Mn doping promotes deep surface reconstruction of CoP nanosheet arrays to drive efficient water splitting

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Experimental

1. Chemicals

All chemical reagents were utilized without purification. Coal powder (Heishan, Xinjiang, China) was used as the precursor. Sulfuric acid (H_2SO_4, 95-98%, Xilong Scientific Co., Ltd.), Nitric acid (HNO_3, 65-68%, Xilong Scientific Co., Ltd.), N, N-dimethylformamide (DMF, AR, 99%, Tianjin Zhiyuan Chemical Reagent Co., Ltd.), Polyacrylonitrile (PAN, average Mw=150, 000, Innochem Technology Co., Ltd.), Cobalt chloride hexahydrate ($CoCl_2{\cdot}6H_2O$, AR, 99%, Tianjin Xinbote Chemical Co., Ltd.), Manganese(II) Nitrate Tetrahydrate ($Mn(NO_3)_2{\cdot}4H_2O$, AR, 98%, Adamas), Potassium hydroxide (KOH, AR, 85%, Tianjin Zhiyuan Chemical Reagent Co., Ltd.), Sodium hypophosphite ($NaH_2PO_2{\cdot}H_2O$, AR, 99%,Tianjin Zhiyuan Chemical Reagent Co., Ltd.), commercial Pt/C (20 wt%, JM, Shanghai Hesen Electric Co., Ltd.) and RuO_2 (Shanghai Hesen Electric Co., Ltd.).

2. Materials Characterization

The morphology and detailed microstructures of the final products were characterized by scanning electron microscopy (SEM) with Hitachi S-4800 scanning electron microscope and transmission electron microscopy (TEM) with FEI F30 transmission electron microscope. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 advance X-ray diffractometer with Cu Kα radiation source (λ = 1.54178 Å). Raman spectroscopy was performed on a Bruker Senterra microscope-confocal Raman spectrometer at the excitation wavelength of 532 nm. X-ray photoelectron spectroscopy (XPS) was performed using Thermo Fisher Scientific Escalab 250 Xi with monochromatic Al Kα at 15 kW. Element analysis was performed by inductively coupled plasma-mass spectrometry (ICP-MS) using Agilent 7900.

3. Electrochemical Measurements

Accurately cut 0.5 cm × 1 cm of material to be directly used as self-supporting electrode for testing. The Pt/C and RuO_2 electrodes were prepared as follows: accurately weighed the same loading amount of Pt/C and RuO_2 as the final product, and then dispersed them in a mixture of ethanol and deionised water for sonication, and then dropped the Pt/C and RuO_2 onto the 0.5 cm × 1 cm coal-based carbon nanofibers to produce the Pt/C and RuO_2 electrodes, respectively. fibers to produce Pt/C and RuO_2 electrodes.

In this paper, a standard three-electrode test system was used for testing, where the prepared self-supporting electrode was used as the working electrode, the Hg/HgO electrode was used as the reference electrode, and the graphite rod was used as the counter electrode. The electrochemical data were tested on an electrochemical workstation (CHI 660E). The tests of HER performance and OER performance were carried out in 1.0 M KOH electrolyte. A sweep rate of 5 mV s^{-1} was used for the polarisation curves of the samples in this thesis. All test results were corrected according to the reversible hydrogen electrode (RHE), E (RHE) = E (Hg/HgO) + (0.098 + 0.059 pH) V (1.0 M KOH, pH=14). The voltage interval for the HER performance test was -0.9--1.6 V, the voltage interval for the OER performance test was 0-1.2 V, and the voltage interval for the test of water electrolysis performance was 1.2-2 V. Meanwhile, in order to accurately obtain the overpotentials of the electrocatalysts, the polarisation curves of the HER and the OER in this paper were subjected to 90% iR correction.

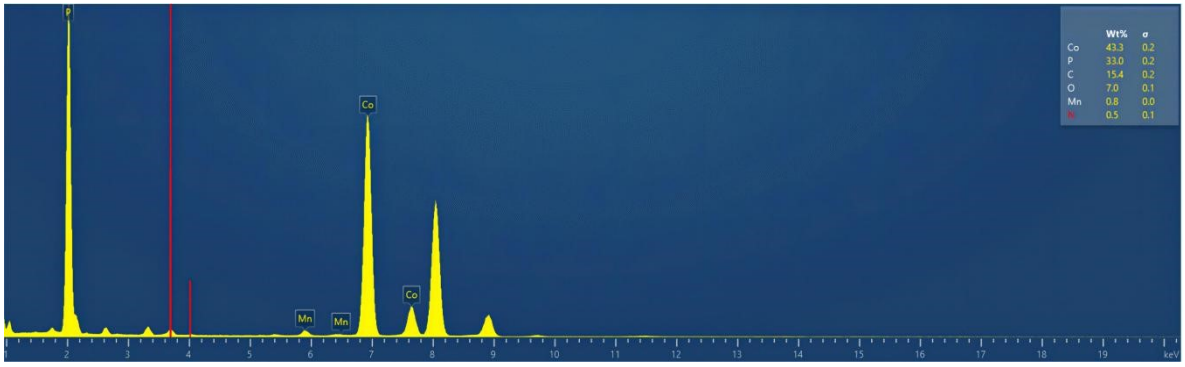

Fig S1. EDX image of Mn_{10}-CoP@C-CNFs.

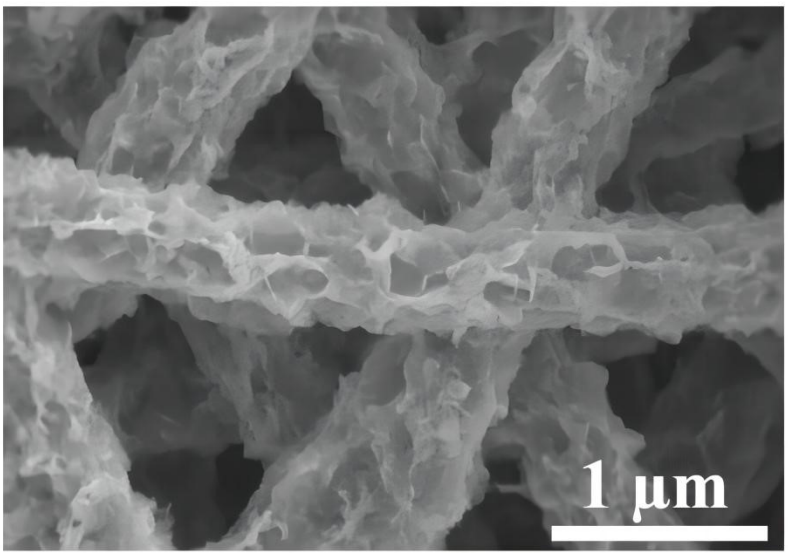

Fig S2. SEM image of the Mn_{10}-CoP@C-CNFs after stability test of HER.

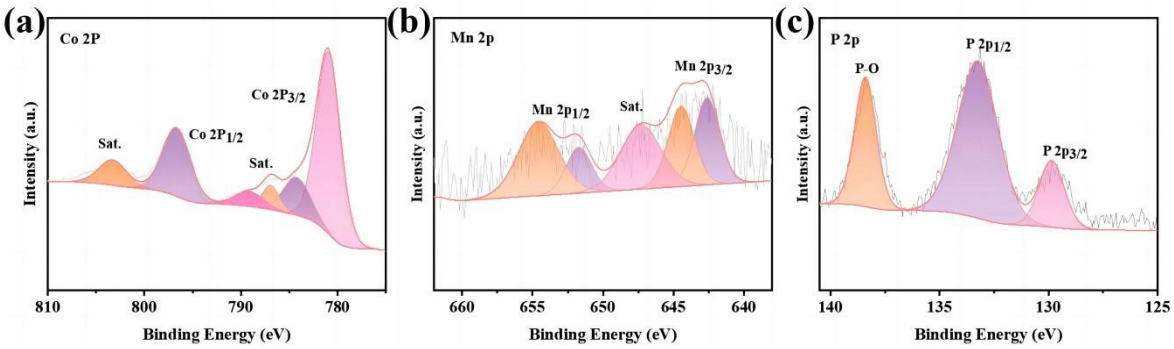

Fig S3. High-resolution XPS spectra of (a) Mn 2p, (b) Co 2p, and (c) P 2p of the Mn_{10}-CoP@C-CNFs after HER stability tests.

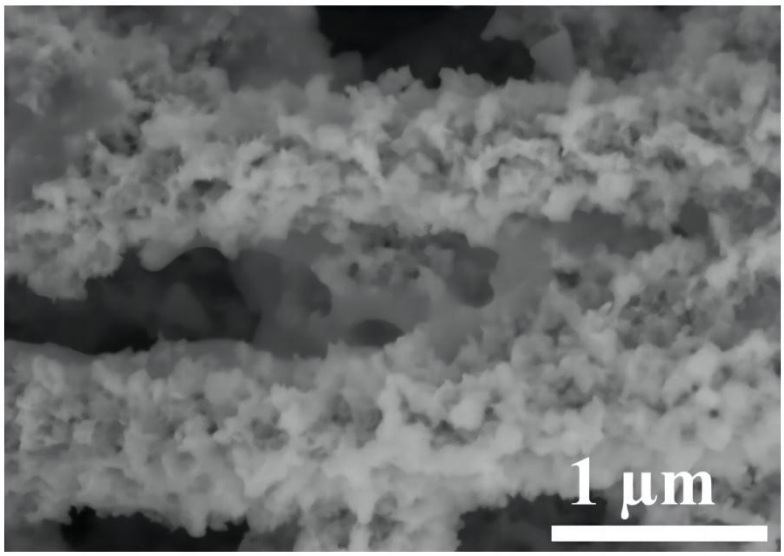

Fig S4. SEM image of the Mn_{10}-CoP@C-CNFs after stability test of OER.

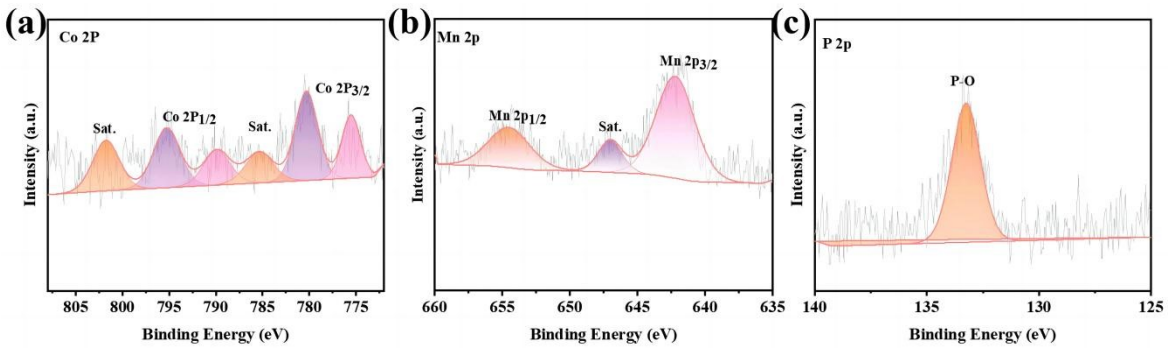

Fig S5. High-resolution XPS spectra of (a) Mn 2p, (b) Co 2p, and (c) P 2p of the Mn_{10}-CoP@C-CNFs after OER stability tests.

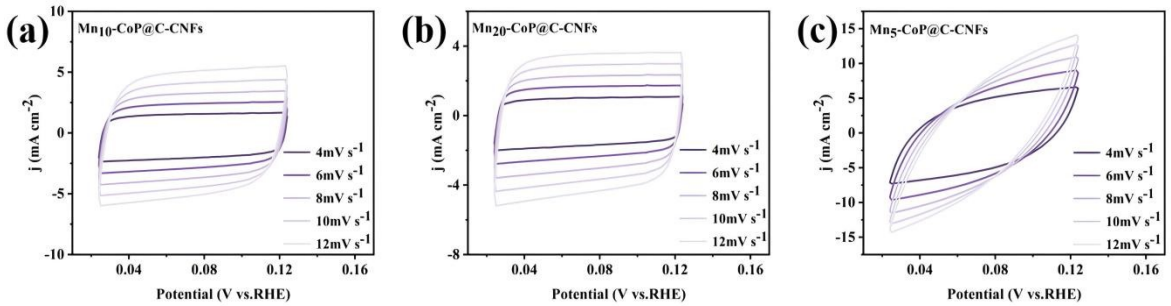

Fig S6. CV scans of (a) Mn_{10}-CoP@C-CNFs, (b) Mn_{20}-CoP@C-CNFs, (c) Mn_5-CoP@C-CNFsat various scan rate for HER.

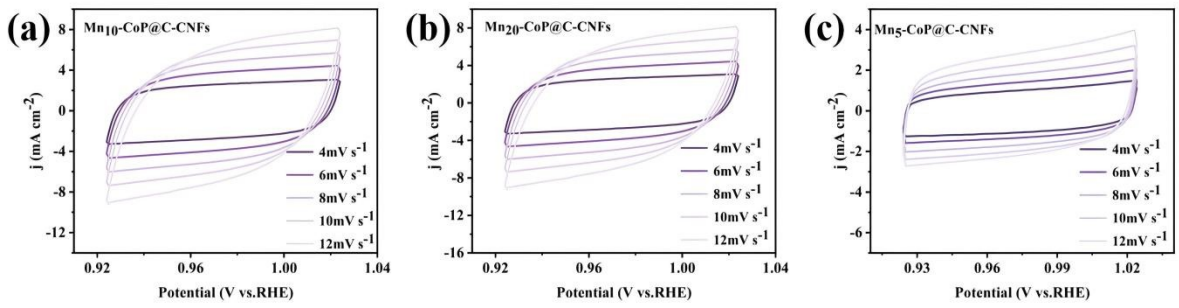

Fig S7. CV scans of (a) Mn_{10}-CoP@C-CNFs, (b) Mn_{20}-CoP@C-CNFs, (c) Mn_5-CoP@C-CNFsat various scan rate for OER.

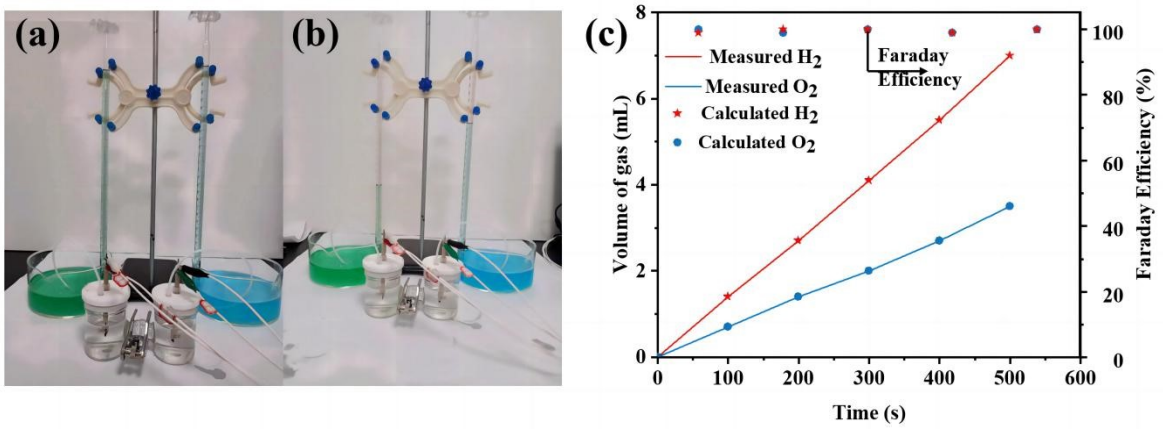

Fig S8. (a, b) Photograph of volume changes during electrocatalytic water splitting, (c) Experimental and theoretical volumes of H_2 and O_2 gases at a current density of 10 mA cm^{-2} and Faraday efficiency of the Mn_{10}-CoP@C-CNFs.

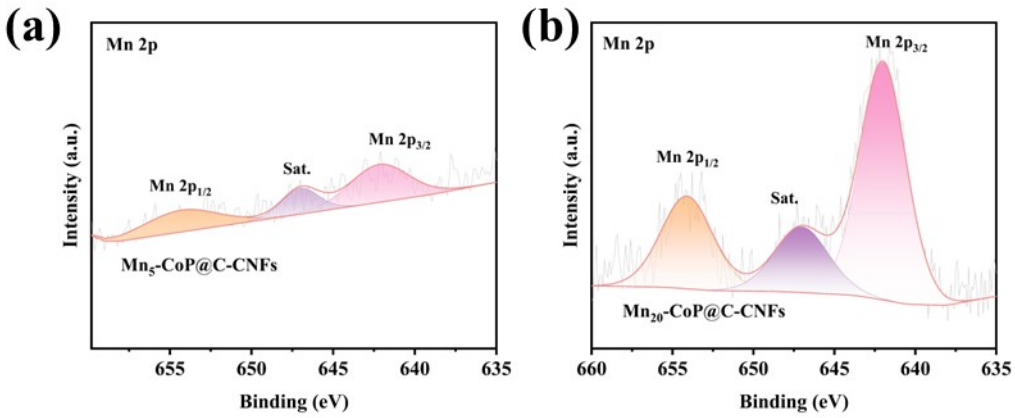

Fig S9. High-resolution XPS spectra of Mn 2p of the (a) Mn_5-CoP@C-CNFs and Mn_{20}-CoP@C-CNFs.

Table S1. Comparison of HER and OER properties of Mn_{10}-CoP@C-CNFs with those of reported representative electrocatalysts under alkaline conditions.

Catalysts	HER	OER	Reference
Mn_{10}-CoP@C-CNFs	62	230	This Work
MnCoP/CC	65	261	[1]
Mn-CoP/CC	90	/	[2]
Mn-doped CoP/NF	60	/	[3]
Mn-Co-P/Ti	76	/	[4]
Mn-CoP/Co_2P	82	309	[5]
Mn-Ni_2P/NF	205	330	[6]

Table S2. Actual mass ratio of elements in catalysts were acquired by ICP-OES.

Catalyst	Mn/Co
Mn_5-CoP@C-CNFs	**1: 64.5**
Mn_{10}-CoP@C-CNFs	**1: 55.7**
Mn_{20}-CoP@C-CNFs	**1: 45.9**

Reference:

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