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# **Electronic Supplementary Information (ESI)**

# In situ surface engineering of nickel inverse opal for enhanced overall electrocatalytic water splitting

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Fig. S1. Schematic of the in-situ phosphorization process.

#### Electrochemical area measurement:



**Fig. S2.** (a) CV curves for Ni inverse opal between 0.1 and 0.2 V at 2, 4, 6, 8 and 10 mV s<sup>-1</sup> and (b) the relation of the capacitive currents with respect to scan rates.

To estimate the surface of inverse opal, we measured the double-layer capacitance ( $C_{dl}$ ) of Ni inverse opal. According to the previously reported approach,<sup>[1,2]</sup> we calculated the specific surface area by considering the relative roughness factor of the Ni inverse opal.

To measure the double-layer capacitance, CV scanning is conducted between 0.10 and 0.20 V (vs RHE) at varied scan rates (2, 4, 6, 8 and 10 mV s<sup>-1</sup>). A potential range of 0.1-0.2 V is selected for the capacitance measurements because no obvious faradaic reactions can be observed in this region for all electrodes. The capacitive currents of  $\Delta J/Ja-Jc/2$  are plotted with respect to the CV scan rates. The trend follows the good linear relation. The slope of the fitted line is the double layer capacitance (C<sub>dl</sub>), which is proportional to the surface area of the electrode. As shown in Fig. S2, we determined the specific capacitance to be 3.7 mF cm<sup>-2</sup> for Ni inverse opal.

The C<sub>dl</sub> is directly used to estimate the relevant specific surface area by using the specific capacitance value for a flat electrode with real surface area 1 cm<sup>2</sup>. We assumed 40  $\mu$ F cm<sup>-2</sup> for a flat electrode provided in Jaramillo et al<sup>[2,3]</sup> and Kim et al<sup>[4]</sup> for calculation here. The nickel loading (*m*) on the Ni inverse opal

electrode is about 4.5 mg cm<sup>-2</sup>. Thus, the specific surface area (*S*) of Ni inverse opal can be calculated as follows:

$$S = \frac{A}{m} = \frac{\frac{3.7 \times 1000}{40}}{\frac{4.5}{1000}} \frac{m^2}{g} \approx 2.06 \frac{m^2}{g}$$

The specific surface area of Ni inverse opal can be approximately considered to be 2.06 m<sup>2</sup> g<sup>-1</sup>.

Characterization of Fe:Ni<sub>2</sub>P catalysts:



**Fig. S3.** XRD of Fe:Ni/Ni<sub>2</sub>P inverse opal.



Fig. S4. SEM image and elemental mapping of  $Fe:Ni/Ni_2P$  inverse opal.



Fig. S5. EDX element distribution of a) Ni/Ni<sub>2</sub>P and b) Fe:Ni/Ni<sub>2</sub>P inverse opal, respectively, under the

## STEM mode.

To investigate the Fe doping in STEM, we dissolved the metallic Ni scaffold of inverse opals by HCl and collected Ni<sub>2</sub>P and Fe:Ni/Ni<sub>2</sub>P nanosheets. The cleaned nanosheets were loaded for the EDX

characterization. Fig. S5a shows that  $Ni_2P$  nanosheets have the distribution of Ni and P elements. In the Fe: $Ni_2P$  sample (Fig. S5b), Fe distribution follows the trends of Ni and P elements. In conjunction with XRD in Fig. S3 and the SEM observation of the whole sample in Fig. S4, we deduced that Fe is doped into  $Ni_2P$ .



Fig. S6. XPS spectra of Fe 2p from Ni/Ni<sub>2</sub>P and Fe:Ni/Ni<sub>2</sub>P inverse opal.

The XPS spectra in Fig. S6 present the Fe signals of Ni/Ni<sub>2</sub>P and Fe:Ni<sub>2</sub>P inverse opals. The broad Fe  $2p_{3/2}$  signal could be fitted into two peaks at 710.4 and 713.4 eV, which correspond to Fe<sup>2+</sup> and Fe<sup>3+</sup>, respectively.<sup>[5-7]</sup>

## Fabrication and characterization of bulk Ni/Ni<sub>2</sub>P(TOP):

To verify the roles of the exposed  $\{001\}$  planes in the electrocatalysis, a bulk Ni/Ni<sub>2</sub>P sample with random plane exposure was prepared using a TOP as the phosphorus source. During the high-temperature treatment, Ni<sub>2</sub>P was formed on the surface of metallic Ni foil. Fig. S7 shows the SEM morphologies of the obtained Ni<sub>2</sub>P. The TOP-derived Ni<sub>2</sub>P has very different morphologies as compared to the Ni<sub>2</sub>P which was prepared with PH<sub>3</sub>. The surface Ni<sub>2</sub>P particles were ultrasonicated and collected for TEM observation. Fig. S8a,b present the TEM images of the TOP-derived Ni<sub>2</sub>P particles. The lattice fringes in Fig. S8b and SAED pattern in Fig. S8c indicate that the TOP-derived particles actually consist of Ni<sub>2</sub>P polycrystals. No particular crystallographic planes are favorably exposed. Basically, an aggregate of multiple planes exposure was obtained. The XRD pattern in Fig. S8d confirms that the TOP phosphorization procedure produces the well-crystallized Ni<sub>2</sub>P.



Fig. S7. (a, b) SEM images of bulk Ni/Ni<sub>2</sub>P(TOP).



Fig. S8. (a) TEM image, (b) HRTEM image, (c) SAED pattern, and (d) XRD patterns of bulk Ni/Ni<sub>2</sub>P(TOP).



Fig. S9. (a) LSV polarization curves and (b) Tafel plots of bulk Ni/Ni<sub>2</sub>P and Ni/Ni<sub>2</sub>P(TOP).

Ni/Ni <sub>2</sub> P(TOP).					
Sample —	HER				
	$\eta_{20}\left[mV\right]$	$\eta_{100} \left[mV\right]$	Tafel slope [mV dec <sup>-1</sup> ]		
Ni/Ni <sub>2</sub> P inverse opal	73	145	76		
Bulk Ni/Ni <sub>2</sub> P	306	387	98		
Bulk Ni/Ni <sub>2</sub> P(TOP)	394	489	125		

Table S1. Summary of the electrocatalytic properties of Ni/Ni<sub>2</sub>P inverse opal, bulk Ni/Ni<sub>2</sub>P, and



Fig. S10. Cyclic voltammograms between 0.1 and 0.2 V at 2, 4, 6, 8 and 10 mV s<sup>-1</sup> and the corresponding linear fitting of the capacitive currents with respect to scan rates: (a) and (b) Ni/Ni<sub>2</sub>P inverse opal, (c) and (d) bulk Ni/Ni<sub>2</sub>P. The calculated C<sub>dl</sub> values are shown in the upper-left corner of (b) and (d) for Ni/Ni<sub>2</sub>P inverse opal and bulk Ni/Ni<sub>2</sub>P, respectively.

To compare the surface area of bulk Ni/Ni<sub>2</sub>P and Ni/Ni<sub>2</sub>P inverse opal, the double-layer capacitances were measured using the same method as shown in Fig. S2. Because the material surface properties are

the same, the double-layer capacitances are proportional to their surface area.



Fig. S11. (a) HER and (b) OER LSV polarization curves of the Ni/Ni<sub>2</sub>P and Fe:Ni/Ni<sub>2</sub>P inverse opal

## samples, respectively, before and after grinding.

To elucidate what role the inverse opal structure plays on the electrocatalytic activities, a control sample was prepared by grinding the inverse opals and destroying the inverse opal structures. The collected particles together with Nafion were coated on a titanium foil for HER and OER tests. Fig. S11 shows that the resulted particles exhibit much lower HER and OER activities than the integrated inverse opals. In particular, the ground Ni/Ni<sub>2</sub>P particles require 156 mV more overpotential to drive the HER at 20 mA cm<sup>-2</sup>. The large difference on overpotentials may mainly originate from the accessible active sites, which the inverse opal structure is able to provide. The limited mass transport underneath the surface Ni/Ni<sub>2</sub>P particles may also contribute to the overall overpotential. Therefore, the Ni/Ni<sub>2</sub>P inverse opal fabricated by the in situ phosphorization is able to provide the more active sites because of the 3D inverse opal structures and {001} planes exposure.



Fig. S12. Nyquist plots (a) and Bode plots (b) of Ni/Ni<sub>2</sub>P inverse opal at three different applied overpotentials during HER tests. Nyquist plots (c) and Bode plots (d) of Ni/Ni<sub>2</sub>P inverse opal at three different applied overpotentials during OER tests.



Fig. S13. Nyquist plots (a) and Bode plots (b) of Ni inverse opal at three different applied overpotentials during HER tests. Nyquist plots (c) and Bode plots (d) of Ni inverse opal at three different applied overpotentials during OER tests.



Fig. S14. Nyquist plots (a) and Bode plots (b) of bulk Ni/Ni<sub>2</sub>P at three different applied overpotentials during HER tests. Nyquist plots (c) and Bode plots (d) of bulk Ni/Ni<sub>2</sub>P at three different applied overpotentials during OER tests.

	$R_{ct}[\Omega]$					
		HER			OER	
	$\eta_{onset}$ -50 mV	$\eta_{\text{onset}}mV$	$\eta_{onset}$ +50 mV	$\gamma \eta_{onset}$ -50 mV	$\eta_{\text{onset}}mV$	$\eta_{onset}$ +50 mV
Ni/Ni <sub>2</sub> P inverse opal	532	198	86	9.33	2.62	1.39
Ni inverse opal	1783	834	232	83.2	27.93	8.42
bulk Ni/Ni <sub>2</sub> P	2683	1159	316	168.79	86.55	11.59

Table S2. Charge-transfer impedances at different overpotentials for various catalysts.

Material Characterization prior to and after HER/OER tests:

To evaluate the stability of HER/OER catalysts, additional characterizations on Ni/Ni<sub>2</sub>P and Fe:Ni/Ni<sub>2</sub>P inverse opal were conducted prior to and after HER/OER tests.

Fig. S15 shows the XPS characterization of Ni/Ni<sub>2</sub>P inverse opal prior to and after the HER tests. The high-resolution XPS spectra of Ni and P signals of the Ni/Ni<sub>2</sub>P inverse opal after HER tests resembles those of untested samples except the slight intensity changes, indicating the retention of the electrocatalyst. The peak around 852.7 eV in the Ni  $2p_{3/2}$  spectrum (Fig. S15a) is typically due to Ni phosphide.<sup>[8,9]</sup> The peak at a higher binding energy of 855.5 eV is usually attributed to NiO<sub>x</sub>, indicating the surface oxidation.<sup>[9,10]</sup> The weak and broad peak around 860.2 eV is regarded as the satellite of the Ni  $2p_{3/2}$  component that originates from nickel phosphide.<sup>[9]</sup> The P 2p spectrum (Fig. S15b) has two characteristic peaks around 129.5 and 133.4 eV, which have been attributed to phosphorus in phosphide and phosphate species, respectively.<sup>[11,12]</sup> These results are in agreement with previous reports.<sup>[9]</sup>



Fig. S15. (a) Ni 2p<sub>3/2</sub> and (b) P 2p XPS spectra for untreated and post-HER Ni/Ni<sub>2</sub>P inverse opal.

Fig. S16 shows the XPS characterization of Fe:Ni/Ni<sub>2</sub>P inverse opal prior to and after the OER testing.

The high-resolution Ni  $2P_{3/2}$  XPS spectrum for the post-OER Fe:Ni/Ni<sub>2</sub>P inverse opal displays a significant intensity decrease at 852.7 eV while an increase at 855.2 eV, confirming the partial oxidation of Ni<sub>2</sub>P to nickel oxides (Fig. S16a). This oxidation phenomenon is also revealed by the increased intensity of the peaks that is ascribed to oxidized P species in the high-resolution P 2p XPS spectrum (Fig. S16b).



Fig. S16. (a) Ni 2p<sub>3/2</sub> and (b) P 2p XPS spectra for untreated and post-OER Fe:Ni/Ni<sub>2</sub>P inverse opal.

For the Fe 2P XPS spectrum, Fe:Ni/Ni<sub>2</sub>P inverse opal shows a tilted baseline. A smooth base line is observed for Ni/Ni<sub>2</sub>P inverse opal (Fig. S17), suggesting the Fe incorporation. The peaks of Fe 2p3/2 appear at around 710 and 713 eV, which are assigned to Fe<sup>2+</sup> and Fe<sup>3+</sup>, respectively.<sup>[5-7]</sup> After the OER tests, the increased peak area ratio of Fe<sup>3+</sup>/Fe<sup>2+</sup> for Fe:Ni/Ni<sub>2</sub>P inverse opal may be caused by the oxidation phenomenon during the anodic polarization.



Fig. S17. XPS spectra of Fe 2p from the inverse opal electrodes.



Fig. S18. Raman spectra of the inverse opal electrodes.

Fig. S18 shows the Raman spectra (Fig. S18) of the inverse opal electrodes prior to and after the electrolysis tests. It should be noted that no Raman vibration modes are detected on the Ni<sub>2</sub>P crystals from 200 to 900 cm<sup>-1</sup>, which is consistent with the previously reported results.<sup>[13,14]</sup> The similar base line signal

for Ni/Ni<sub>2</sub>P inverse opal prior to and after HER tests suggests the stability of the electrocatalyst. However, for Fe:Ni/Ni<sub>2</sub>P inverse opal, there has an obvious peak around 546 cm<sup>-1</sup> after the OER testing. We can assign the peak to the longitudinal optical phonon modes of Ni oxides,<sup>[15,16]</sup> indicating the surface oxidation of the catalyst during OER process. These Raman results agree with the above XPS analyses.



Faradaic efficiency measurements:

Fig. S19. Optical images of the H shape cell with two separate compartments: (a) side view, (b) top view.c) Optical image of the homemade water splitting device. A is the Ag/AgCl reference electrode, B is the working electrode, C and G are the gas outlets, D and F are the gas inlets, H is the Nafion membrane, and E is the counter electrode.

The Faraday efficiencies of HER or OER are calculated based on the ratio of the amount of evolved  $H_2$  or  $O_2$  over the theoretical amount of  $H_2$  or  $O_2$ .<sup>[17,18]</sup>

The amount of  $H_2$  evolution is measured by a water displacement method (as shown in Fig. S19). To avoid the mixing of  $O_2$  and  $H_2$ , an H-cell was used with a Nafion membrane to separate the two compartments. The theoretical gas evolution is determined by assuming that 100% of the current efficiencies during the electrolysis based on the Faraday law. Fig. S20 shows the amount of  $H_2$  and  $O_2$ evolved experimentally versus the amount of  $H_2$  and  $O_2$  theoretically expected in the electrolysis for 90 min, respectively. The average Faraday efficiencies of Ni/Ni<sub>2</sub>P and Fe:Ni<sub>2</sub>P inverse opals in 90 min are 96.3% and 95.4%, respectively.



Fig. S20. Faraday efficiency of  $Ni/Ni_2P$  and Fe: $Ni_2P$  inverse opal for (a) HER and (b) OER, respectively.

Table S3. Comparison of electrocatalytic activity of IrO2 and Pt/C electrodes cell for alkaline full water

splitting.

Electrodes cell	J (mA cm <sup>-2</sup> )	η (mV)	Ref.
	10	~1.55	
IrO <sub>2</sub> //Pt/C	20	~1.59	Adv. Mater. 2017 29, 1606200.
	100	~1.86	
IrO <sub>2</sub> //Pt/C	7.2	1.61	<i>Adv. Funct. Mater.</i> <b>2016</b> , 26, 3314.

IrO <sub>2</sub> /C//Pt/C	10	1.52	ACS Catal. <b>2017</b> , 7,2357.
	10	~1.60	Angew. Chem. Int. Ed.
$IIO_2//Pt/C$	20	~1.70	<b>2016</b> , 128, 6814.
	10	1.549	
IrO <sub>2</sub> //Pt/C	20	1.604	This work
	100	1.858	

Table S4. Comparison of electrocatalytic HER activity of various non-precious catalysts in 1 M KOH

electrol	yte.
	Т

Material	J (mA cm <sup>-2</sup> )	η (mV)	Tafel slop (mV dec <sup>-1</sup> )	Ref.
C CN	10	138	<i>c c</i>	J. Am. Chem. Soc. 2015
Co-C-N	100	212	22	137, 15070.
Co@NC/NG	20	200	79.3	<i>Chem. Mater.</i> <b>2015</b> , 27, 2026.
Co-NRCNTs	10	260	80	Angew. Chem. Int. Ed. <b>2014</b> , 53,4372.
Ni <sub>5</sub> P <sub>4</sub> /NF	15	150	83	Angew. Chem. Int. Ed. <b>2015</b> , 54, 12361.
NiSe/NF	10	≈96	120	Angew. Chem. Int. Ed.
	20	≈160	120	<b>2015</b> , 54, 9351.
FeP NAs/CC	20	250	146	ACS Catal. <b>2014</b> , 4, 4065.
np-CoP/Ti	20	150	71	<i>Phys. Chem. Chem. Phys.</i> <b>2014</b> , 16, 16909.
NED NE/CC	10	102	0.4	Nanoscale <b>2014</b> , 6,
$N1P_2 NS/CC$	100	270	04	13440.
α-CoSe/Ti	100	≈200	84	<i>Chem. Commun.</i> <b>2015</b> , 51, 16683.
NiMoN	10	109	95	<i>Adv. Energy Mater.</i> <b>2016</b> 6, 1600221.

Co(OH)2@PANI NSs/NF	100	240	91.6	<i>Adv. Mater.</i> <b>2015</b> , 27, 7051.	
Ni-P film	15	≈100	81	<i>ChemCatChem</i> <b>2016</b> 8, 106.	
Ni/Ni <sub>2</sub> P	20	73	76	This work	
Inverse Opal	100	145	70	I IIIS WOLK	

 Table S5. Comparison of electrocatalytic OER activity of various non-precious catalysts in 1 M KOH electrolyte.

Material	J (mA cm <sup>-2</sup> )	η (mV)	Tafel slop (mV dec <sup>-1</sup> )	Ref.
NiCo <sub>2</sub> O <sub>4</sub> NA/CC	20	390	90	Nanoscale
	100	470		2015,7, 13122.
Co <sub>3</sub> O <sub>4</sub> film	20	≈390	58.1	ACS Appl. Mater. Interfaces <b>2015</b> , 7, 24550.
	10	345		Angew. Chem. Int.
Co-P film	100	413	47	<i>Ed.</i> <b>2015</b> , 54, 6251.
NiO/Ni foam	10	345	53	J. Mater. Chem. A <b>2016</b> , 4, 9797.
NF@CoO LNSA@G	10	≈330		J Power Sources
	20	≈415	79	<b>2016</b> , 319, 159.
Co-Mn LDHs	20	340	54	<i>J. Am. Chem. Soc.</i> <b>2014</b> , 136, 16481.
NiCo LDH	100	>420	76	Nano Lett. 2015, 15, 1421.
Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub> /CNFs	10	430	61	<i>Adv. Mater.</i> <b>2015</b> , 27, 4752.
FeNC-800	10	410	137	<i>J. Phys. Chem. C</i> <b>2016</b> , 120, 11006.
N-G-CoO	10	340	87	<i>Energy Environ.</i> <i>Sci.</i> <b>2014</b> , 7, 609.
CP/CTs/Co-S	20	≈340	72	ACS Nano, <b>2016</b> , 10, 2342.
Fe:Ni/Ni <sub>2</sub> P Inverse Opal	20	285	48	This work

100

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Material	J (mA cm <sup>-2</sup> )	Cell voltage (V)	Ref.
Ni-P/CF	10	1.68	<i>J. Power Sources</i> <b>2015</b> , 299, 342.
$FeS_x$	10	≈2	<i>Adv. Energy Mater.</i> <b>2016</b> , 6, 1502095.
	10	1.71	Chem. Mater. 2015,
CO-r/INC	50	1.85	27, 7636.
NiSe <sub>2</sub> /Ti	10	1.66	ACS Appl. Mater. Interfaces, <b>2016</b> , 8, 4718.
Ni <sub>2</sub> P/NF	10	1.63	<i>Energy Environ. Sci.</i> <b>2015</b> , 8, 2347.
α-CoSe/Ti	10	1.65	<i>Chem. Commun.</i> <b>2015</b> , 51, 16683.
CoO <sub>x</sub> @CN	50	1.90	J. Am. Chem. Soc. <b>2015</b> , 137, 2688.
	10	1.63	Adv. Funct. Mater.
Cr @M-r	20	1.73	<b>2016</b> , 26, 4067.
Ni <sub>3</sub> S <sub>2</sub> /NF	13	1.76	J. Am. Chem. Soc. <b>2015</b> , 137, 14023.
NF-Ni <sub>3</sub> Se <sub>2</sub> /Ni	10	1.61	Nano Energy <b>2016</b> , 24, 103.
CP/CTs/Co-S	10	1.74	ACS Nano, <b>2016</b> , 10, 2342.
	10	1.441	
Fe:Ni/Ni <sub>2</sub> P//Ni/Ni <sub>2</sub> P Inverse Opal	20	1.523	This work
	50	1.629	

 Table S6. Comparison of electrocatalytic overall water splitting activity of various non-precious

 bifunctional catalysts in 1 M KOH electrolyte.

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