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Supporting Information:

Metal-Organic Framework-Derived $Zn_{0.975}Co_{0.025}S/CoS_2$ Embedded in N, S-codoped Carbon nanotube/nanopolyhedra as Efficient Electrocatalyst for Overall Water Splitting

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1 EXPERIMENTAL

1.1 Synthesis of ZnCo-ZIFs and ZIF-67

All the chemicals were directly used after purchase without further purification. In a typical preparation, 4 mmol $Co(NO_3)_2\cdot 6H_2O$ and 2 mmol $Zn(NO_3)_2\cdot 6H_2O$ were dissolved into 40 mL of methanol (MeOH) and solution was then added into 30 mL of MeOH containing 24 mmol 2-methylimidazole (MeIM) under string. The mixed solution was placed at 25 °C for 24 h. The as-obtained powders were centrifuged with ethanol and dried in vacuum overnight to obtain the ZnCo-ZIFs. The preparation of ZIF-67 was performed with a similar process to ZnCo-ZIFs in the absence of $Zn(NO_3)_2\cdot 6H_2O$.

1.2 Synthesis of Co_3ZnC/Co-NCNT/NP, Co-NCNT/NP and Co_3ZnC/Co-NCNP

The as-prepared ZnCo-ZIFs precursors were placed in a ceramic boat, and then heated in a tube furnace at a ramp rate of 5 °C/min to 600 °C under Ar/H_2 flow (95%/5% in volume ratio) for 1 h. After cooling naturally, the black product of Co_3ZnC/Co-NCNT/NP was finally collected. The Co-NCNT/NP was obtained by treating ZIF-67 in the similar chemical vapor reduction and deposition process. The same procedure was conducted to convert ZnCo-ZIFs to Co_3ZnC/Co-NCNP by calcination under Ar_2 atmosphere.

1.3 Synthesis of ZnCoS-NSCNT/NP, CoS_2-NSCNT/NP and ZnCoS-NSNP

The resulting Co_3ZnC/Co-NCNT/NP (0.1 g) was put in a tube furnace, and 0.6 g S powder was placed at the upstream side. Then, the temperature of the furnace was elevated to 600 °C at a rate of 2 °C min^{-1} and maintained for 2 h in a tube furnace under a N_2 flow. After the furnace was cooled to room temperature, the ZnCoS-NSCNT/NP was obtained. The CoS_2-NSCNT/NP and ZnCoS-NSNP products were obtained using similar preparation process with Co-NCNT/NP and Co_3ZnC/Co-NCNP as the precursor, respectively

1.4 Characterization

Field emission scanning electron microscopy (FESEM) images were obtained on a Hitachi S-8010 scanning electron microscope. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-dispersive X-ray (EDX) elemental mapping images were all recorded on a FEI Tecnai G2 F30 (200 kV) high-resolution transmission electron microscope. X-ray diffraction (XRD) characterization was carried out on a PANalytical X'Pert PRO with Cu Ka radiation. X-ray photoelectron spectra (XPS) were obtained with a K-Alpha electron spectrometer (Thermofish Scientific Company) using Al Kα (1486.6 eV) radiation. The surface area was measured by the Brunauer-Emmett-Teller (BET) method using ASAP2020.

1.5 Electrochemical test

Electrocatalytic activity evaluations were performed in a O_2-purged within the solution of 1 M KOH with a three-electrode system. The glassy carbon (GC) electrode (3 mm diameter) was utilized as the working electrode. The saturated Ag/AgCl electrode (SCE) was used as the reference electrode, and Pt mesh or a graphite electrode was used as the counter electrode. 2 mg sample was dispersed in 500 μL Nafion (5 wt%) -water-isopropyl alcohol mixture solution with a volume ratio of 0.05 : 4 : 1 by sonicating. Then, 6 μL of the dispersion was deposited onto a GC and dried in air overnight (loading ~0.21 mg cm^{-2}). The linear sweep voltammetry (LSV) was measured at 5 mV s^{-1} scanning rate. All the applied potentials were referenced to a reversible hydrogen electrode (RHE) scale. The long-term durability test was performed using chronoamperometry measurements. Cyclic voltammograms (CVs) were measured from 0.20 to 0.30 V *vs*. Ag/AgCl at scanning rates of 5, 10, 20, 40, 60, 80 and 100 mV s^{-1}. The overall water splitting performance was measured by Ni (1×1 cm) foam (NF) as the working electrode to reach a high catalyst loading (1 mg cm^{-2}). For comparison, the same amount of Pt/C and RuO_2 were also supported on the NF as cathode and anode, respectively, to drive the overall water splitting process.

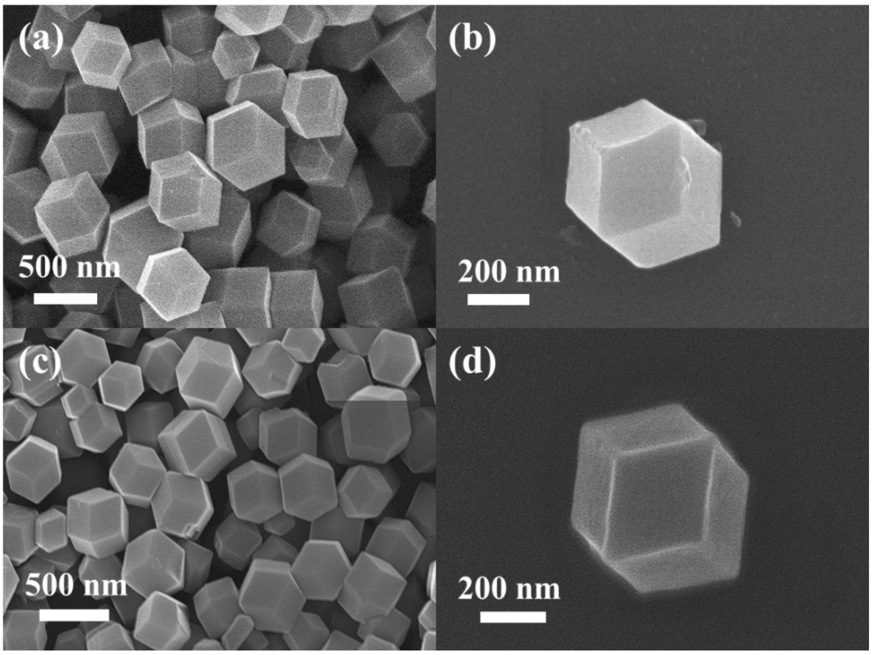

Fig. S1 SEM images of (a-b) ZnCo-ZIFs and (c-d) ZIF-67.

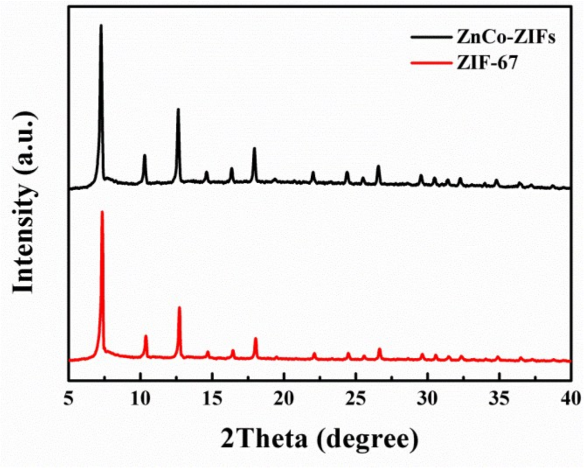

Fig. S2 XRD patterns of ZnCo-ZIFs and ZIF-67.

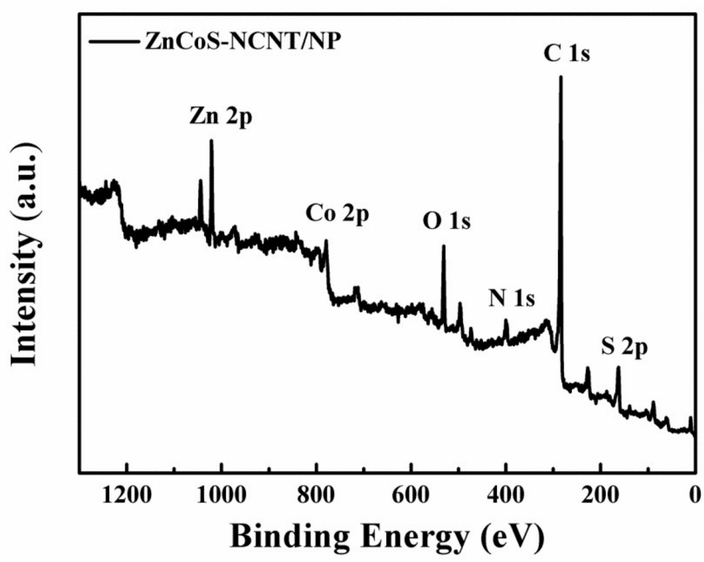

Fig. S3 Full scan XPS spectrum of ZnCoS-NSCNT/NP.

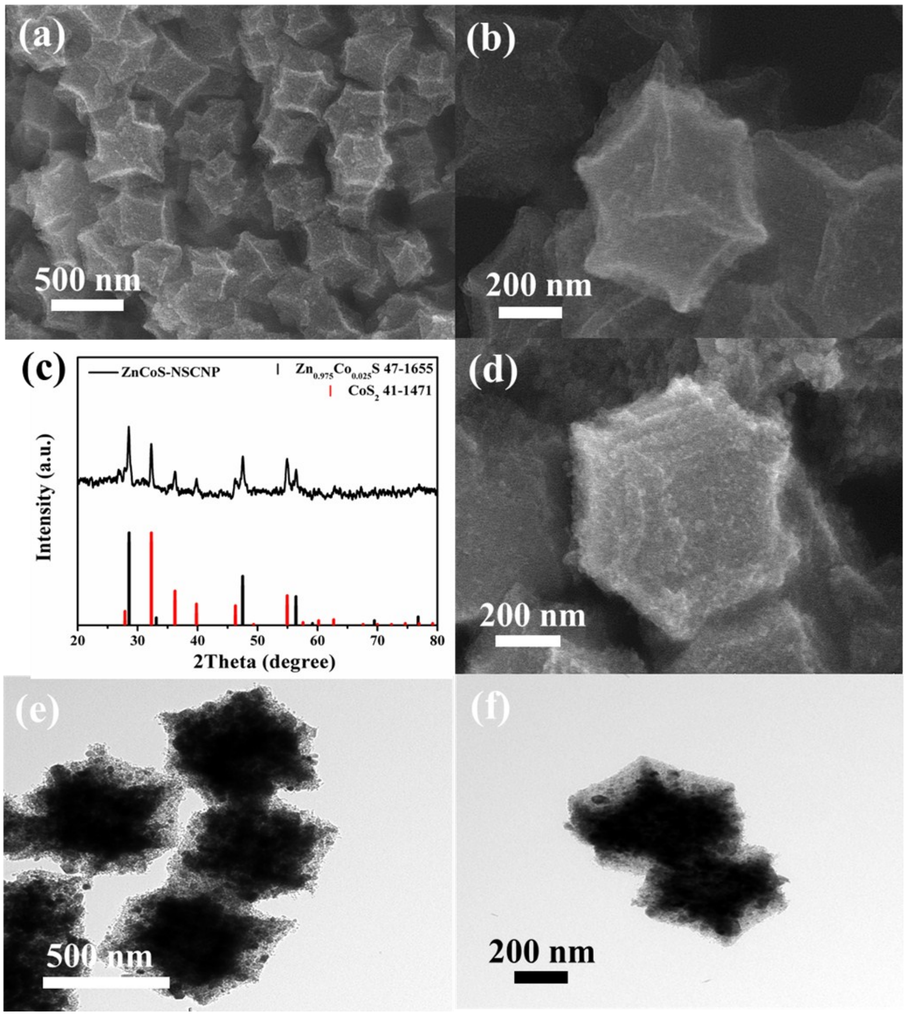

Fig. S4 (a,b) SEM images of Co_3ZnC/Co-NCNP. (c) XRD pattern, (d) SEM images, and (e, f) TEM image of ZnCoS-NSCNP.

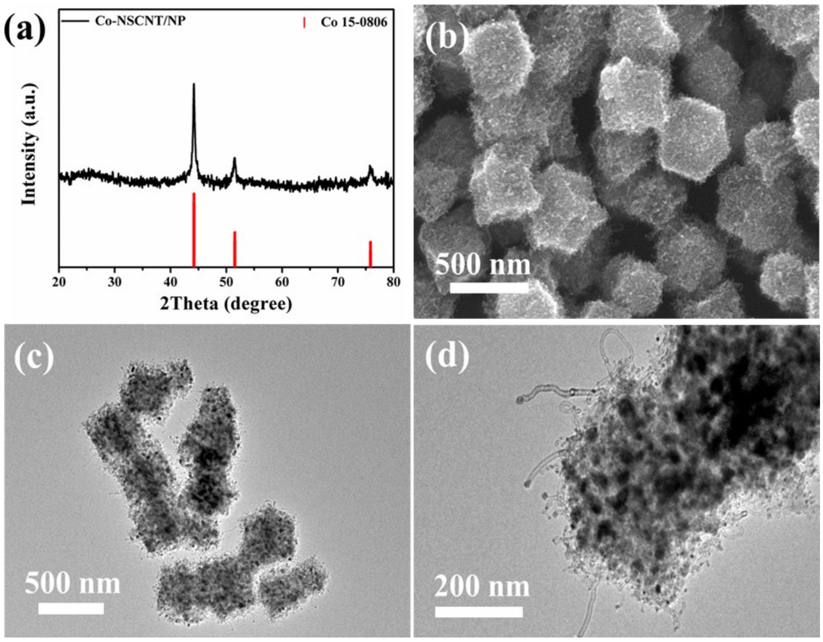

Fig. S5 (a) XRD patterns, (b) SEM image, and (c, d) TEM images of Co-NSCNT/NP.

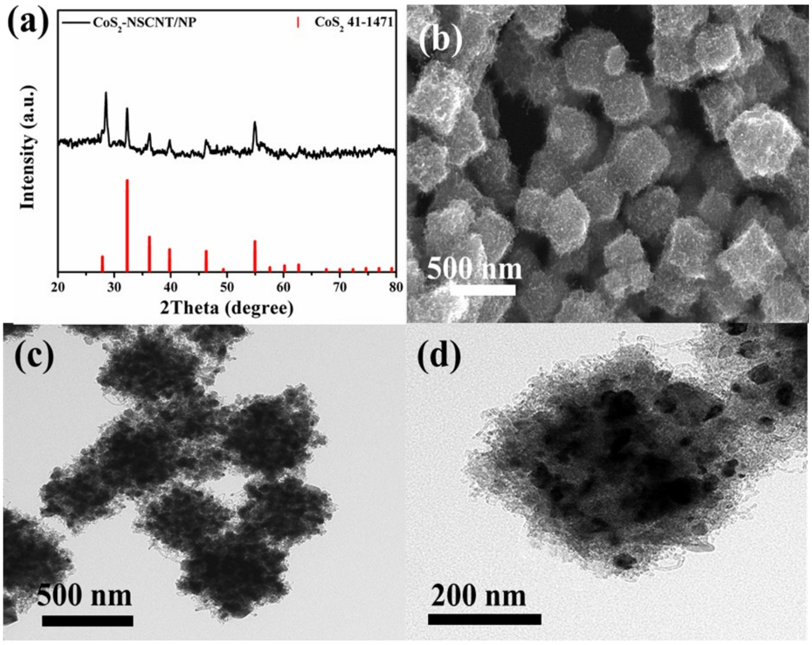

Fig. S6 (a) XRD patterns, (b) SEM image, and (c, d) TEM images of CoS_2-NSCNT/NP.

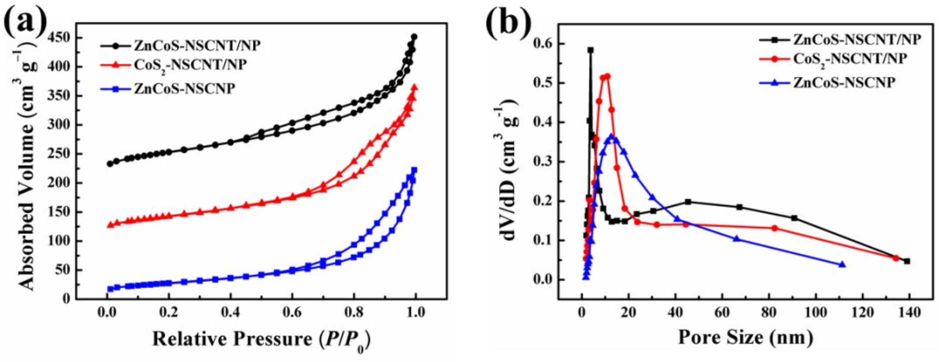

Fig. S7 (a) Nitrogen adsorption−desorption isotherm, and (b) BJH pore size distribution of ZnCoS-NSCNT/NP, CoS_2-NSCNT/NP and ZnCoS-NSCNP.

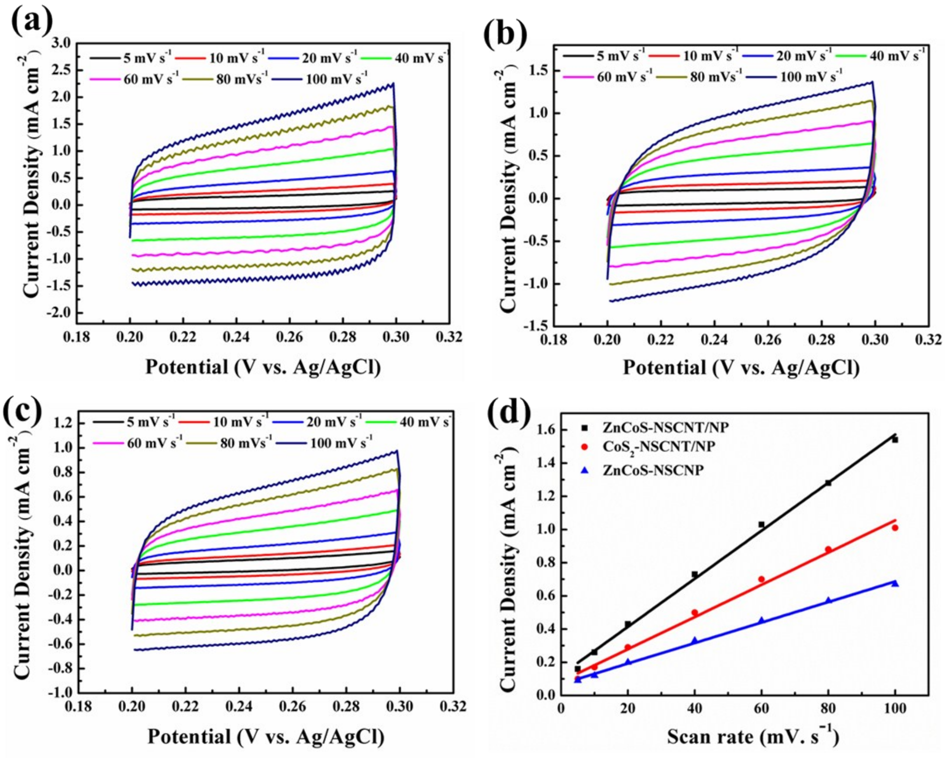

Fig. S8 Cyclic voltammograms in the double-layer region of the electrodes loaded with (a) ZnCoS-NSCNT/NP, (b) CoS_2-NSCNT/NP, and (c) ZnCoS-NSCNP. (d) plot of current density vs. scan rate at 0.25 V vs. Ag/AgCl.

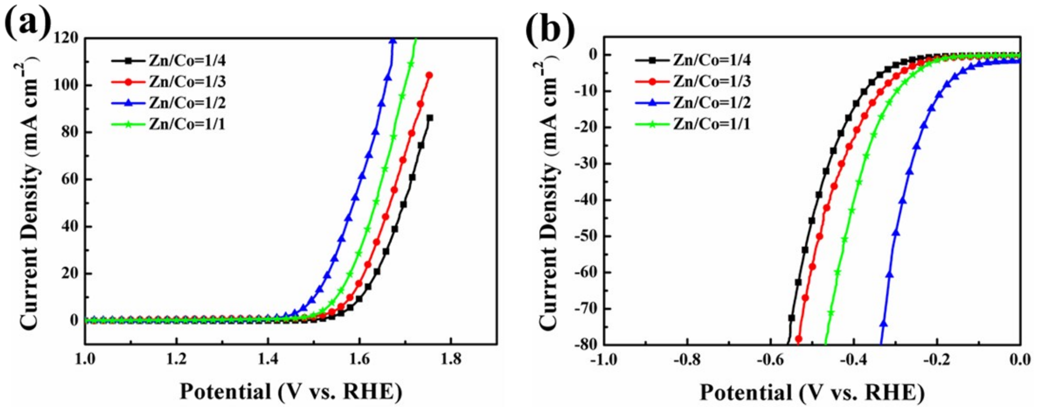

Fig. S9 (a) and (b) LSV curves of samples prepared with different Zn/Co molar ratios in precursor.

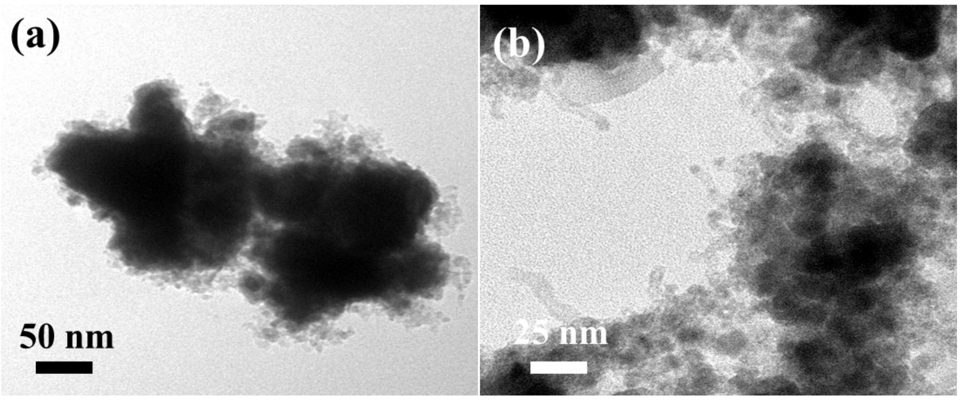

Fig. S10 (a, b) TEM image of ZnCoS-NSCNT/NP after 40 h of electrolysis in 1M KOH .

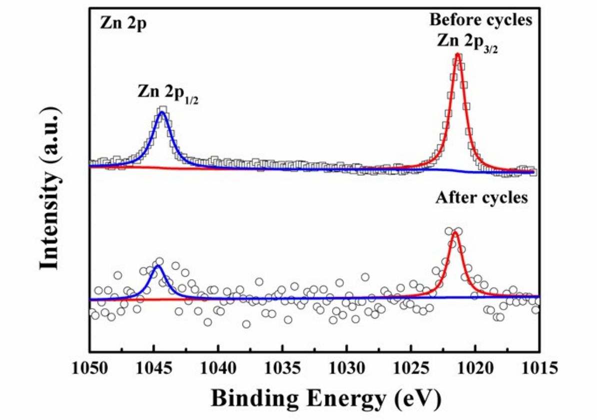

Fig. S11 High-resolution XPS spectra of Zn 2p before and after cycles in alkaline solution.

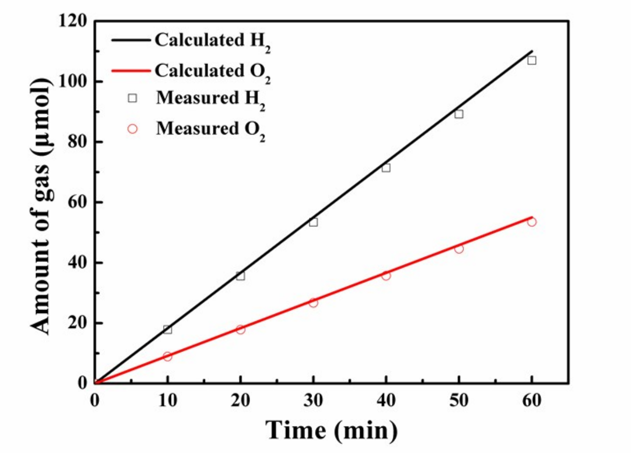

Fig. S12 The amount of gas theoretically calculated and experimentally measured versus time for overall water splitting of ZnCoS-NSCNT/NP.

Table S1. Comparison of electrochemical parameters of Co_3ZnC/Co-NCCP and other reported OER catalysts in 1M KOH

Electrocatalysts	**Overpotential (mV *vs*. RHE) at 10 mA·cm^{-2}**	**Tafel slope**	**Ref**
ZnCoS-NSCNT/NP	270 mV	67 mV dec^{-1}	This work
CoP/rGO	340 mV	66 mV dec^{-1}	S1
$NiCo_2S_4$	337 mV	64 mV dec^{-1}	S2
$Ni_xCo_{2x}(OH)_{6x}$@Ni	305 mV	78 mV dec^{-1}	S3
Zn-Co-S/TM	330 (20 mA cm^{-2})	79 mV dec^{-1}	S4
N-CG-CoO	340 mV	71 mV dec^{-1}	S5
CoS_2 NTA	276 mV	81 mV dec-1	S6
Co@Co_3O_4-NC	391 mV	102 mV dec^{-1}	S7

Table S2. Comparison of electrochemical parameters of Co_3ZnC/Co-NCCP and other reported HER catalysts in 1M KOH.

Electrocatalysts	**Overpotential (mV *vs.* RHE) at 10 mA·cm^{-2}**	**Tafel slope**	**Ref**
ZnCoS-NSCNT/NP	152 mV	103 mV dec^{-1}	This work
Zn-Co-S NN/CFP	234 mV	109 mV dec^{-1}	S8
MoS_{2+x} nanoparticles	310 mV	84 mV dec^{-1}	S9
$NiSe_2$ nanosheets	184 mV	184 mV dec^{-1}	S10
Co_9S_8@MoS_2/C	190 mV	110 mV dec^{-1}	S11
Ni_3S_2 particles	335 mV	97 mV dec^{-1}	S12
CP/CTs/Co-S	190 mV	131 mV dec^{-1}	S13
$NiCo_2S_4$	260 mV	141 mV dec^{-1}	S14

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