Supporting information

High-efficiency hydrogen evolution catalyzed by iron phosphide nanocrystals

Zhichao Gao,[a] Qian Gao,[a] Zhipeng Liu,[a] Cong Zhang,[a] Xiaoting Zhang,[a] Xin Liu,[a] Runwei Wang[b] and Nan Li*[a]

[a]College of Material Science and Engineering, Key Laboratory of Automobile Materials of Ministry of Education, Jilin University, 2699 Qianjin Street, Changchun, 130012, P. R. China.

[b]State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun, 130012, P. R. China.

*Corresponding author. Phone: +86 43185094856. Fax: +86 43185094856.

E-mail address: lin@jlu.edu.cn

Synthesis of CoP/C NCs

1.455 g of cobalt nitrate hexahydrate ($Co(NO_3)_3 \cdot 6H_2O$) was ground with 0.787 g of ammonium bicarbonate (NH_4HCO_3) in a mortar. The reagents were ground until the bubbling ceased (~5-10 min) and then 0.24 g carbon black (Carbot Vulcan XC72R) (with Co/C mole ratio of 1/4) was added to the slurry. The following processes were the same as that of Fe_2O_3/C.

Synthesis of Ni_2P/C NCs

1.454 g of nickel nitrate hexhydrate ($Ni(NO_3)_3 \cdot 6H_2O$) was ground with 0.787 g ammonium bicarbonate (NH_4HCO_3) in a mortar. After ~10 min, 0.24 g of carbon black (Carbot Vulcan XC72R) (with Ni/C mole ratio of 1/4) was added to the slurry. The following processes were the same as that of Fe_2O_3/C except that both the calcination and

the phosphidation step were prolonged from 1h to 2h.

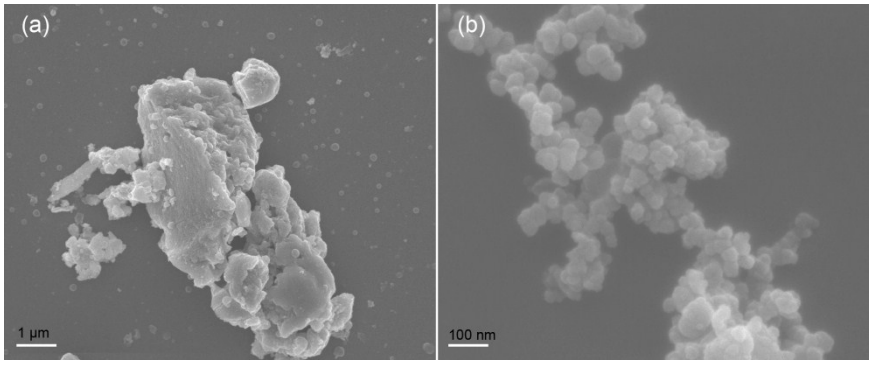

Fig. S1 SEM image of pure FeP (a) and bare carbon black (b).

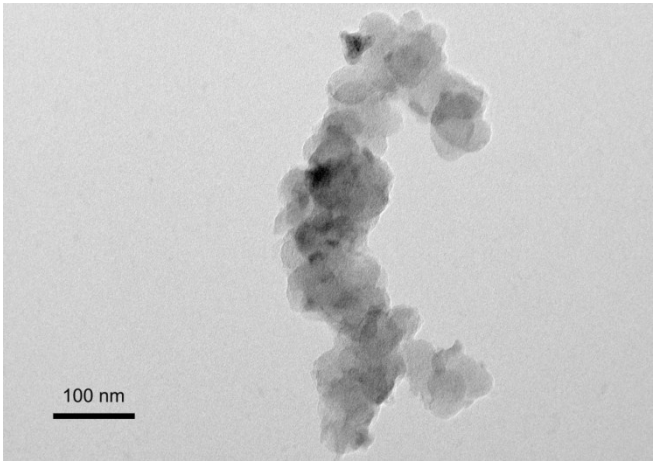

Fig. S2 Low-resolution TEM image of FeP/C NCs.

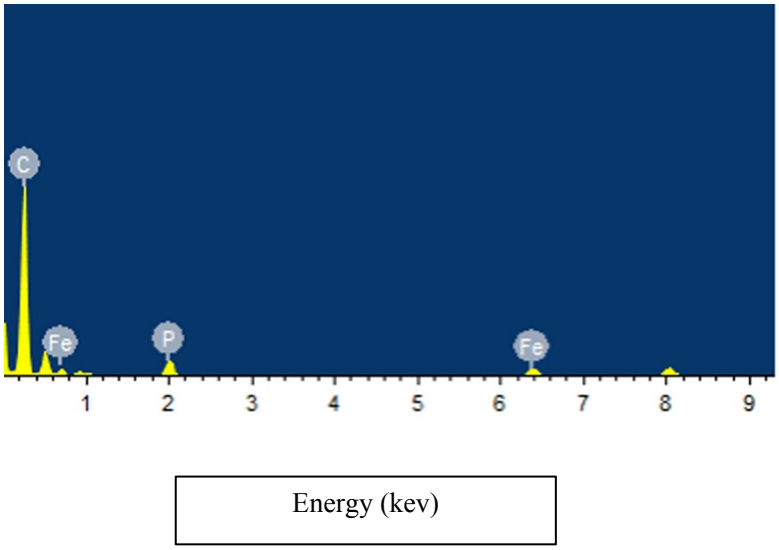

Fig. S3 EDS spectrum of FeP/C NCs.

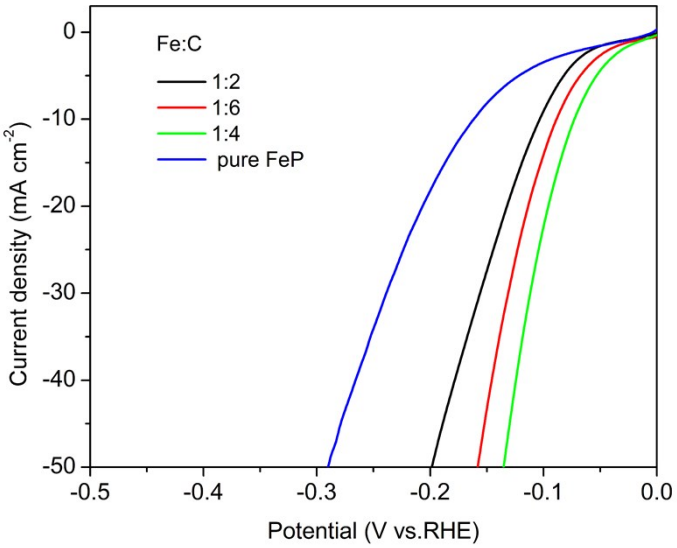

Fig. S4 Polarization curves of FeP/C NCs catalysts synthesized with various Fe/C mole ratio.

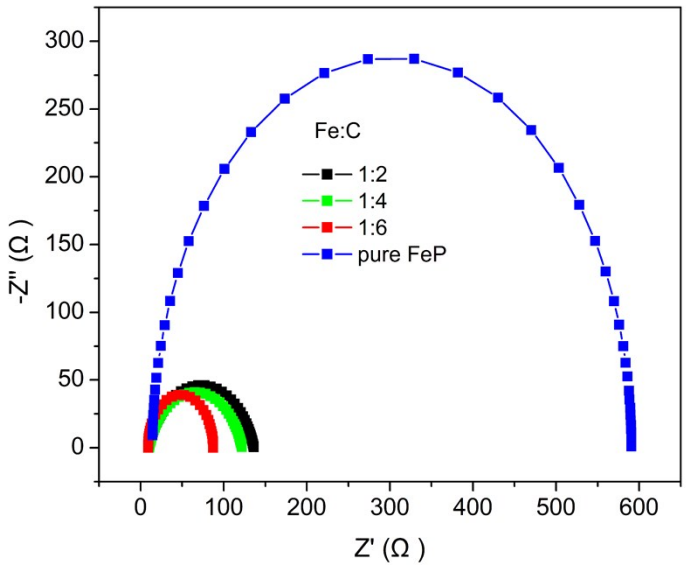

Fig. S5 Nyquist plots of FeP/C NCs catalysts synthesized with various Fe/C mole ratio.

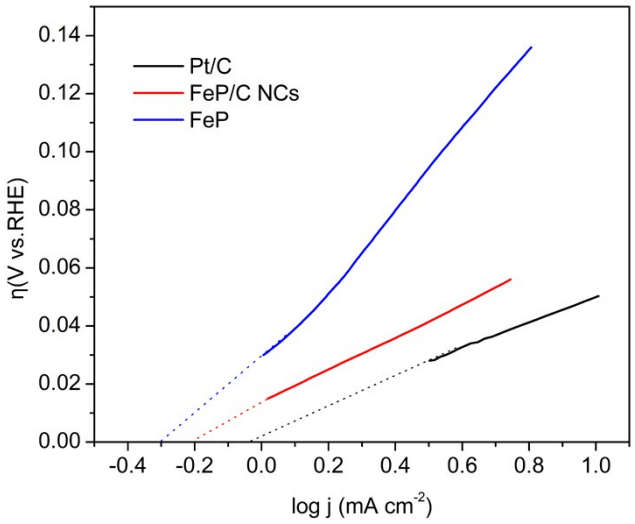

Fig. S6 Calculation of exchange current density for FeP/C NCs, pure FeP and Pt/C.

Exchange current density (j_0) was calculated using extrapolation methods. When the value of overpotential (η) is 0, the log j values of FeP/C, FeP and Pt/C are -0.2, -0.3 and -0.02 respectively. Based on Tafel equations, j_0 was calculated to be 0.631, 0.501 and 0.955 mA cm^{-2} for FeP/C, FeP and Pt/C respectively.

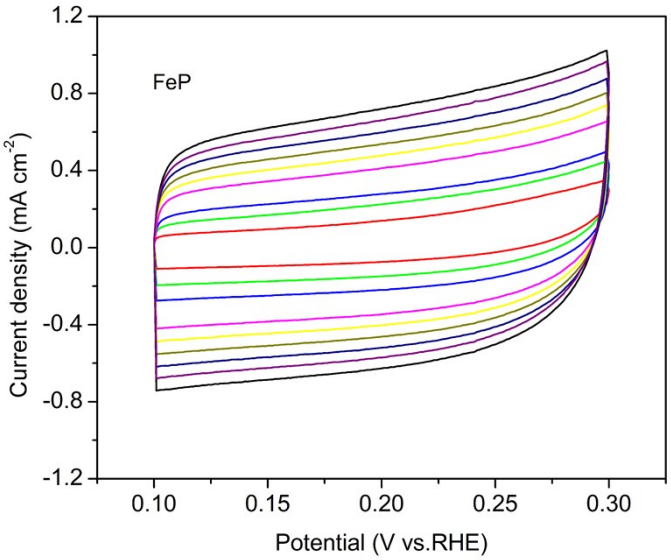

Fig. S7 Cyclic voltammograms (CV) recorded for pure FeP at various scan rates.

Table S1 Comparison of the HER performances for recently reported transition metal phosphide-based catalysts (in 0.5M H_2SO_4 electrolyte).

Catalyst	Current density (j, mA/cm^2)	η at the corresponding j (mV)	Exchange Current density (mA/cm^2)	Tafel slope (mV/dec)	Ref.
FeP/C NCs	10	70	0.631	56	This work
Pure FeP	10	157	0.501	138	This work
CoP/C NCs	10	117	--	58	This work
Ni_2P/C NCs	10	253	--	92	This work
FeP-GS	10	123	0.12	50	[33]
FeP array	10	96	0.17	39	[35]
FeP_2 array		61	0.55	31	
FeP/CC	10	39	0.59	32	[36]
FeP nanosheets	10	~240	--	67	[37]
FeP NRs	10	120	0.062	55	[38]
FeP nanrod /Ti	10	85	--	60	[39]
FeP NPs	10	112	0.22	58	[40]
FeP/NCNT	10	113	0.15	59	[41]
FeP NA/Ti	10	55	0.42	38	[44]
$Fe_{0.5}Co_{0.5}P$/CC	10	37	--	30	[45]
CoP/CNT	10	122	0.13	54	[16]
CoP NWs	10	110	0.15	54	[17]
CoP NSs		164	0.032	61	
CoP NPs		221	0.054	87	

CoP nanotube	10	129	--	60	[18]
u-CoP/Ti	10	45	--	49.3	[19]
CoP/Ti	10	90	--	43	[20]
CoP/CC	10	67	0.288	51	[21]
CoP-RGO	10	156.87	0.057	70.2	[22]
Ni_2P/Ti	20	138	--	60	[23]
Cu_3P NW/CF	10	143	0.18	67	[24]
Amorphous MoP nanoparticles	10	90	0.12	45	[29]
WP NAs/CC	10	130	0.29	69	[30]
FeS_2 film	4	190 ~ 270	$5.2e^{-4}$	62.5	[9]
$FeSe_2$ film	4	190 ~ 270	$3.0e^{-4}$	65.3	[9]