Electronic Supplementary Information

NiP₂ nanosheet arrays supported on carbon cloth: an efficient 3D hydrogen evolution cathode in both acidic and alkaline solutions

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Experimental Section

Materials: Sodium hypophosphite (NaH₂PO₂) was purchased from Aladdin Ltd. (Shanghai, China). Nitric acid (HNO₃), nickel nitrate hexahydrate (Ni(NO₃)₂.6H₂O), hexamethylene tetramine (HMT) were bought from Beijing Chemical Corporation. CC was provided by Hongshan District, Wuhan Instrument Surgical Instruments business. All the reagents were used as received. The water used throughout all experiments was purified through a Millipore system.

*Synthesis of Ni(OH)*₂ *NS/CC:* Typically, CC was carefully cleaned with concentrated HNO₃ to remove impurity of surface, and then deionized water and ethanol were used for several times to ensure the surface of the CC was well cleaned. The cleaned CC ($2 \text{ cm} \times 3 \text{ cm}$) was immersed into a 36 mL aqueous solution containing 5 mmol Ni(NO₃)₂.6H₂O and 10 mmol HMT at room temperature. The aqueous solution and the CC were transferred to a 40 mL Teflon-lined stainless-steel autoclave and maintained at 100 °C for 10 h, and then allowed to cool down. Then the CC with precursor was wished with water several times and dried in air.

*Synthesis of NiP*₂*NS/CC*: Ni(OH)₂ NS/CC and NaH₂PO₂ with 5:1 mole ratio of P/Ni were placed at two separate positions in one closed porcelain crucible with NaH₂PO₂ at the upstream side of the furnace. Subsequently, the samples were heated at 300 °C for 2 h with a heating speed of 2 °C/min in a static Ar atmosphere. After that, NiP₂ NS/CC was collected after cooled to ambient temperature under Ar. The loading for NiP₂ on CC was determined to be 4.3 mg/cm² with the use of a high precision microbalance. *Characterizations:* Powder XRD data were acquired on a RigakuD/MAX 2550 diffractometer with Cu

K α radiation (λ =1.5418 Å). SEM measurements were carried out on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV.

BET SSA and pore size were analyzed using a Quantachrome NOVA 1000 system at liquid N₂ temperature. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The generated gas was confirmed by gas chromatography (GC) analysis and measured quantitatively using a calibrated pressure sensor to monitor the pressure change in the cathode compartment of a H-type electrolytic cell. The FE was calculated by comparing the amount of measured hydrogen generated by potentiostatic cathodic electrolysis with calculated hydrogen (assuming 100% FE). The rough agreement of both values suggests nearly 100% FE for hydrogen evolution in both acidic and basic solutions. GC analysis was carried out on GC–2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of 1 point per second.

Electrochemical measurements: All electrochemical measurements were conducted in a typical threeelectrode setup with an electrolyte solution of 0.5 M H₂SO₄ or 1.0 M KOH, using NiP₂ NS/CC as the working electrode, a graphite plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. In all measurements, the SCE reference electrode was calibrated with respect to reversible hydrogen electrode (RHE). LSV measurements were conducted in electrolyte with scan rate of 2 mV/s. All the potentials reported in our work were vs. RHE. In 0.5 M H₂SO₄, E (RHE) = E (SCE) + 0.281 V. In 1.0 M KOH, E (RHE) = E (SCE) + 1.068 V. Onset overpotentials were determined based on the beginning of linear regime in the Tafel plot and no iR compensation was applied for all the electrochemical measurements.



Fig. S1 (a) Low- and (b) high-magnification SEM images of $Ni(OH)_2 NS/CC$ after sonication for 30 min.



Fig. S2 (a) Nitrogen adsorption/desorption isotherm plot and (b) the BJH pore–size distribution curve of NiP₂ nanosheets.



Fig. S3 (a) SEM image, (b) EDX spectrum, and (c) XRD pattern for Ni(OH)₂ MPs.



Fig. S4 (a) SEM image, (b) HRTEM image, (c) EDX spectrum, and (d) XRD pattern for NiP₂MPs.



Fig. S5 (a) Nitrogen adsorption/desorption isotherm plot and (b) the BJH pore–size distribution curve of NiP₂ MPs.

Table S1 Comparison of HER performance in acid media for of NiP $_2$ NS/CC with other non-noble-metalHER electrocatalysts (a catalysts directly grown on current collectors).

Catalyst	Current density (j, mA cm ⁻²)	η at the correspondi ng j (mV)	Exchange current density (mA cm ⁻²)	Ref.
double-gyroid MoS ₂ /FTO ^a	2	190	6.9×10 ⁻⁴	Nat. Mater., 2012, 11, 963-969
metallic MoS ₂ nanosheets	10	195	-	J. Am. Chem. Soc., 2013, 135, 10274-10277
defect-rich MoS ₂	13	200	8.9×10 ⁻³	Adv. Mater, 2013, 25, 5807-5813
MoO ₃ -MoS ₂ /FTO ^a	10	310	8.2×10 ⁻⁵	Nano Lett., 2011, 11 , 4168-4175
bulk Mo ₂ C	1	~150	1.3×10-3	Angew. Chem. Int. Ed., 2012, 51 , 12703- 12706
bulk MoB	1	~150	1.4×10 ⁻³	Angew. Chem. Int. Ed., 2012, 51 , 12703- 12706
nanoporous Mo ₂ C nanowires	60	200	-	Energy Environ. Sci., 2014, 7, 387-392
NiMoN _x /C	5	220	0.24	Angew. Chem. Int. Ed., 2012, 51 , 6131- 6136
$Co_{0.6}Mo_{1.4}N_2$	10	200	0.23	J. Am. Chem. Soc., 2013, 135, 19186-19192
Co-NRCNTs	10	260	0.01	Angew. Chem. Int. Ed., 2014, 126 , 4372- 4376
exfoliated WS2 nanosheets	10	~220	0.02	Nat. Mater., 2013, 12, 850-855
WS ₂ /graphene	10	~270	-	Angew. Chem. Int. Ed., 2013, 52 , 13751- 13754
CoSe ₂ NP/CP ^a	10	139	(4.9±1.4) ×10 ⁻³	J. Am. Chem. Soc., 2014, 136, 4897-4900
Ni ₂ P hollow nanoparticles	10	116	0.033	J. Am. Chem. Soc., 2013, 135, 9267-9270
Ni ₂ P/Ti ^a	10	120	-	Nanoscale, DOI: 10.1039/c4nr03037k
Ni ₂ P nanoparticles	20	140	-	Phys. Chem. Chem. Phys., 2014, 16 , 5917- 5921
FeP nanosheets	10	~240	-	Chem. Commun., 2013, 49, 6656-6658
CoP nanoparticles	20	95	0.14	Angew. Chem. Int. Ed., 2014, 53 , 5427- 5430-
CoP nanotubes	10	144	-	J. Mater. Chem. A, 2014, 2, 14812-14816
CoP/CNT	10	122	0.13	Angew. Chem. Int. Ed., 2014, 53 , 6710- 6714
CoP/CC ^a	10	67	0.288	J. Am. Chem. Soc., 2014, 136, 7587-7590
CoP/Ti ^a	10	90	-	Chem. Mater., 2014, 26, 4326-4329
interconnected network of MoP nanoparticles	10	125	0.086	Adv. Mater., 2014, 26, 5702-5707
bulk MoP	30	180	0.034	Energy Environ. Sci., 2014, 7, 2624-2629
amorphous WP nanoparticles	10	120	-	Chem. Commun., 2014, 50 , 11026-11028
	10	75		
NiP ₂ NS/CC ^a	20	99	0.26	This work
	100	204		



Fig. S6 Calculated exchange current density for $NiP_2 NS/CC$ in 0.5 M H_2SO_4 by applying extrapolation method to the Tafel plot.



Fig. S7 (a) XRD pattern, (b, c) SEM images, and (d) EDX spectrum of Ni_2P NS/CC. (e) HRTEM image and (f) SAED pattern of the Ni_2P NS.



Fig. S8 Polarization curves for NiP₂ NS/CC and Ni₂P NS/CC in 0.5 M H_2SO_4 with a scan rate of 2 mV/s.

The number of active sites (n) was determined using cyclic voltammograms (CVs) data (Fig. S9) collected between -0.2 V and +0.6 V *vs*. RHE in 1.0 M PBS solution with a scan rate of 50 mV/s. While it is difficult to assign the observed peaks to a given redox couple, n should be proportional to the integrated charge over the whole potential range. Assuming a one-electron process for both reduction and oxidation, the upper limit of n could be calculated with the following equation:

n = Q/2F

where Q is the voltammetric charge, F is Faraday constant (96480 C mol⁻¹). For Ni₂P NS/CC, Q is 7.017×10^{-3} C, n (mol) = $7.017 \times 10^{-3}/(2 \times 96480)$ mol = 3.63×10^{-8} mol. For Ni₂P NS/CC, the calculated number of active site is 1.06×10^{-7} , which was nearly three times for Ni₂P NS/CC.



Fig. S9 CVs of the CC, NiP₂ NS/CC and Ni₂P NS/CC recorded at pH = 7 between -0.2 V and +0.6 V vs. RHE at a scan rate of 50 mV/s.



Fig. S10 Polarization curves for NiP₂ MPs/CC and NiP₂ NS/CC in 0.5 M H_2SO_4 with a scan rate of 2 mV/s.



Fig. S11 Nyquist plots for NiP₂NS/CC and NiP₂MPs/CC at an overpotential of 50 mV.



Fig. S12 (a, b) SEM images, (c) EDX spectrum, and (d) XRD pattern (the peaks marked "*" arise from the CC substrate) for NiP₂NS/CC after durability test.

Catalyst	Current density (j, mA cm ⁻²)	Overpotential at the corresponding <i>j</i> (mV)	Ref.	
bulk MoB	10	225	Angew. Chem. Int. Ed., 2012, 54, 12703	
Ni	10	400	Angew. Chem. Int. Ed., 2012, 54, 12703	
Co-NRCNTs	1	160	Anony Cham Int Ed 2014 126 4272	
	10	370	<i>Angew. Chem. Int. Ed., 2014</i> , 120 , 4372	
CoP/CC ^a	1	115	I Am Cham Soc 2014 136 7597	
	10	209	J. Am. Chem. 30C., 2014, 130 , 7387	
Ni ₂ P nanoparticles	20	250	Phys. Chem. Chem. Phys., 2014, 16, 5917	
Co-S/FTO ^a	1	480	J. Am. Chem. Soc., 2013, 135, 17699	
amorphous MoS ₂ /FTO ^a	10	540	Chem. Sci., 2011, 2, 1262	
Ni-Mo alloy/Ti foil ^a	10	80	ACS Catal., 2013, 3 , 166	
Ni wire	10	350	ACS Catal., 2013, 3 , 166	
NiP ₂ NS/CC ^a	10	102	This work	

Table S2 Comparison of HER performance in alkaline media for NiP₂NS/CC with other non-noblemetal HER electrocatalysts (*^a* catalysts directly grown on current collectors).



Fig. S13 The amount of H_2 theoretically calculated (black curve) and experimentally measured (red curve) versus time for NiP₂NS/CC at (a) pH 0 and (b) pH 14 under overpotentials of 200 mV for 5000 seconds.



Fig. S14 XPS spectra in the (a) Ni(2p) and (b) P(2p) regions for NiP₂.