

Electronic Supplementary Information

Boosting oxygen evolution reaction rates with mesoporous Fe-doped MoCo-phosphide nanosheets

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Experimental section:

In this study, we fabricated a series of Co-based phosphides mesoporous nanosheets (PNSs) via a simple one-step hydrothermal reaction and chemical vapor deposition-based phosphorization under 350 °C annealing temperatures. Herein, mixture of Oleylamine, ethanol and water is used as precipitating agent.

Materials and Chemicals

All chemicals used in this study were of high purity and analytical grade. The study procured cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; 99.0 wt. %), sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$; 99.0 wt. %), iron (II) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$; wt. 98.0%), sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$; 99.9 wt. %), from Sinopharm Chemical Reagent Co., Ltd. Oleylamine ($\text{C}_{18}\text{H}_{37}\text{N}$; 99.0 wt. %), ethanol ($\text{C}_2\text{H}_5\text{OH}$; 99.9 wt. %), and Nafion solution (5% wt.%) were purchased from Aladdin Reagent Co. Ltd, while potassium hydroxide [KOH, $\geq 95\%$] was obtained from Alfa Aesar. The study utilized ultrapure DI water from a Millipore Autopure system with a resistivity of 18.25 M Ω . All other materials used for electrochemical measurements were also of analytical grade and did not require further purification prior to use.

1-Synthesis of Co-precursor nanosheets

The Co-precursor nanosheets were prepared using a straightforward hydrothermal technique. In a typical procedure, a solution was created by dissolving cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) containing 0.5 mmol in 20 mL of deionized (DI) water. A mixture of Oleylamine (0.5 mL) and ethanol (20 mL) was added drop by drop to the solution. The resulting mixture was stirred for more than 30 minutes to ensure homogeneity. Subsequently, the solution was transferred to a Teflon-lined stainless-steel autoclave with a capacity of 50 mL. The autoclave was sealed and gradually heated to 180°C at a rate of 2°C per minute. The solution was maintained at this temperature for 12 hours before being cooled to room temperature. The resulting product was then subjected to centrifugation, washed multiple times with ethanol and ultrapure (UP) water, and finally dried under vacuum overnight.

2- Synthesis of Molybdenum-Cobalt layered double hydroxide nanosheets (MoCoLDH)

The MoCoLDH precursor nanosheets were synthesized using a simple hydrothermal method. In a typical procedure, a solution was prepared by dissolving sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) with a quantity 0.2 mmol and cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) with a quantity of 0.3 mmol in 20 mL of deionized (DI) water. A mixture composed of Oleylamine (0.5 mL) and ethanol (20 mL) was added wisely drop by drop to the solution. The resulting mixture was stirred for more than 30 minutes to ensure uniformity. Afterwards, the solution was transferred to a Teflon-lined stainless-steel autoclave that could hold up to 50 mL. The autoclave was sealed and gradually heated to 180°C at a heating rate of 2°C per minute. The solution was maintained at this temperature

for a duration of 12 hours and then slowly cooled down to room temperature. Subsequently, the resulting product was subjected to centrifugation, followed by multiple washes using ethanol and ultrapure (UP) water. Finally, the product was dried under vacuum overnight.

3- Fabrication of Fe-doped Molybdenum-Cobalt layered double hydroxide nanosheets (MoCoFeLDH)

The MoCoFeLDH precursor nanosheets were synthesized using a straightforward hydrothermal method. In a typical procedure, a solution was prepared by dissolving molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) with a quantity 0.2 mmol, cobalt (II) nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) with a quantity of 0.3 mmol, and iron (II) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$) with a quantity of 0.1 mmol, in 20 mL of deionized (DI) water. A mixture of oleylamine (0.5 mL) and ethanol (20 mL) was added drop by drop to the solution and the resultant mixture was stirred for more than 30 minutes to ensure homogeneity. Then, the solution was transferred to a Teflon-lined stainless-steel autoclave with a maximum capacity of 50 mL. Subsequently, the autoclave was sealed, and a gradual heating process was carried out, increasing the temperature to 180°C at a heating rate of 2°C per minute. The solution was held at this temperature for a duration of 12 hours, followed by a slow cooling process to reach room temperature. The resulting product underwent centrifugation, followed by multiple washes using ethanol and ultrapure (UP) water. Finally, the product was dried under vacuum conditions overnight.

4- Synthesis of Cobalt phosphide (CoP), Molybdenum-Cobalt phosphide (MoCoP), and Fe-doped Molybdenum-Cobalt phosphide (MoCoFeP) nanosheets

The as-prepared samples were converted to the corresponding phosphide to improve the catalytic activity. In a typical procedure, Co-precursor, MoCoLDH, and MoCoFeLDH were obtained and placed in one side of a separate ceramic boats and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ was also placed up stream at the other side of a separate ceramic boats and the systems were covered by another ceramic boats. The ratio between CoLDH, MoCoLDH, MoCoFeLDH and $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ was set at 1:10. Throughout the process, the systems were transferred to tube furnaces exposed to a flow of nitrogen gas (N_2) at a rate of 5 Scm. The temperature inside the furnace was gradually increased at a rate of 5 °C per minute until it reached 350 °C. It was then maintained at this temperature for a duration of two hours before being gradually cooled back to room temperature. The final product obtained was a black substances containing numerous active sites and phosphide defects. To study the effect of Fe concentration on the catalytic activity and the overpotential, we prepared MoCoFeP with different Fe concentration (0.05, 0.1, 0.15, and 0.2 mmol of iron (II) nitrate nonahydrate $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$).

5- Working electrode preparation

To prepare the catalyst ink, 5 mg of catalyst and 1 mL of Nafion solution (0.1 wt%) were dispersed and sonicated for 30 minutes to achieve a homogeneous ink. Prior to loading the catalyst, the surface of the glassy carbon electrode (GCE) with a surface area of 0.2 cm² was polished with successive alumina polishing steps of 500 nm and 50 nm. The electrode surface was then washed with ultrapure water and ethanol. The working electrode was prepared by uniformly drop casting of 12 μL of the ink was carefully suspended to the clean electrode surface and allowed to dry at room temperature. The catalyst loading was determined to be 0.3 mg cm⁻².

6- Electrochemical measurements:

The electrochemical measurements (linear sweep voltammetry (LSV), cyclic voltammetry (CV), electrical double layer capacitance (EDLC), electrochemical impedance spectroscopy (EIS), cyclic stability, chronopotentiometry, and electrochemically active surface area (ECSA) in this study were conducted at room

temperature (30 °C) using an electrochemical workstation (CHI-760E, CH Instruments, Inc.). A three-electrode configuration was employed, consisting of a glassy carbon electrode as the working electrode, a platinum electrode as the counter electrode, and a Hg/HgO electrode filled with 1 M KOH as the reference electrode.

7- Calculation of potential vs. RHE and overpotential (η)

The electrocatalytic performance was investigated at a sweep rate of 5 mV s⁻¹ based on the linear sweep voltammetry method. All recorded voltage values were converted to voltages relative to the reversible hydrogen electrode (RHE) in 1 M KOH by comparing them to the corresponding reference electrode.

$$E \text{ (vs. RHE)} = E \text{ (Hg/HgO)} + 0.92$$

The overpotential (η) were obtained from:

$$\eta = E \text{ (vs. RHE)} - 1.23 \text{ V}$$

Where E (vs. RHE), E (Hg/HgO), and η are potential of reversible hydrogen electrode, experimentally calculated potential of Hg/HgO electrode, and the overpotential respectively. All the curves were recorded without iR correction.

8- Tafel slope

Tafel slope indicates the required amount of overpotential to rise the reaction rate by a factor of ten. The Tafel plots of the catalysts were generated by analyzing the linear sweep voltammograms (LSV) data. The Tafel equation, was used to fit the data,

$$\eta = a + b \times \log j$$

where η represents the overpotential, j represents the steady-state current density normalized to the geometric area of the working electrode, b represents the Tafel slope value, and a represents the equation constant.

8- Electrical double layer capacitance (EDLC), and electrochemically active surface area (ECSA)

The electrical double layer capacitance (EDLC) was evaluated using the cyclic voltammetry (CV) technique within a low potential range of 1.17 to 1.27 V (vs. RHE) at different scan rates ranging from 10 to 50 mV s⁻¹. This range was chosen to avoid the generation of Faradic currents. The double-layer capacitance (C_{dl}), which was estimated by plotting half of the capacitive currents at 1.22 V (vs. RHE) ($\Delta J/2$, where ΔJ is the difference between the anodic current and the cathodic current) against the scan rate. The electrochemically active surface area (ECSA) is proportional to the double-layer capacitance (C_{dl}) and can be measured using the following equation.

$$ECSA = C_{dl} / C_s$$

Where C_{dl}, and C_s are double layer capacitance and specific capacitance of a flat surface respectively.

9- durability test

The durability test was performed using chronopotentiometry measurements at current density 10 mA cm⁻² and cyclic stability in 1M KOH.

10- Physical characterization:

The surface morphology and fine structure of the material were examined using a Zeiss SIGMA field emission scanning electron microscope (FESEM). To further analyze the material, high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and energy dispersive X-ray spectroscopy (EDX) were performed on a FEI Tecnai G2 F20 Field Emission Transmission Microscope. The crystal structure of the samples was determined using a Bruker D8 Advance X-ray diffractometer (XRD) with Cu K α radiation. The scan range was from 10 to 70 degrees with a scan rate of 5 degrees per minute. X-ray photoelectron spectroscopy (XPS) measurements were done using Thermo Fisher's ESCALAB Xi+ instrument, with the C 1s binding energy calibrated at 284.6 eV. The data obtained from XPS was analyzed using Casa XPS Software version 2.3.19.

Supplementary Images characterization:

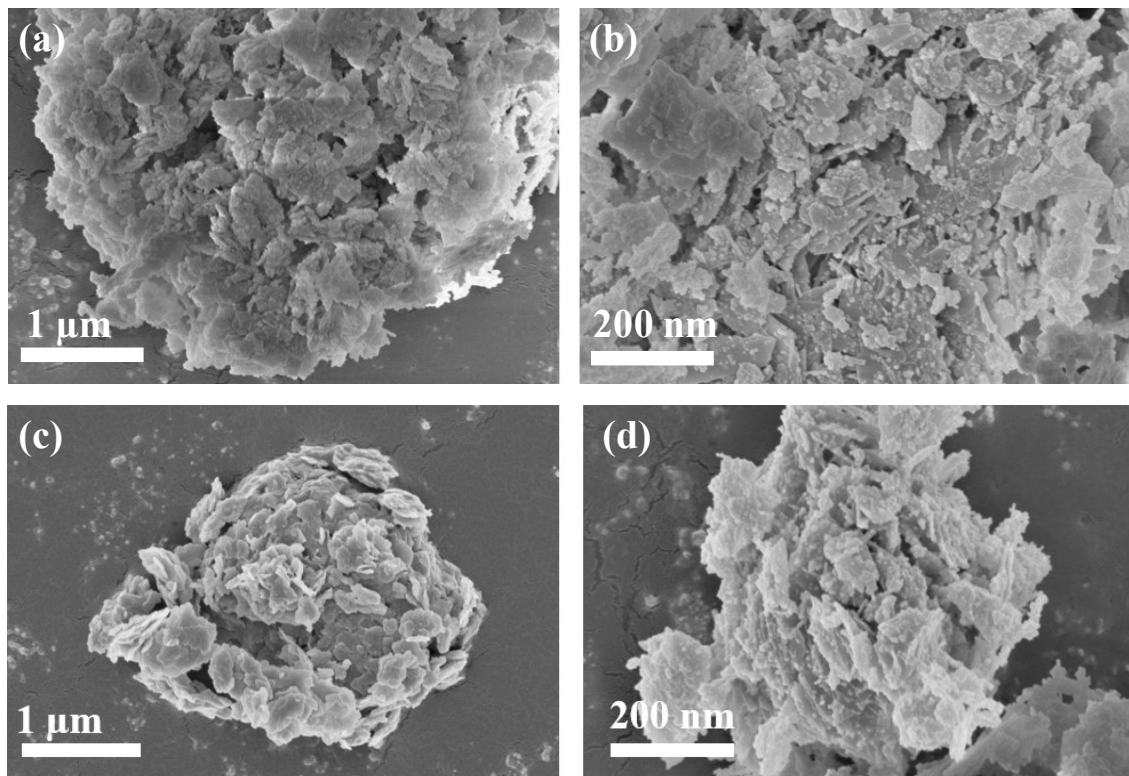


Fig. S1. SEM images of: (a, b) CoLDH, and (c, d) CoP.

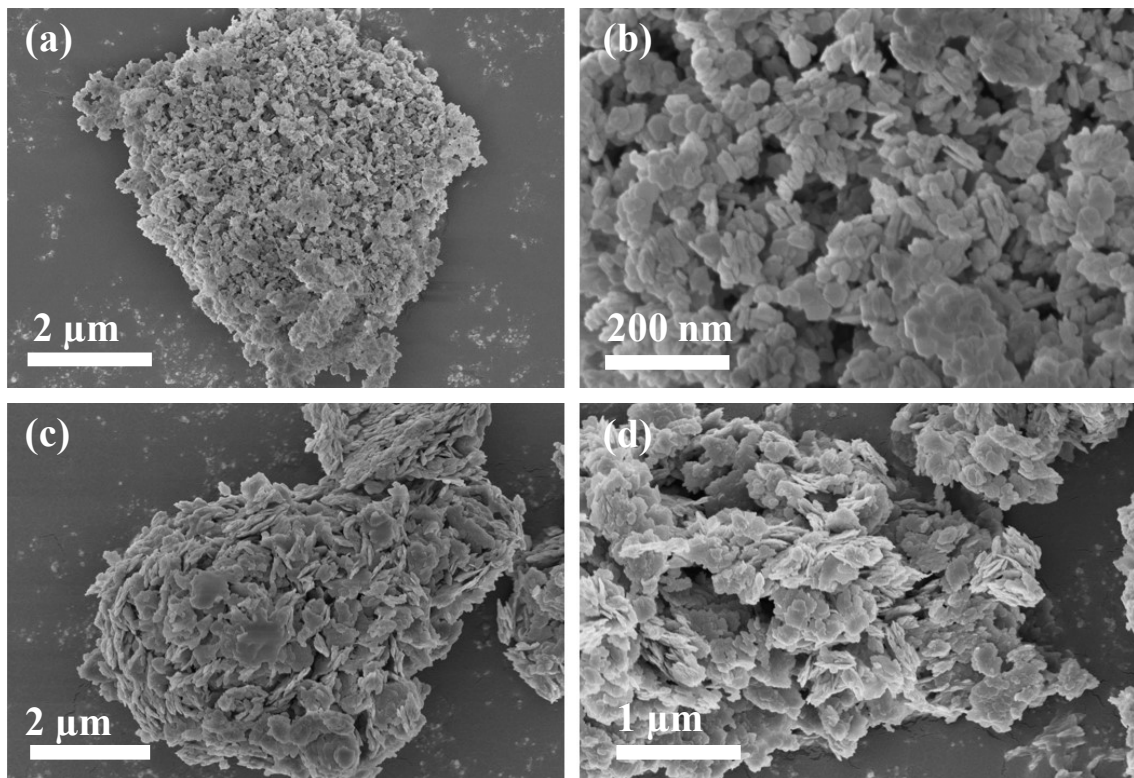


Fig. S2. SEM images of: (a, b) MoCoLDH, and (c, d) MoCoP.

(a)

Supplementary Tables:

Table S1. The metal elements composition (%) of samples determined by ICP.

(b)

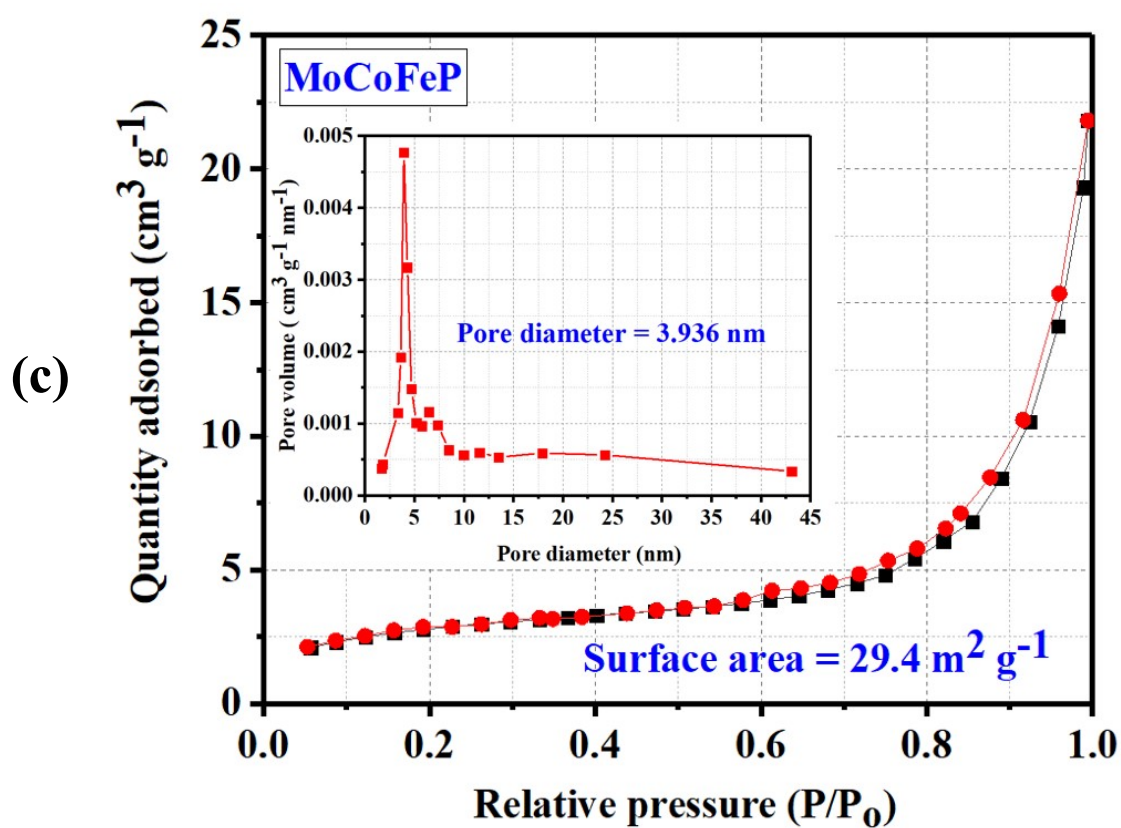
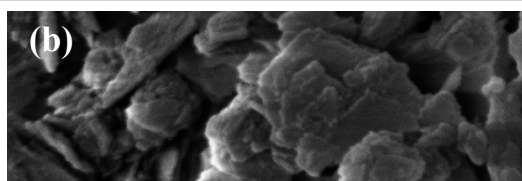
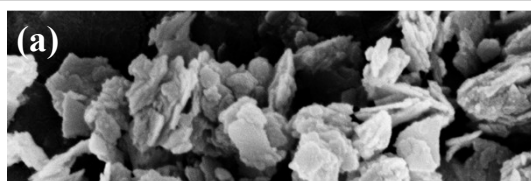


Fig. S4: N₂ adsorption desorption of MoCoFeP PNSs and the inset is Pore size distribution curve corresponding to specific pore volume of MoCoFeP PNSs.



sample	Mo	Co	Fe
CoP	-----	26.78	-----
MoCoP	12.38	16.44
MoCoFeP	9.43	12.47	4.56

Table S2. The metal elements composition (%) of sample's surface determined by XPS.

sample	Mo	Co	Fe	O	P	C
CoP	-----	13.03	-----	54.3	17.06	15.62
MoCoP	2.37	12.76	-----	57.26	15.18	12.42
MoCoFeP	1.63	11.18	1.16	57.78	13.04	15.21

Table S3. Comparison of OER activity of MoCoFeP nanosheets in this work with other reported electrocatalysts in 1 M alkaline solution.

Catalyst	$\eta_{10\text{mA/cm}^2}$ (mV)	Tafel slope (mV dec ⁻¹)	Stability	Reference
MoCoFeP	250	43.38	100 h	This work
CoFeO@BP	266	53	24 h	[1]
Mn-Co phosphide yolk-shell spheres	330	59	8 h	[2]
CoP-B1	297	58.8	11 h	[3]
Mo-Co ₃ O ₄ /CNTs	280	63	30 h	[4]

CoP/Mo₂CT_x	260	51	50 h	[5]
NMCP@NF	250	41	30 h	[6]
Ni-Co-Fe-P	277	85.64	24 h	[7]
FeP nanoparticles with reduced graphene oxide	260	49.6	4 h	[8]
Ni_{0.6}Co_{1.4}P nanocages	300	80	10 h	[9]
Cu-CoP	252	89.1	18 h	[10]
NiFeP-DBD	265	40.9	20 h	[11]

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