Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Monodispersed nickel phosphide nanocrystals with different phases: synthesis, characterization and electrocatalytic properties for hydrogen evolution

Yuan Pan, Yanru Liu, Jinchong Zhao, Kang Yang, Jilei Liang, Dandan Liu, Wenhui Hu, Dapeng Liu, Yunqi Liu, Chenguang Liu*

State Key Laboratory of Heavy Oil Processing, Key Laboratory of Catalysis, China National Petroleum Corporation (CNPC), China University of Petroleum, 66 West Changjiang Road, Qingdao, Shandong 266580, P. R. China

* Corresponding author. E-mail address: liuyq@upc.edu.cn.

Tel.: +86-532-86981861.

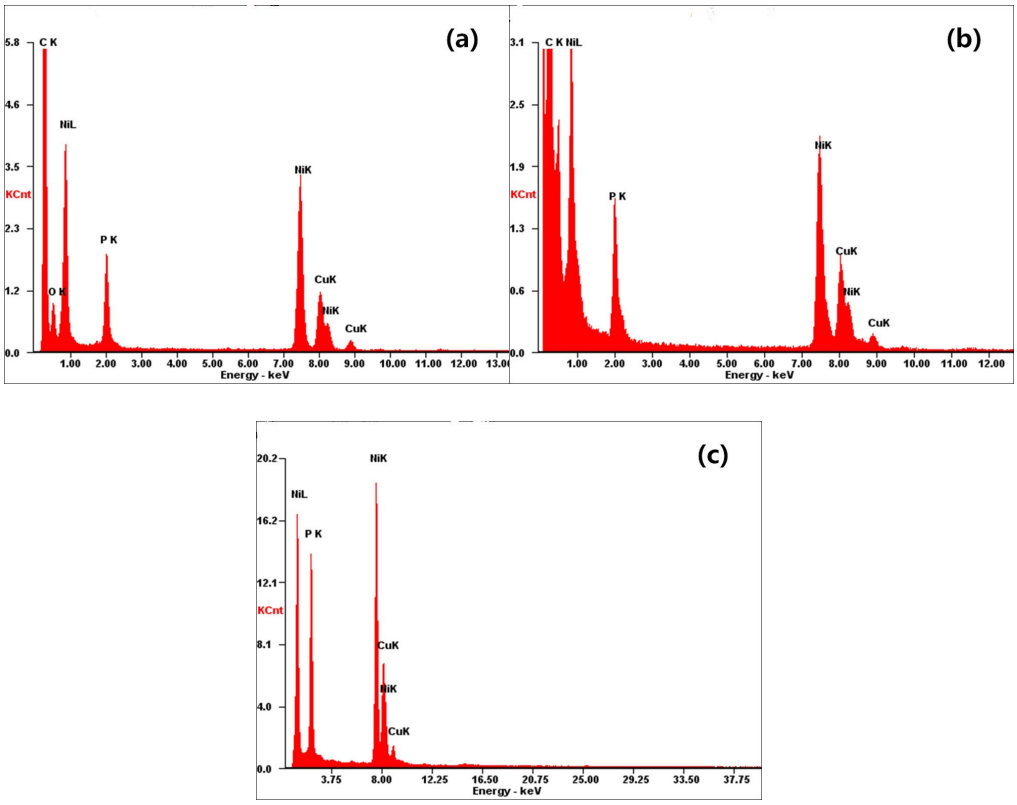
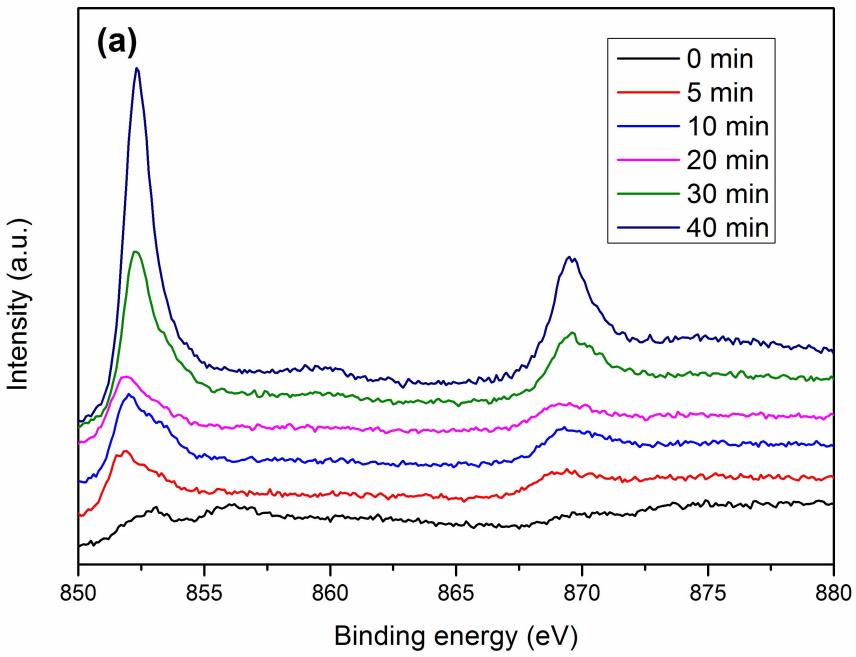
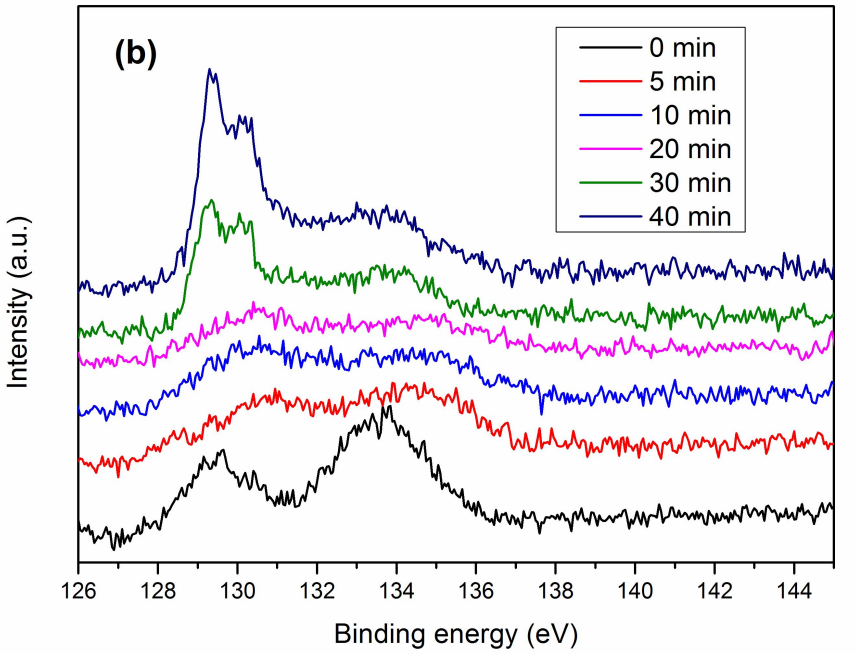
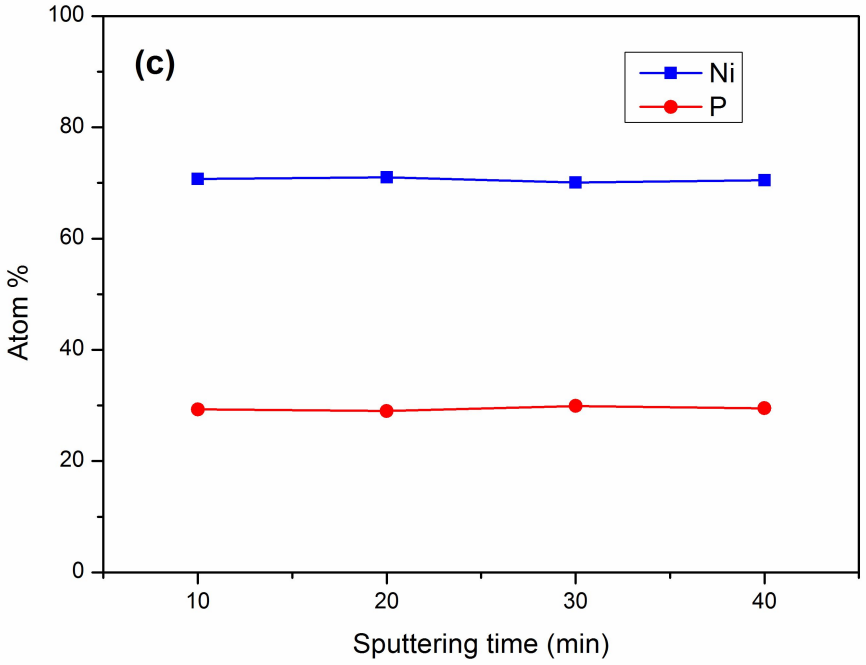
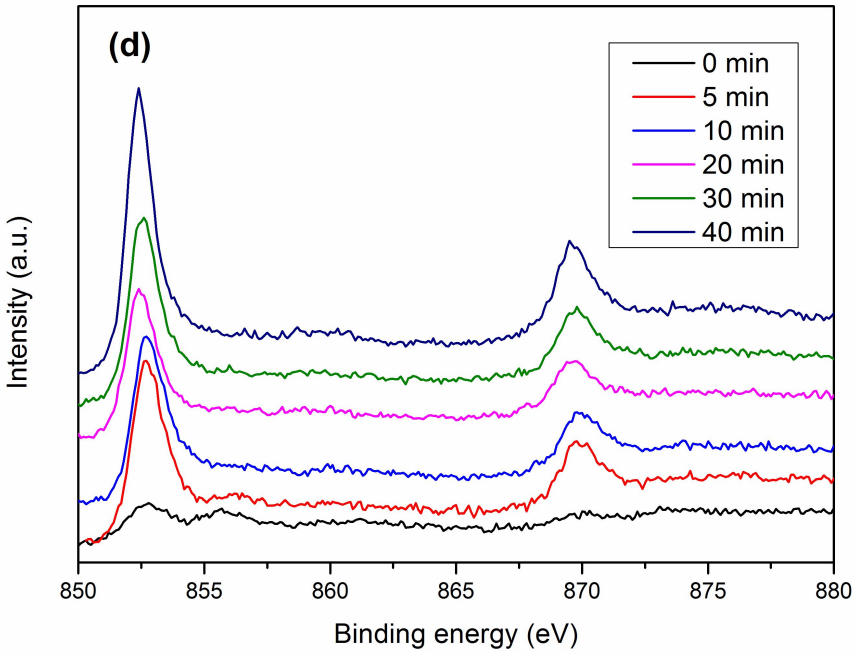


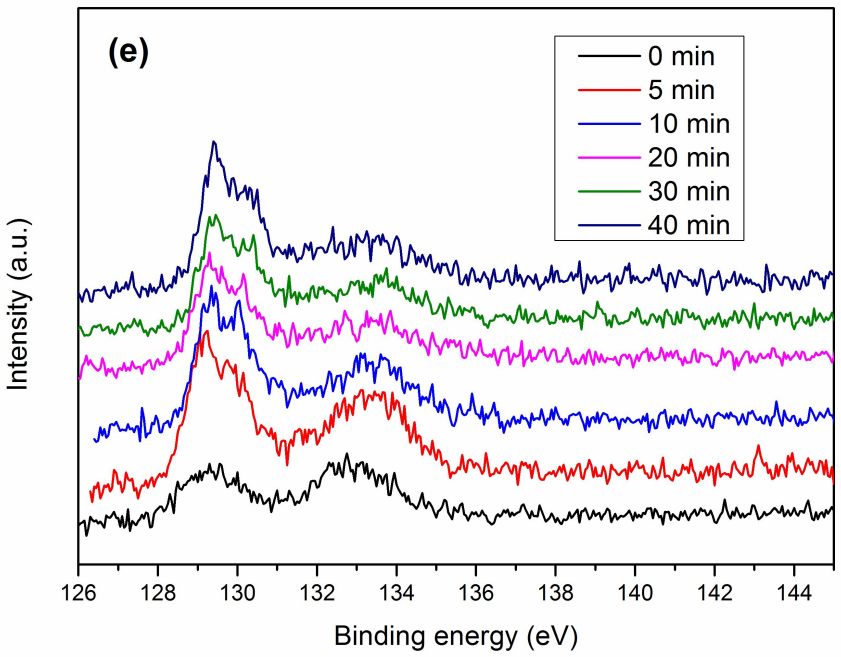
Fig. S1 EDX spectra of nickel phosphide NCs with different phases (a) $Ni_{12}P_5$, (b) Ni_2P and (c) Ni_5P_4 NCs.

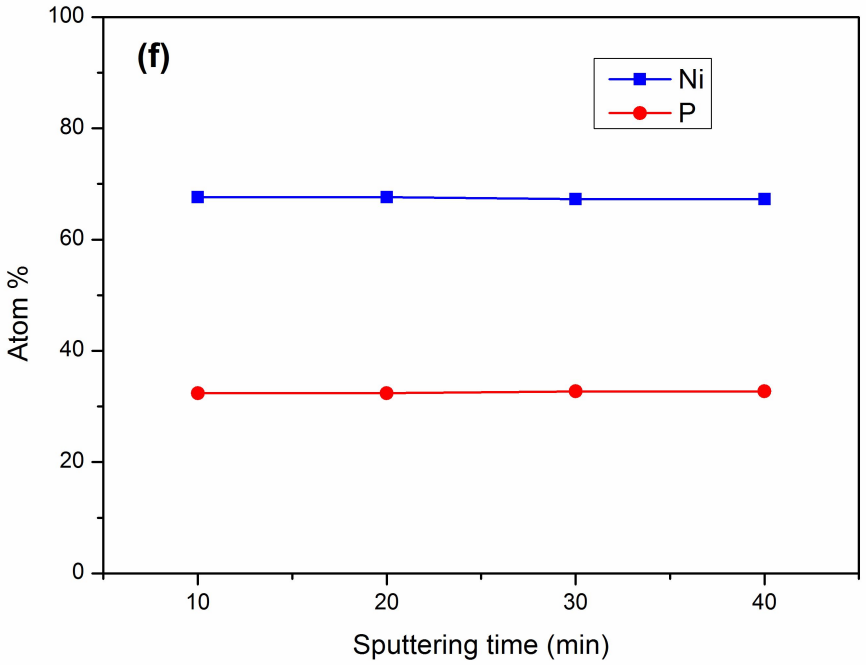

(a)
0 min
5 min
10 min
20 min
30 min
40 min
Intensity (a.u.)
850
855
860
865
870
875
880
Binding energy (eV)

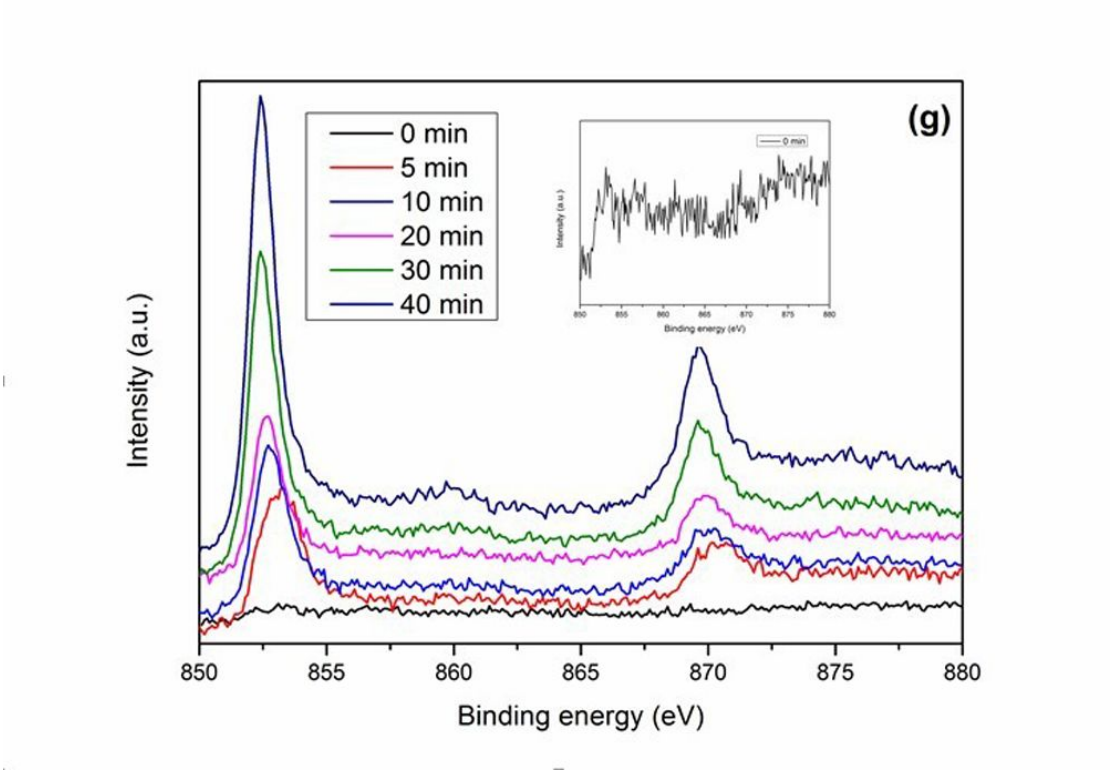

(b)
0 min
5 min
10 min
20 min
30 min
40 min
Intensity (a.u.)
126
128
130
132
134
136
138
140
142
144
Binding energy (eV)

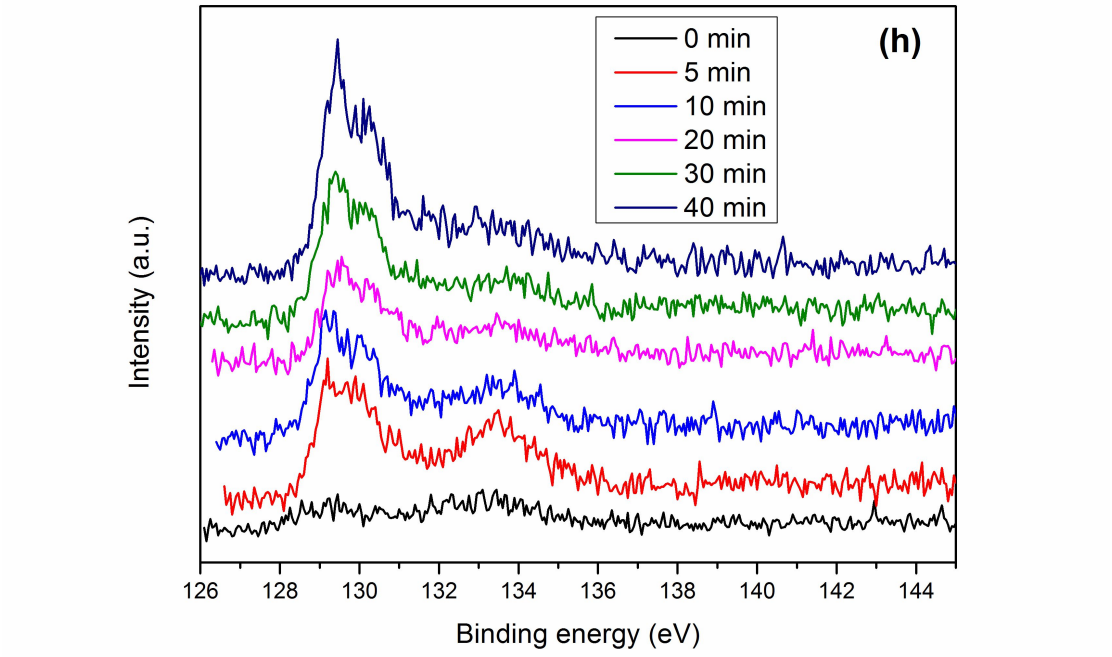

(c)
Ni
P
Atom %
Sputtering time (min)
0
20
40
60
80
100
10
20
30
40


(d)
0 min
5 min
10 min
20 min
30 min
40 min
Intensity (a.u.)
Binding energy (eV)
850
855
860
865
870
875
880


(e)
0 min
5 min
10 min
20 min
30 min
40 min
Intensity (a.u.)
126
128
130
132
134
136
138
140
142
144
Binding energy (eV)


(f)
Ni
P
Atom %
100
80
60
40
20
0
10
20
30
40
Sputtering time (min)


(g)
0 min
5 min
10 min
20 min
30 min
40 min
Intensity (a.u.)
850
855
860
865
870
875
880
Binding energy (eV)


(h)
0 min
5 min
10 min
20 min
30 min
40 min
Intensity (a.u.)
126
128
130
132
134
136
138
140
142
144
Binding energy (eV)

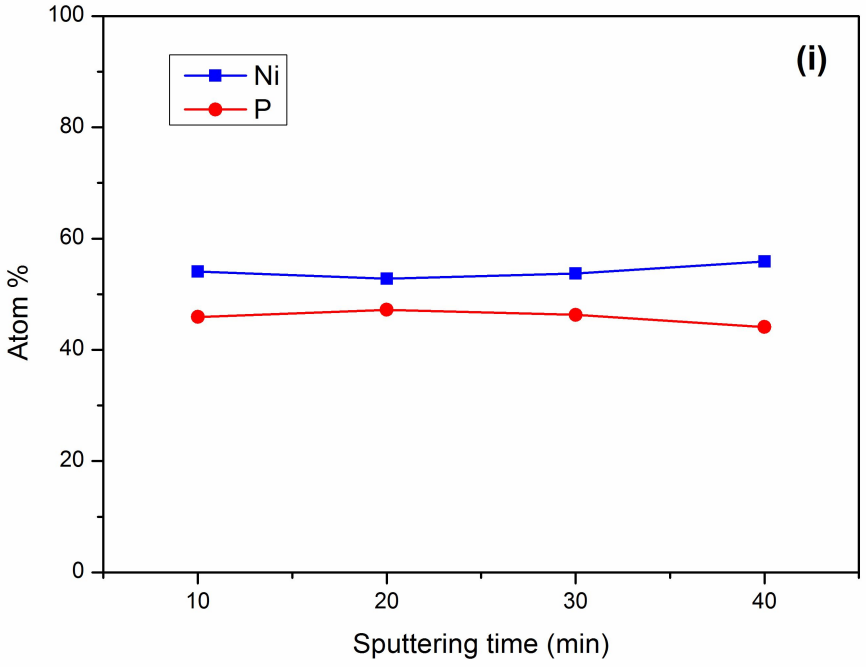


Fig. S2 XPS spectra in the (a) Ni(2p) and (b) P(2p) regions for $Ni_{12}P_5$ NCs, (d) Ni(2p) and (e) P(2p) regions for Ni_2P NCs, (g) Ni(2p) and (h) P(2p) regions for Ni_5P_4 NCs after 0, 5, 10, 20, 30 and 40 min Ar^+ etching. Inserted in (g) is an expansion Ni(2p) region for Ni_5P_4 NCs after 0 min Ar^+ etching. The peaks for oxidized Ni and P species decrease while the peaks for $Ni_{12}P_5$, Ni_2P and Ni_5P_4 increase after 5 min Ar^+ etching. The oxidized Ni and P species nearly completely removed after 10 min Ar^+ etching. (c), (f) and (i) are the corresponding XPS depth profiles of Ni and P elements for the $Ni_{12}P_5$, Ni_2P and Ni_5P_4 NCs, respectivly.

Table S1 Comparison of HER activity of some transition metal phosphides.

Catalyst	Current density ($mA \cdot cm^{-2}$)	Potential (mV)	Electrolyte	Tafel slope ($mV \cdot dec^{-1}$)	Reference
$Ni_{12}P_5$ hollow NPs	10	208	0.5 M H_2SO_4	75	This work
Ni_2P hollow NPs	10	137	0.5 M H_2SO_4	49	This work
Ni_5P_4 solid NPs	10	118	0.5 M H_2SO_4	42	This work
CoP NWs	10	110	0.5 M H_2SO_4	54	22
CoP NSs	10	164	0.5 M H_2SO_4	61	22
CoP NPs	44410	221	0.5 M H_2SO_4	87	22
Amorphous MoP	10	90	0.5 M H_2SO_4	45	23
Bulk CoP	30	180	0.5 M H_2SO_4	54	13
FeP NSs	10	240	0.5 M H_2SO_4	67	24
Ni_2P hollow NPs	10	116	0.5 M H_2SO_4	46	14
Ni_2P NPs	20	140	1 M H_2SO_4	87	25
$Ni_{12}P_5$ NPs	20	141	0.5 M H_2SO_4	63	15
Ni_2P/Ti	20	138	1 M H_2SO_4	60	44
NiP_2 NS/CC	20	99	0.5 M H_2SO_4	51	45
CoP/CNT	10	122	0.5 M H_2SO_4	54	41d
MoP-CA2 NPs	10	125	0.5 M H_2SO_4	54	42b
CoP NPs/CC	10	48	0.5 M H_2SO_4	70	49
CoP/Ti	10	90	0.5 M H_2SO_4	43	41c
MoP/CF	100	200	0.5 M H_2SO_4	67.4	42a

Cu_3P NW/CF	10	143	0.5 M H_2SO_4	67	43
	20	100	0.5 M H_2SO_4	51	
CoP/CC	2	65	1M PBS	93	41b
	10	209	1M KOH	129	
CoP NTs	10	129	0.5 M H_2SO_4	60	41a
np-CoP NWs/Ti	20	95	0.5 M H_2SO_4	65	50
FeP NA/Ti	20	72	0.5 M H_2SO_4	38	46

Table S2 Calculations of the exchange current densities of $Ni_{12}P_5$, Ni_2P and Ni_5P_4 NCs by using extrapolation methods.

Catalyst	log(|j (mA·cm^{-2})|) at η=0 V	Exchange current densities j_0 [μA·cm^{-2}]
$Ni_{12}P_5$	-1.544	28.57
Ni_2P	-1.338	45.92
Ni_5P_4	-1.244	57.02