Electronic Supplementary Information

Experimental section

Materials: NH_4F, hexamethlene tetramine (HMT) and urea were purchased from Beijing Chemical Corp. NaH_2PO_2, $Co(NO_3)_2\cdot 6H_2O$ and $CoCl_2\cdot 6H_2O$ were purchased from Aladdin Ltd (China). Nickel foam was purchased from Shenzhen Green and Creative Environmental Science and Technology Co., Ltd. $RuCl_3\cdot 3H_2O$ was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. The water used throughout all experiments was purified through a Millipore system. All chemicals were used as received without further purification.

Preparation of $Co(H_2PO_4)_2\cdot 2H_3PO_4$ MW/NF, Co(OH)F NW/NF, $Co(OH)CO_3$ NW/NF and $Co(OH)_2$ NS/NF: To synthesize $Co(H_2PO_4)_2\cdot 2H_3PO_4$ MW/NF, NF was treated with 1 M HCl. Water and alcohol are used to remove residual organic species thoroughly. Then 0.475 g $CoCl_2\cdot 6H_2O$ was dissolved in water under vigorous stirring, followed by the addition of 0.283 g NaH_2PO_4. After 15 min stirring, the mixed solution was transferred to a Telfon-lined stainless steel autoclave. The pretreated NF was put into the autoclave and immersed in the reaction solution. The autoclave was sealed and kepted at 120 ºC for 24 h. The as-obtained material was washed with distilled water and ethanol, and dried at 60 ºC overnight. Co(OH)F NW/NF was prepared as follows. $Co(NO_3)_2\cdot 6H_2O$ (0.582 g), NH_4F (0.186 g) and urea (0.61 g) were dissolved in 40 ml water under ultrasonication for 10 min. Then the solution was transferred into a Teflon-lined stainless autoclave (50 ml), and a piece of NF was immersed into the autoclave contained reaction solution. The autoclave was sealed and maintained at 120 °C for 6 h. For synthesis of $Co(OH)CO_3$ NW/NF, 0.87 g $Co(NO_3)_2\cdot 6H_2O$, 0.296 g NH_4F and 0.9 g urea were dissolved in 50 ml deionized water and all transferred into a 50 ml polytetrafluoro-ethylene Teflon-lined stainless steel autoclave. The pretreated NF was immersed in the solution, sealed and kept at 120 °C for 6 h. To prepare $Co(OH)_2$ NS/NF, 1.4 g HMT and 1.45 g $Co(NO_3)_2\cdot 6H_2O$ were dissolved in 40 ml distilled water. After ultrasonication for 10 min, the solution was transferred to a 50 ml Teflon-lined stainless steel autoclave with a pretreated NF (3 cm × 2 cm), and kepted at 100 °C for 10 h in an oven.

Synthesis of CoP NS@MW/NF, CoP NW/NF and CoP NS/NF: The $Co(H_2PO_4)_2·2H_3PO_4$ MW/NF and 1.0 g NaH_2PO_2 were put into a porcelain boat and annealed at 300 °C for 2 h under Ar atmosphere. The resulting samples were immersed in water for 10 min to obtain CoP NS@MW/NF. CoP NW/NF and CoP NS/NF were prepared by phosphidation of Co(OH)F NW/NF and $Co(OH)_2$ NS/NF, respectively.

Synthesis of RuO_2: RuO_2 was prepared according to previous report.[1] Briefly, 2.61 g $RuCl_3·3H_2O$ and 1.0 ml NaOH (1.0 M) were added into 100 ml distilled water and stirred for 45 min at 100 °C. Then the solution was centrifuged for 10 min. The precipitate was collected and washed with water for several times. Finally, as-product was dried at 60 °C overnight and then annealed at 300 °C in air for 3 h.

Characterizations: XRD data were collected on a Rigaku X-ray diffractometer equipped with a Cu Kα radiation source. Scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) measurements were carried out on a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurements: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using a CoP NS@MW/NF, CoP NW/NF and CoP NS/NF as the working electrodes, respectively, a platinum wire as the counter electrode and Hg/HgO as the reference electrode. The potentials reported in this work were calibrated to reversible hydrogen electrode (RHE), with the following equation: $E\ (RHE) = E\ (Hg/HgO) + (0.098 + 0.059\ pH)\ V$. Polarization curves were obtained using linear sweep voltammetry with a scan rate of 5 mV s^{-1}. All experiments were carried out at room temperature (~25 °C).

Ion chromatographic measurements: All ion chromatographic measurements were carried out with a Dionex ICS 1100 instrument with suppressed conductivity detection. The suppressor (AERS 500, Dionex) was regenerated with an external water module. The system was equipped with the analytical column IonPac AS 14 or IonPac AS 22 from Dionex (4250 mm) with the corresponding guard column AG 14 or AG 22 (450 mm), respectively. The injection volume was 25 µl.

Determination of Faradaic efficiency (FE): The generated gas was confirmed by gas chromatography (GC) analysis and quantified by monitoring the pressure change in the anode compartment of a H-type electrolytic cell using a calibrated pressure sensor. FE was calculated by comparing the amount of measured oxygen generated by potentiostatic anodic electrolysis with calculated oxygen (assuming 100% FE). 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.

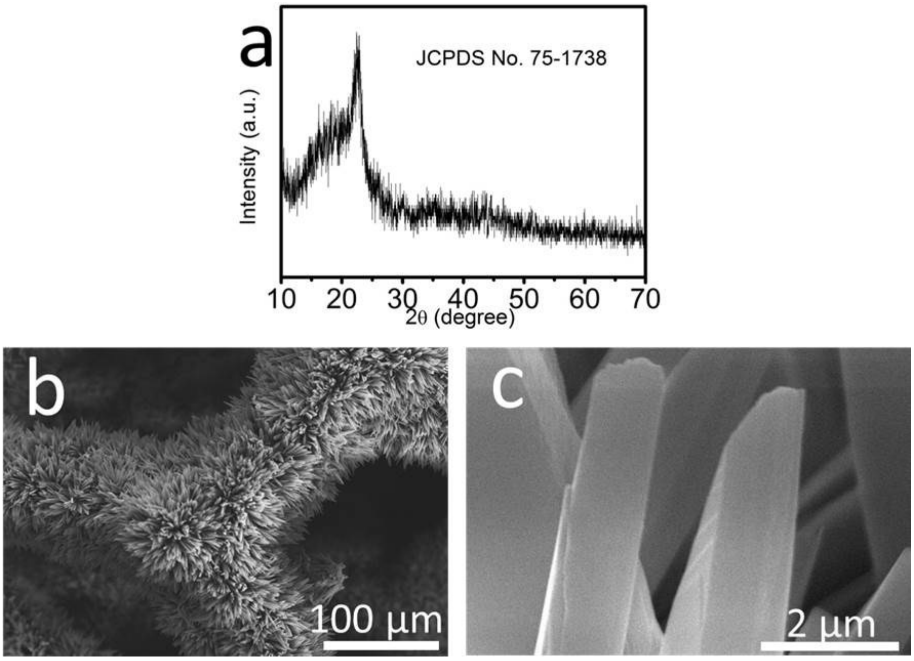

Fig. S1. (a) XRD pattern of $Co(H_2PO_4)_2{\cdot}2H_3PO_4$. (b) Low- and (c) high-magnification SEM images of $Co(H_2PO_4)_2{\cdot}2H_3PO_4$ MW/NF.

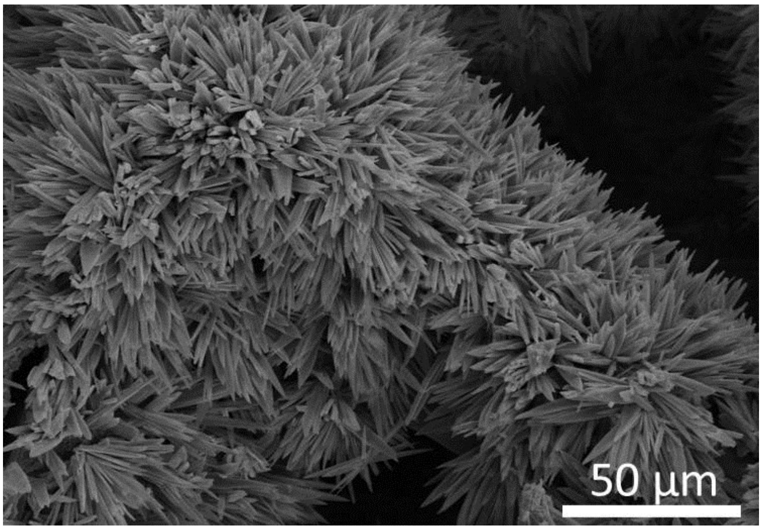

Fig. S2. Low-magnification SEM image of the phosphided product of $Co(H_2PO_4)_2{\cdot}2H_3PO_4$ MW/NF after water immersion.

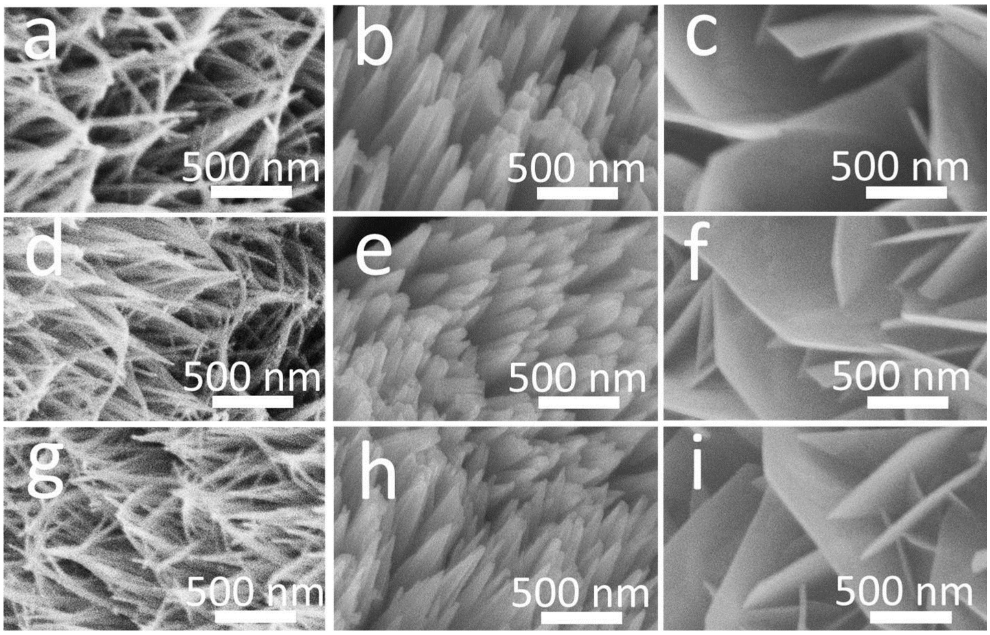

Fig. S3. SEM images for (a) Co(OH)F NW/NF, (b) Co(OH)CO_3 NW/NF, (c) Co$(OH)_2$ NS/NF. SEM images for the phosphided products of (d, g) Co(OH)F, (e, h) Co(OH)CO_3 and (f, i) Co$(OH)_2$ before (d-f) and after (g-i) water immersion.

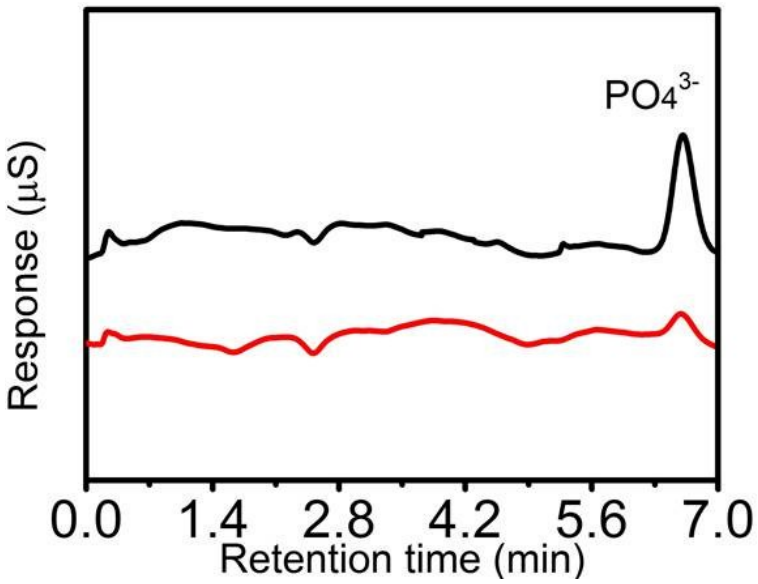

Fig. S4. Chromatograms of standard H_3PO_4 solution (black line) and water after immersion process (red line).

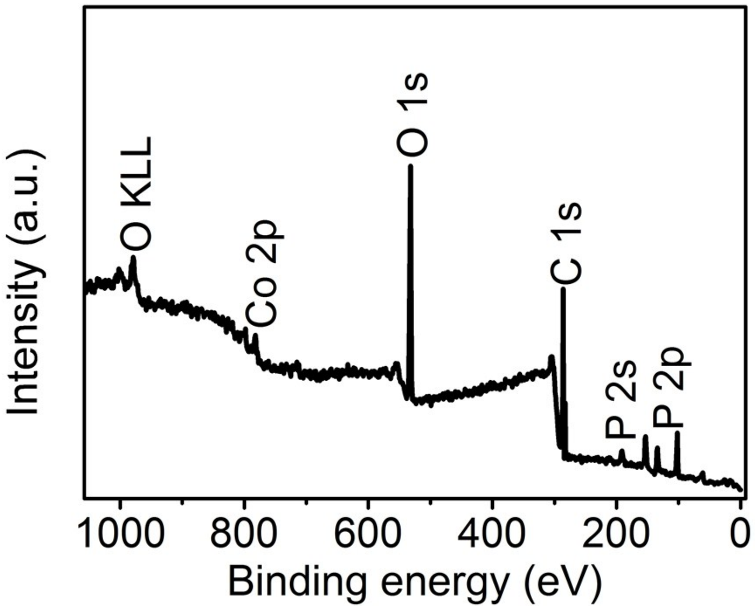

Fig. S5. XPS survey spectrum for CoP NS@MW.

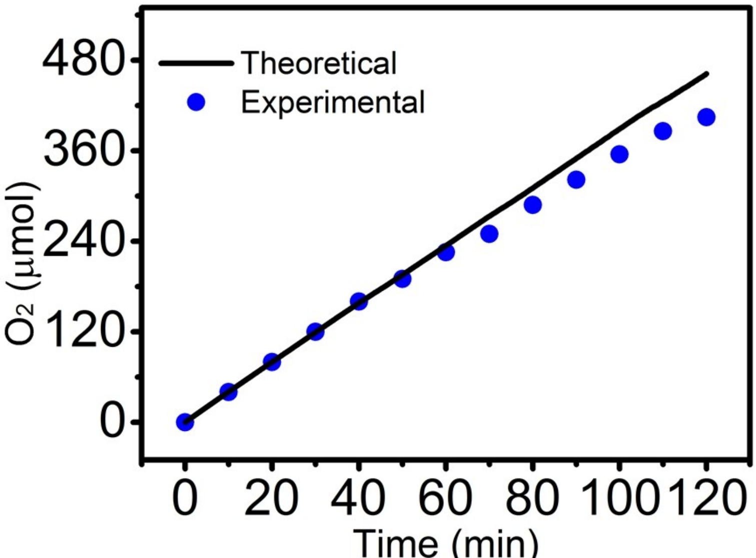

Fig. S6. The amount of oxygen theoretically calculated and experimentally measured versus time for CoP NS@MW/NF in 1.0 M KOH.

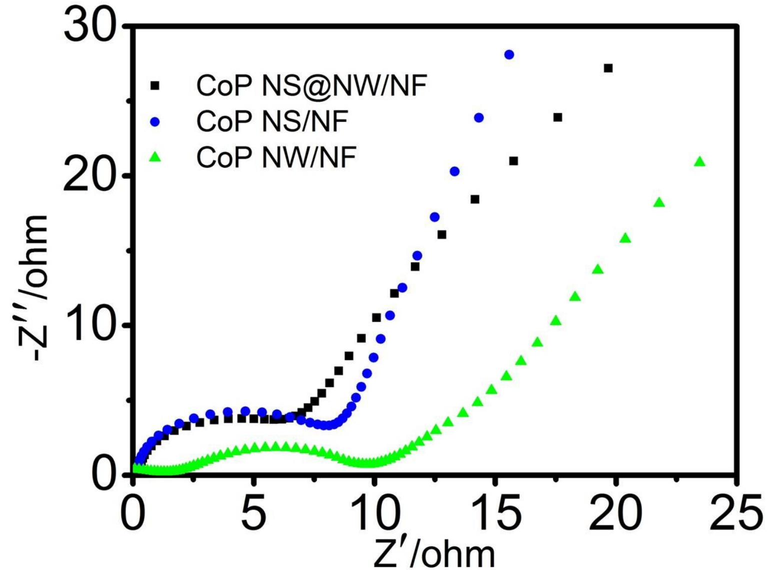

Fig. S7. Nyquist plots of CoP NS@MW/NF, CoP NS/NF and CoP NW/NF.

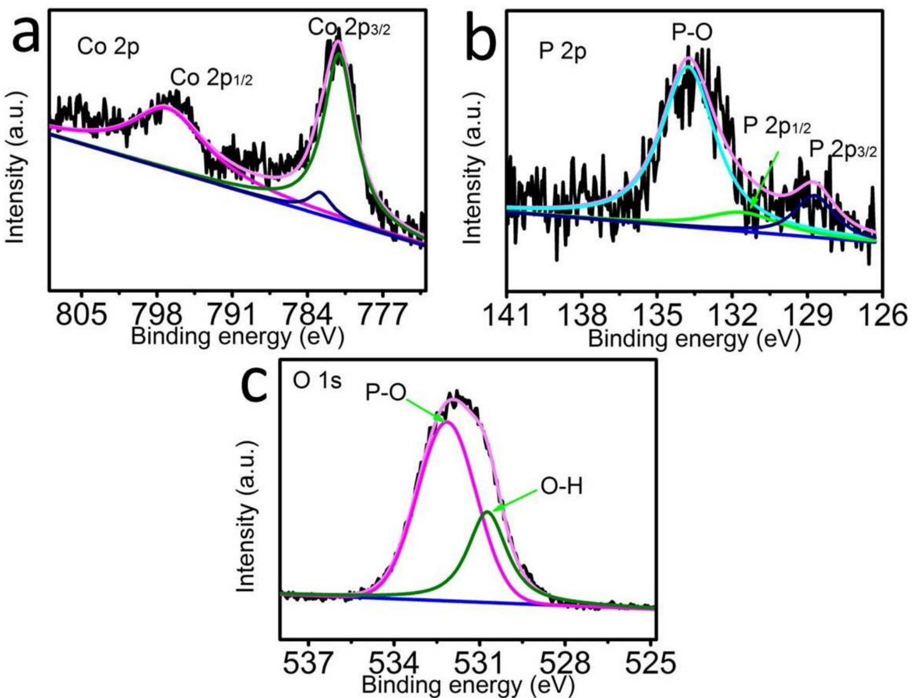

Fig. S8. XPS spectra for post-OER CoP NS@MW in the (a) Co 2p, (b) P 2p, and (c) O 1s regions.

Table S1. Comparison of OER performance for CoP NS@MW/NF with other nonprecious metal OER electrocatalysts in alkaline media.

Catalyst	**j (mA cm^{-2})**	**Overpotential (mV)**	**Electrolyte**	**Ref.**
CoP NS@MW/NF	50	260	1.0 M KOH	This work
	100	296		
CoP nanorod arrays	10	290	1.0 M KOH	2
CoP nanoneedle arrays	10	281	1.0 M KOH	3
CoP nanorod	10	320	1.0 M KOH	4
CoP NA/CC	10	300	1.0 M KOH	5
CoP_2/RGO	10	300	1.0 M KOH	6
Co_2P nonowires	20	290	1.0 M KOH	7
Ni_2P nanoparticles	10	290	1.0 M NaOH	8
Ni_5P_4/Ni plate	10	290	1.0 M KOH	9
PCPTF	10	300	1.0 M NaOH	10
Co-S/Ti mesh	10	340	1.0 M KOH	11
Co_3O_4 NW/CFP	10	330	1.0 M KOH	12
Co_3O_4/N-rmGO	10	310	1.0 M KOH	13
Fe/mCo_3O_4	10	380	1.0 M KOH	14
Co_3O_4/SWNTs	10	570	1.0 M KOH	15
Co_3O_4	10	340	1.0 M KOH	16
Mesoporous Co_3O_4	10	476	1.0 M KOH	17
N-CG–CoO	10	340	1.0 M KOH	18
NiO on Ni foam	10	440	1.0 M KOH	19
β-$Ni(OH)_2$ nanosheets	10	415	1.0 M KOH	20
Ni/NiO	10	345	1.0 M KOH	21
β-$Ni(OH)_2$	10	340	1.0 M KOH	22

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