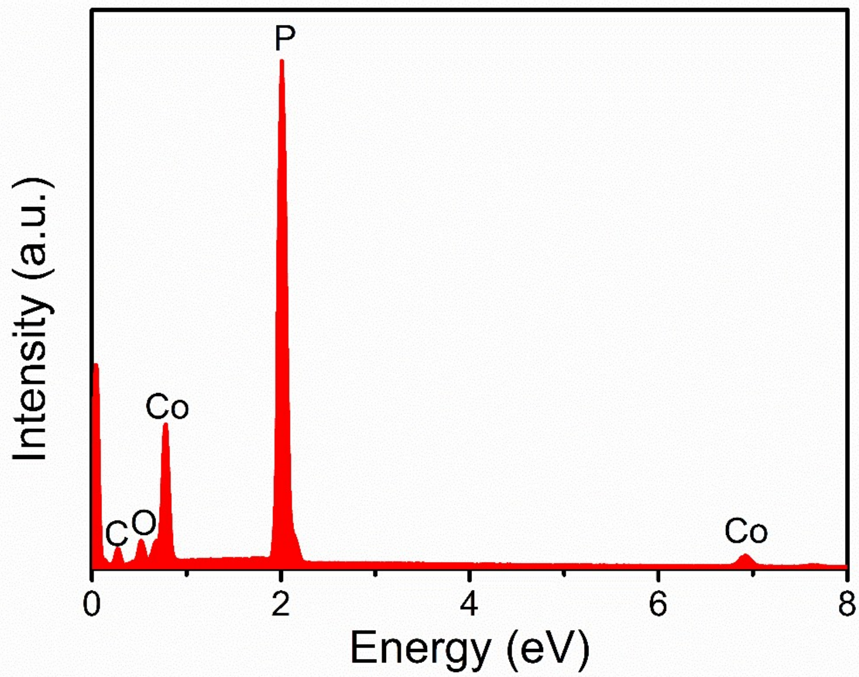

Fig. S4 EDX spectrum of CoP_3 CPs.

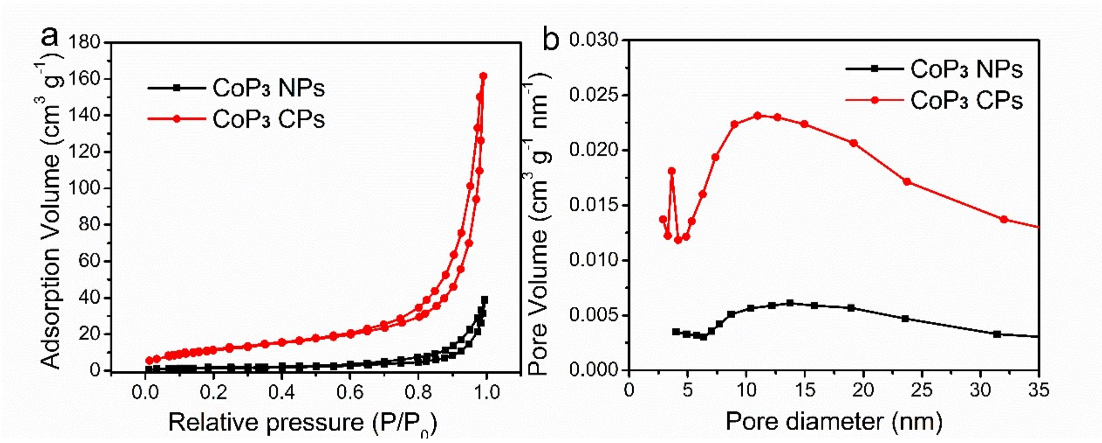

Fig. S5 (a) Nitrogen adsorption/desorption isotherm and (b) the BJH pore-size distribution curve of CoP_3 NPs and CoP_3 CPs.

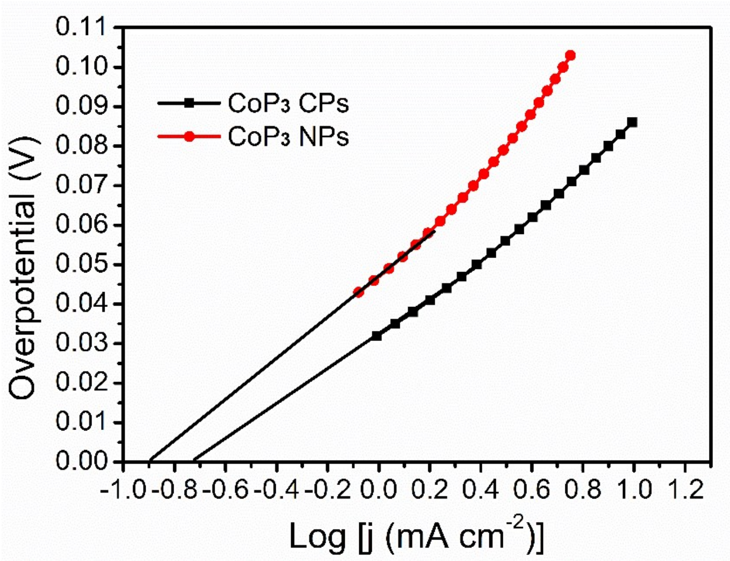

Fig. S6 Calculated exchange current density of the CoP_3 CPs and CoP_3 NPs by applying extrapolation method to the Tafel plot.

Table S1. Comparison of HER performance in acid media for CoP_3 CPs/CFP with other TMPs HER electrocatalysts.

Catalyst	Onset η (mV)	Current density (*j*, mA cm^{-2})	η at the corresponding *j* (mV)	Exchange current density (mA cm^{-2})	Ref.
FeP nanosheets	100	10	240	-	*Chem. Commun.*, 2013, 49, 6656
FeP NWs/Ti	38	10	55	0.42	*Angew. Chem. Int. Ed.*, 2014, 53, 12855
FeP NWs	-	10	96	0.17	*Chem. Commun.*, 2016, 52, 2819.
FeP NPs	38	10	112	-	*Nanoscale*, 2015, 7, 4400
FeP NAs	-	10	85	-	*J. Mater. Chem. A*, 2014, 2, 17263
FeP_2/C	-	5	500	$1.75*10^{-3}$	*J. Mater. Chem. A*, 2015, 3, 499
Ni_2P NPs	-	20	130	$2.7*10^{-3}$	*J. Am. Chem. Soc.*, 2013, 135, 9267
Ni_2P/graphene	37	10	102	0.049	*J. Power Sources*, 2015, 297, 45
Ni_2P/CNs	40	10	92	-	*J. Power Sources*, 2015, 285, 169
NiP_2/CC	-	10	116	0.26	*Nanoscale*, 2014, 6, 13440
Se doped NiP_2	-	10	84	-	*ACS Catal.*, 2015, 5, 6355
Cu_3P NWs	62	10	143	0.18	*Angew. Chem. Int. Ed.*, 2014, 53, 9577
MoP Bulk	50	30	180	0.034	*Energy Environ. Sci.*, 2014, 7, 2624
MoP NPs	40	10	125	0.086	*Adv. Mater.*, 2014, 26, 5702
MoP_2 NPs/Mo	-	10	143	0.06	*Nanoscale, 2016, 8, 8500*
MoP_2 nanosheets	-	10	58	-	*J. Mater. Chem. A*, 2016, 4, 7169
WP	50	10	120	-	*Chem. Commun.*, 2014, 50, 11026

α-WP_2	**54**	**10**	**161**	**0.017**	***ACS Catal.*, 2015, 5, 145**
β-WP_2	**56**	**10**	**148**	**0.013**	***J. Power Sources*, 2015, 278, 540**
Co2P	**-**	**10**	**95**	**-**	***Chem. Mater.*, 2015, 27, 3769**
CoP/CC	**38**	**10**	**67**	**0.288**	***J. Am. Chem. Soc.*, 2014, 136, 7587**
CoP NPs	**-**	**20**	**85**	**-**	***Angew. Chem. Int. Ed.*, 2014, 53, 5427**
CoP/CNs	**40**	**10**	**122**	**0.13**	***Angew. Chem. Int. Ed.*, 2014, 53, 6710**
CoP_3 CPs	**30**	**10**	**78**	**0.209**	**This work**
		50	**127**		

NPs (Nanoparticles); CNs (Carbon Nanotubes); CC (Carbon Cloth); NWs (Nanowires); NAs (Nanoneedle Arrays); CPs (Concave Polyhedrons)

Table S2. Comparison of HER performance in neutral media for CoP_3 CPs/CFP with other HER electrocatalysts.

Catalyst	Current density (j, mA cm^{-2})	Potential at the corresponding j (mV)	Ref.
Mo_2B	1	250	*Angew. Chem. Int. Ed.*, 2012, 51, 12703
Mo_2C	1	200	*Angew. Chem. Int. Ed.*, 2012, 51, 12703
H2-CoCat/FTO	2	385	*Nat. Mater.*, 2012, 11, 802
Co-S/FTO	2	83	*J. Am. Chem. Soc.*, 2013, 135, 17699
$CuMoS_4$	2	210	*Energy Environ. Sci.*, 2012, 5, 8912
WP	10	200	*ACS Appl. Mater. Interfaces*, 2014, 6, 218740
WP_2	10	298	*J. Power Sources*, 2015, 278, 540
MoP_2 NPs/Mo	10	211	*Nanoscale*, 2016, 8, 8500
MoP_2 nanosheets	10	67	*J. Mater. Chem. A*, 2016, 4, 7169
CoP NWs	2	65	*J. Am. Chem. Soc.*, 2014, 136, 7587
CoP_3 CPs	10	179	This work

Table S3. Comparison of HER performance in alkaline media for CoP_3/CFP with other HER electrocatalysts.

Catalyst	Current density (*j*, mA cm^{-2})	Potential at the corresponding *j* (mV)	Ref.
Ni wire	10	350	*ACS Catal.*, 2013, 3, 166
MoB	10	225	*Angew. Chem. Int. Ed*, 2012, 51, 12703
NiP_2	10	102	*Nanoscale*, 2014, 6, 13440
WP	10	250	*ACS Appl. Mater. Interfaces*, 2014, 6, 218740
WP_2	10	225	*J. Power Sources*, 2014, 136, 7587
MoP_2 nanosheets	10	85	*J. Mater. Chem. A*, 2016, 4, 7169
MoP_2 NPs/Mo	10	194	*Nanoscale*, 2016, 8, 8500
CoP nanowires	10	209	*J. Am. Chem. Soc.*, 2014, 136, 7587
CoP_3 CPs	10	124	This work

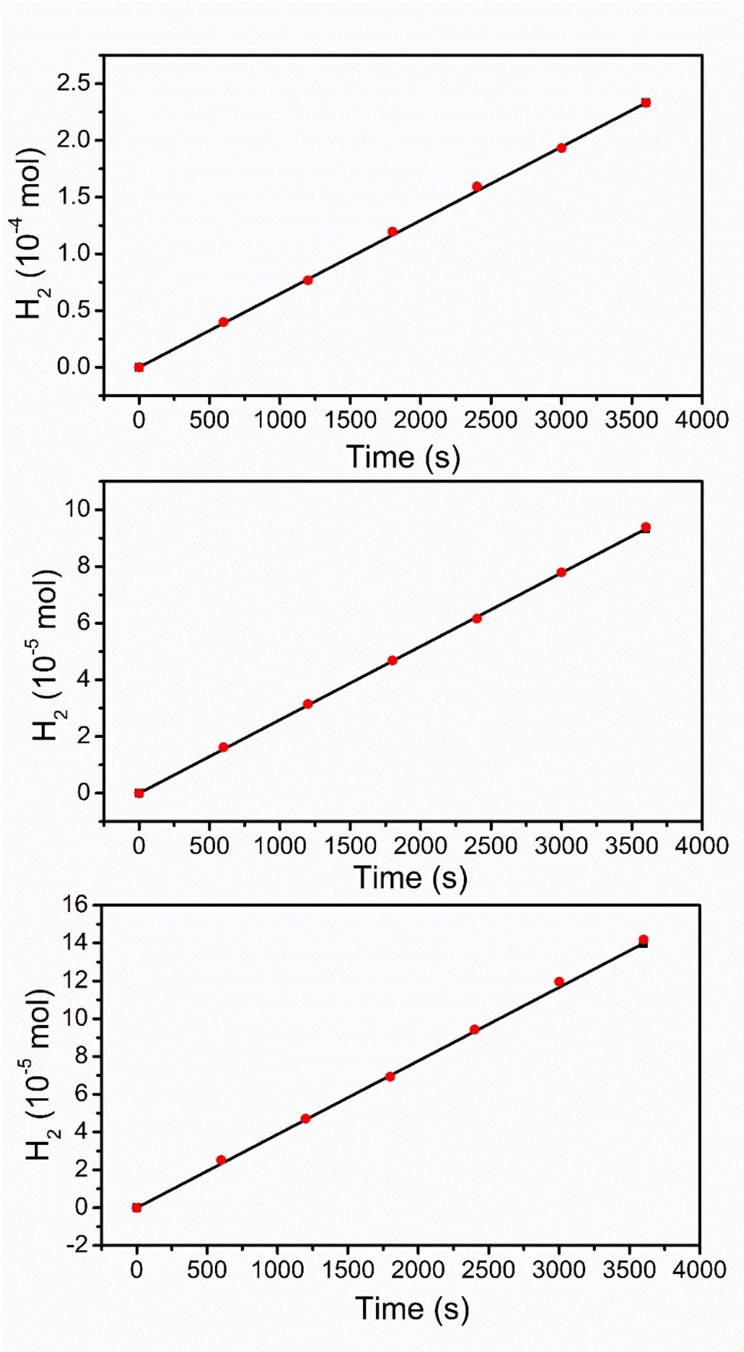

Fig. S7 The amount of H_2 theoretically calculated (solid) and experimentally measured (red sphere) versus time for CoP_3 CPs at (a) pH 0 under an overpotential of 127 mV (50 mA cm^{-2}) for 60 min, (b) pH 6.8 under overpotentials of 223 mV (20 mA cm^{-2}) for 60 min. and (c) pH 14 under overpotentials of 173 mV (30 mA cm^{-2}) for 60 min.

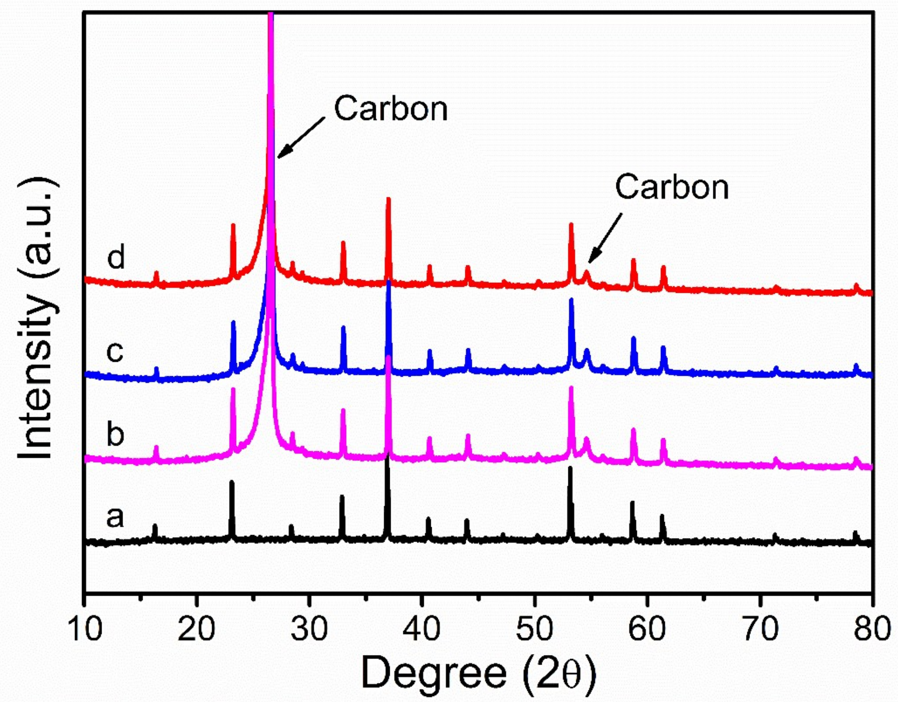

Fig. S8 (a) XRD patterns of CoP_3 CPs and (b), (c), (d) the XRD patterns of CoP_3 CPs/CFP electrode after 3000 cycles CV scanning at pH 0, pH 6.8, and pH 14, respectively.

Table S4. Comparison of OER performance in alkaline media for CoP_3/CFP with other OER electrocatalysts.

Catalyst	Current density (j mA cm^{-2})	Potential at the corresponding j (mV)	Ref
$NiOOH/Ni_5P_4$	**10**	**290**	***Angew. Chem. Int. Ed*, 2015, 54, 12361**
Ni-P/CF	**10**	**325**	***J. Power Sources*, 2015, 299, 342**
Co-P film	**10**	**345**	***Angew. Chem. Int. Ed*, 2015, 54, 6251**
CoP NPs	**10**	**360**	***ACS Catal.*, 2015, 5, 4066**
CoP nanorods	**10**	**320**	***ACS Catal.*, 2015, 5, 6874**
CoP hollow	**10**	**427**	***ACS Appl. Mater. Interfaces*, 2016, 8, 2158**
CoP_2/RGO	**10**	**300**	***J. Mater. Chem. A*, 2016, 4, 4686**
CoP_3 NAs/CFP	**10**	**343**	**This work**
	30	**393**	

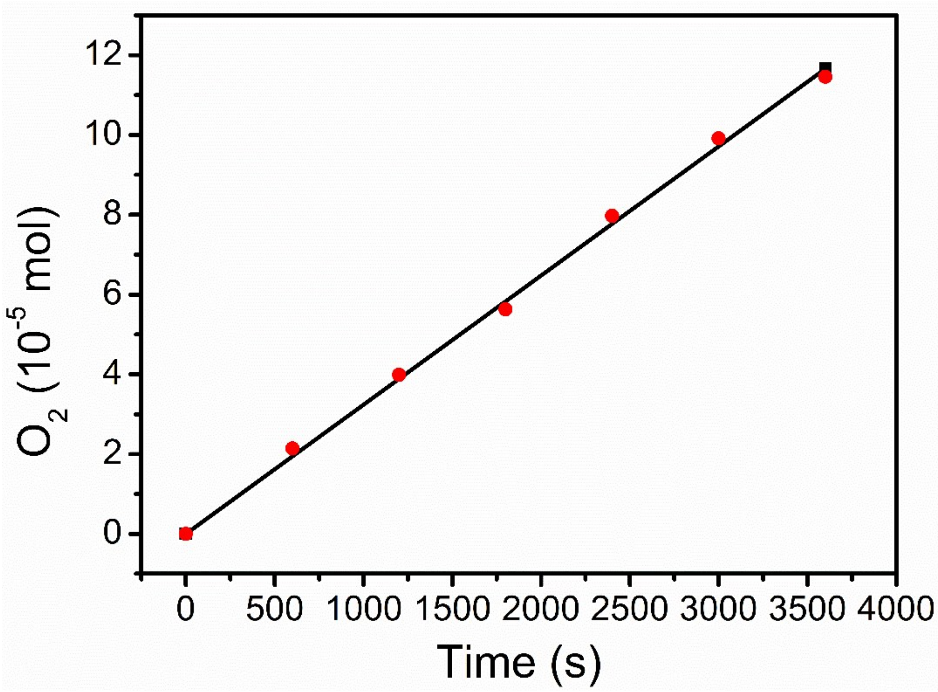

Fig. S9 The amount of O_2 theoretically calculated (solid) and experimentally measured (red sphere) versus time for the CoP_3 CPs at pH 14 under overpotentials of 420 mV (50 mA cm^{-2}) for 60 min.

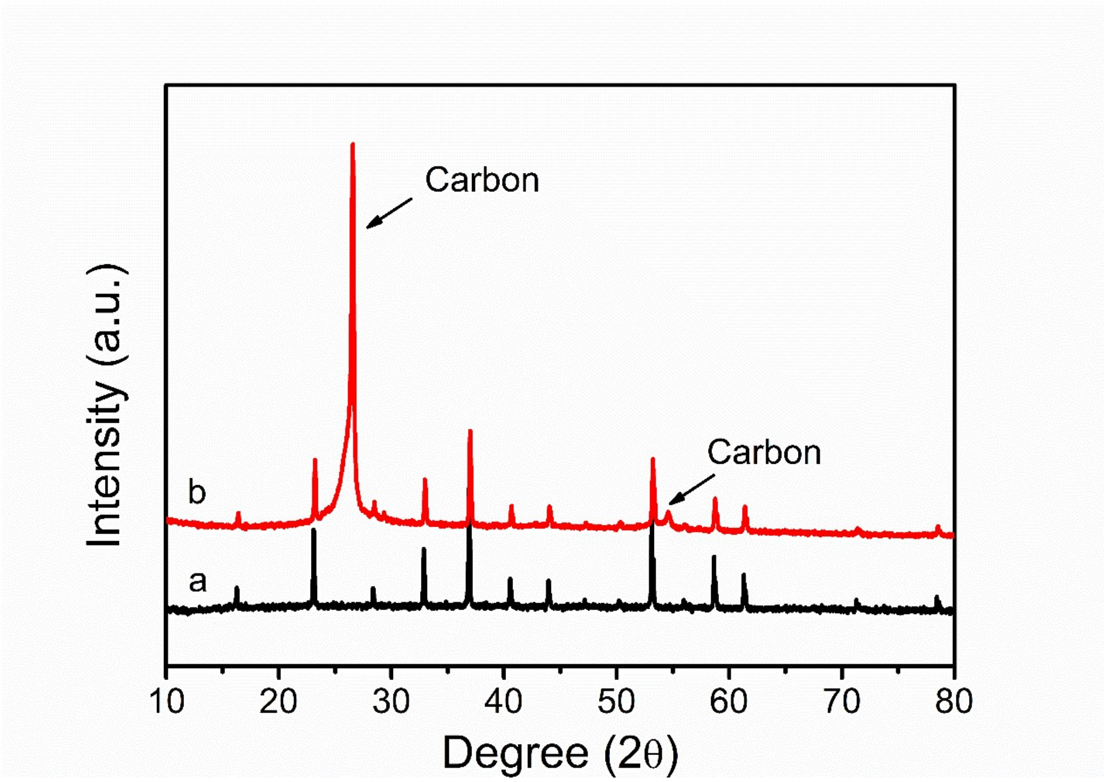

Fig. S10 (a) XRD patterns of CoP_3 CPs and (b) the XRD patterns of CoP_3

CPs/CFP electrode after 3000 cycles CV scanning at pH 14.