Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Surface Phosphorization of $NiCo_2S_4$ as Efficient Bifunctional Electrocatalyst for Full Water Splitting

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1. Characterization details

X-ray diffraction test (XRD) was performed on a PANalytical X-ray Diffractometer (Aeris) equipped with a Cu Kα radiation. The field emission scanning electron microscope (FE-SEM) images were obtained on a Hitachi SU8220 instrument. Transmission electron microscopy (TEM) images and energy-dispersive spectrometer elemental mapping (EDS-mapping) were acquired on a FEI Talos F200S with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) was test on a Thermo Fisher Escalab 250Xi spectrometer. The XPS in-depth test uses a 3 keV Ar ion gun for sputtering, the sputtering area is 1mm*1mm, the sputtering rate is calibrated by thermally oxidized SiO_2 (standard sample) to 25 nm/min, and each sputtering time is 120 s (for 50 nm). The total etching depth is 200 nm.

2. Electrochemical measurements

The electrochemical experiments were carried out on an electrochemical workstation (German, ZAHNER ZENNIUM) using a standard three-electrode system. The Ni-Co-S-P/CFP with area of 1 cm^2 served as the working electrode, and graphite rod and Pt foil served as counter electrodes for HER and OER, respectively. The Ag/AgCl (3.5 M KCl, 0.2046 V vs. RHE) electrode was used as a reference electrode in alkaline media (1.0 M KOH, pH≈14). The measured potentials were converted to the reversible hydrogen electrode (RHE) using the following equation: $E_{RHE} = E_{Hg/HgO} + 0.059pH + E^{0}_{Hg/HgO}$ and $E_{RHE} = E_{SCE} + 0.059pH + E^{0}_{SCE}$, and all potentials were not iR-corrected to avoid the effects of large differences in iR compensation. All electrochemical tests were first activated by continuous cyclic voltammetry (CV), and the linear sweep voltammetry (LSV) tests were at a slow scan rate of 1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) measurement was carried out at different overpotentials in the frequency range of 10 kHz to 10 mHz with a 5 mV ac amplitude. According to Polarization curves, the Tafel plots were plotted by fitting to the Tafel equation: $\eta = a + b \log j$ (where η is the overpotential, a is the intercept relative to the exchange current density (j_0), j is the current density and b is the Tafel slope). The long-term stability was tested by a galvanostatic method at current density of 10 mA cm^{-2} (in 1 M KOH). The electrochemical active surface areas (ECSA) of catalysts were estimated by the double layer capacitance (C_{dl}), which is linearly proportional to the ECSA. The

C_{dl} was determined by using the cyclic voltammograms (CVs) recorded at non-Faradaic potentials (0.43-0.59 V vs. RHE for HER) at different scan rates.

The overall water-splitting test was performed in a two-electrode system by directly using Ni-Co-S-P/CFP as both the cathode and anode. The LSV curves were recorded in 1.0 M KOH with a scan rate of 1 mV s^{-1}. The long-term durability was tested by the galvanostatic method.

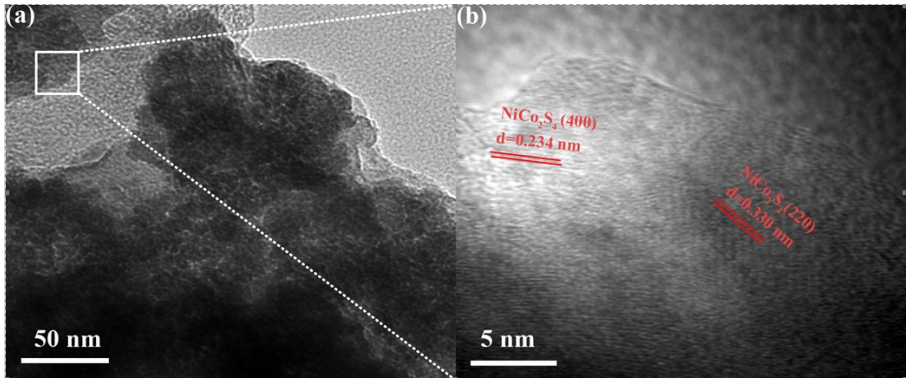

Fig. S1 HRTEM images of Ni-Co-S

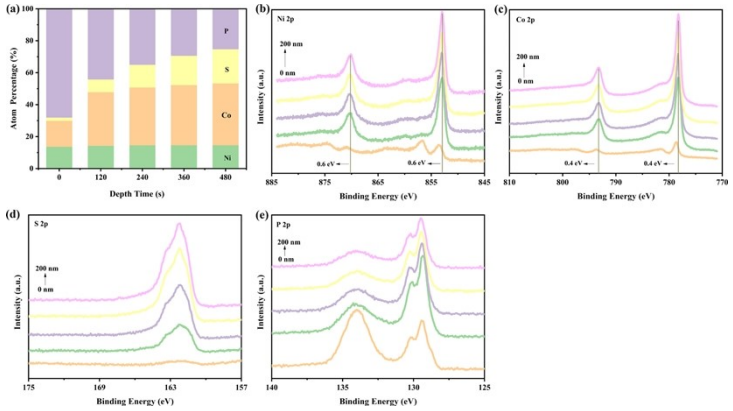

Fig.S2 XPS in-depth analysis using Ar ion etching

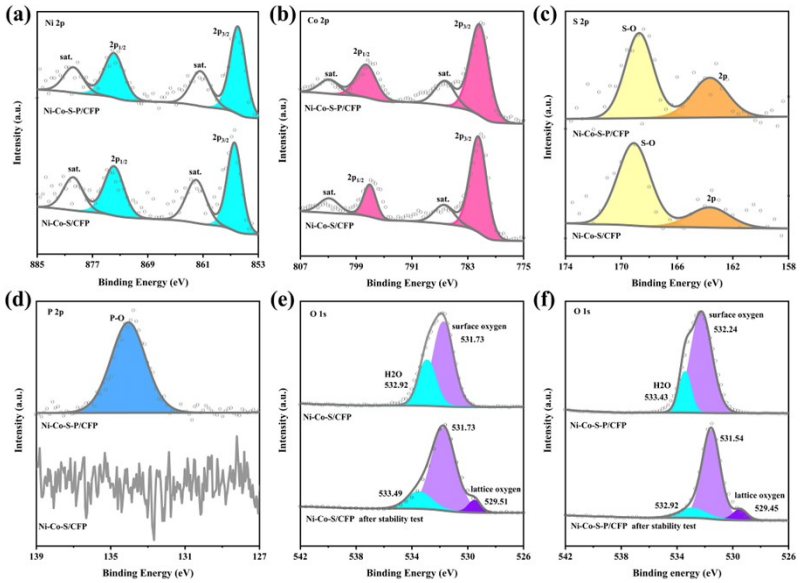

Fig.S3 High-resolution XPS spectra after stability test：(a) Ni 2p, (b) Co 2p, (c) S 2p ,(d) P 2p, O 1s spectra of (e) Ni-Co-S/CFP and (f) Ni-Co-S-P/CFP .

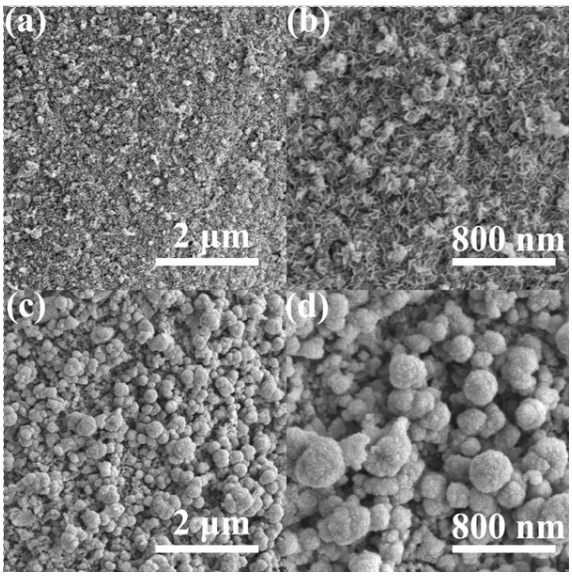

Fig. S4 SEM images of Ni-Co-S-P/CFP after (a,b) HER, (c,d) OER stability test.

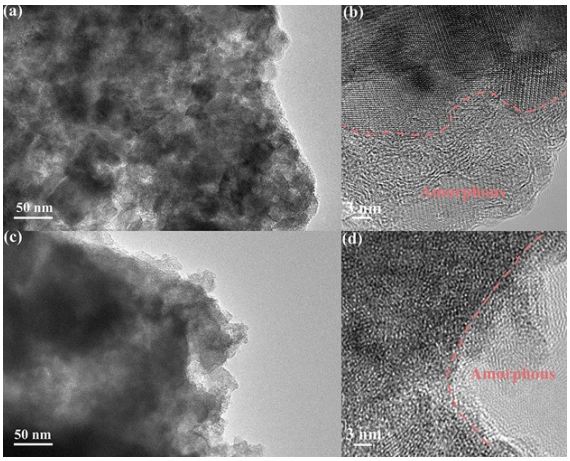

Fig. S5 HRTEM images of Ni-Co-S-P/CFP after (a,b) HER, (c,d) OER stability test.

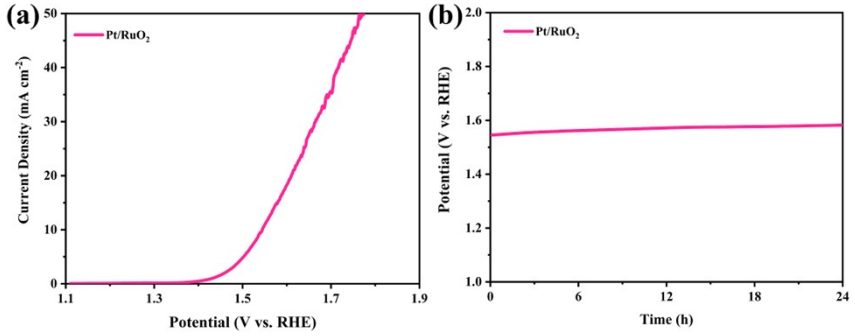

Fig.S6 (a) Polarization curve of overall water-splitting using Pt/RuO_2 as both anode and cathode electrocatalysts in a two-electrode system.

(b) Long-term stability at 10 mA cm^{-2} .

Table S1. Comparison of OER activity of various TMPs based catalysts.

electrocatalysts	Media	η_{10} /m V	η_{100} /m V	Reference
Ni-Co-S-P/CFP	1 M KOH	265	413	This Work
Co-P	1 M KOH	345		[1]
Ni_3S_2/NF	1 M KOH	312	467	[2]
Ni-Co-S-P	1 M KOH	280		[3]
CoP/NCNHP	1 M KOH	310		[4]
NiCo/NiCoO@FeOOH	1 M KOH	278		[5]
Co_9S_8	1 M KOH	299	430	[6]
NiCo/CNF@NC	1 M KOH	350		[7]
$NiCo_2O_4$/CN	1 M KOH	383		[8]
Ni–Co–Fe (NCF)-MOF	0.1 M KOH	320		[9]
P,S-CoxOy /Cu@CuS NWs	1 M KOH	280		[10]
Co_2B/NG	0.1 M KOH	380		[11]
FeCoNi-2	1 M KOH	288		[12]
NiFe LDH/NGF	0.1 M KOH	340		[13]

Table S2. Comparison of HER activity of various TMPs based catalysts.

electrocatalysts	Media	η_{10} /m V	η_{100} /m V	Reference
Ni-Co-S-P/CFP	1 M KOH	176	342	This Work
$Cu_{0.3}Co_{2.7}P$/NC	1 M KOH	220		[14]
Co_9S_8	1 M KOH	217		[6]
NiCoS/C	1 M KOH	232		[15]
NiCo/CNF@NC	1 M KOH	220		[7]
Ni–Co–Fe-MOF	0.1 M KOH	270		[9]
$NiCo_2S_4$ /NF	1 M KOH	220		[16]
NiCoP/CNTs	1 M KOH	267		[17]
NGO/Ni_7S_6	1 M KOH	370		[18]
NiCoP	0.5 M H_2SO_4	230		[19]
CoO @CN	1 M KOH	232		[20]
Ni-Co_2 P/NCNTs	0.5 M H_2SO_4	230	278（η_{20}）	[21]
CoMoP	0.5 M H_2SO_4	215		[22]
Cu-MoS_2 /rGO	0.5 M H_2SO_4		400（$\eta_{83.6}$）	[23]
Co_2B/NG	1 M KOH	230		[11]

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