Cobalt and nitrogen co-doped Ni_3S_2 nanoflowers on nickel foam as high-efficiency electrocatalysts for overall water splitting in alkaline media

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DFT calculation

In this study, the Cambridge Serial Total Energy Package module of Materials Studio was used for DFT calculation. The interactions of electrons were calculated by the generalized gradient approximation functions of Perdew-Burke-Emzerh (GGA-PBE). The (010) plane optimal structures of Ni_3S_2/NF, Co-Ni_3S_2/NF, N-Ni_3S_2/NF and Co-N-Ni_3S_2/NF were calculated by setting a cutoff energy of 480 eV and 8×8×1 k-points grid. The structures were also optimized for energy and force convergence choosing as 2.0×10^{-5} eV/atom and 0.05 eV/A, respectively. The vacuum space was up to 0.002 A to eliminate periodic interactions.

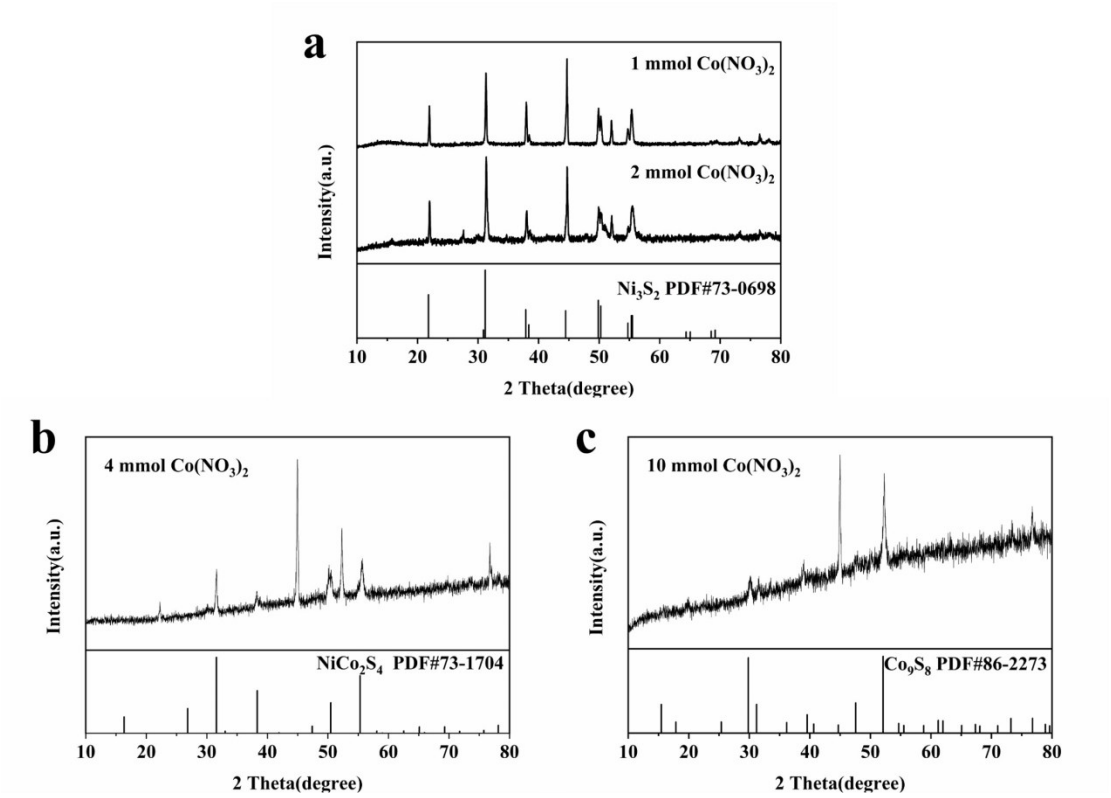

Fig. S1 XRD patterns of different cobalt contents for resulting materials (a) 1 mmol and 2 mmol $Co(NO_3)_2\cdot6H_2O$; (b) 4 mmol $Co(NO_3)_2\cdot6H_2O$ and (c) 10 mmol $Co(NO_3)_2\cdot6H_2O$.

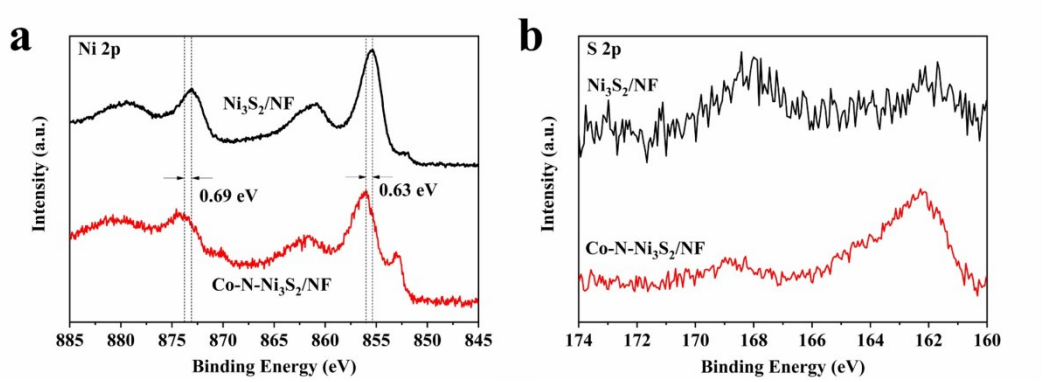

Fig. S2 High resolution XPS spectra (a) Ni 2p and (b) S 2p for Ni_3S_2/NF and Co-N-Ni_3S_2/NF, respectively.

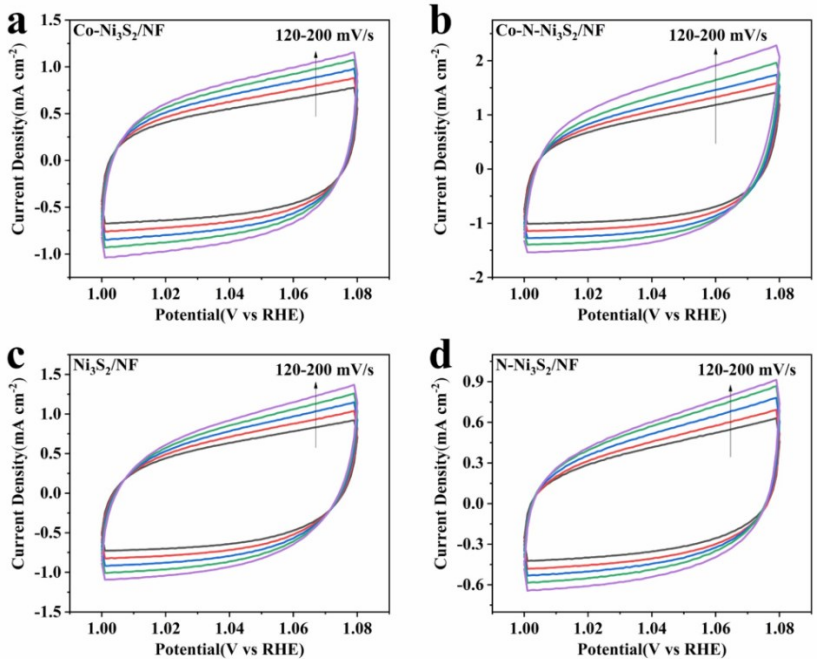

Fig. S3 The cyclic voltammetric curves of the catalyst at scanning speeds of 120, 140, 160, 180, 200 mV/s when the catalyst was used as an anode. (a)Co-Ni_3S_2/NF, (b) Co-N-Ni_3S_2/NF, (c) Ni_3S_2/NF and (d) N-Ni_3S_2/NF.

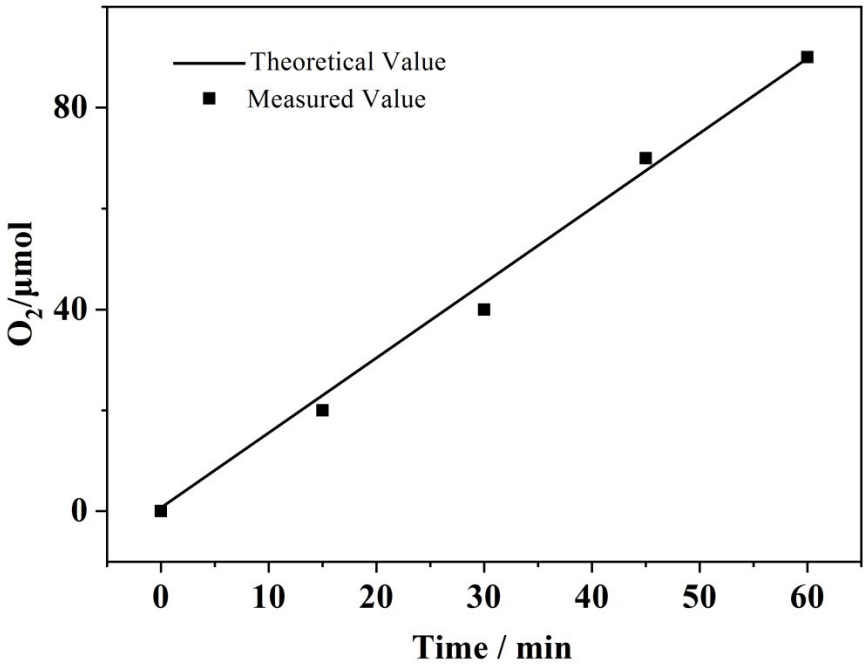

Fig. S4 Electrocatalytic efficiency of O_2 production over Co-N-Ni_3S_2/NF.

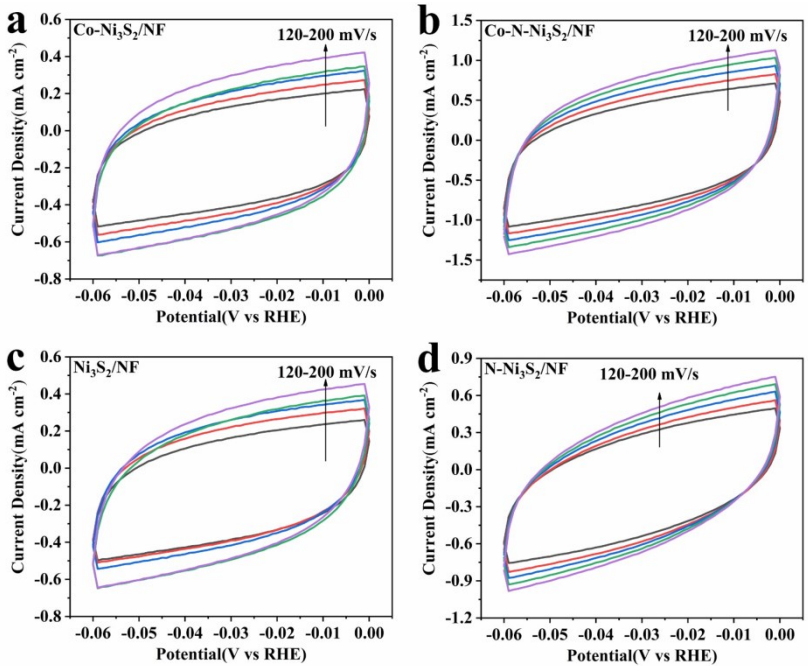

Fig. S5 The cyclic voltammetric curves of the catalyst at scanning speeds of 120, 140, 160, 180, 200 mV/s when the catalyst was used as a cathode. (a)Co-Ni_3S_2/NF, (b) Co-N-Ni_3S_2/NF, (c) Ni_3S_2/NF and (d) N-Ni_3S_2/NF.

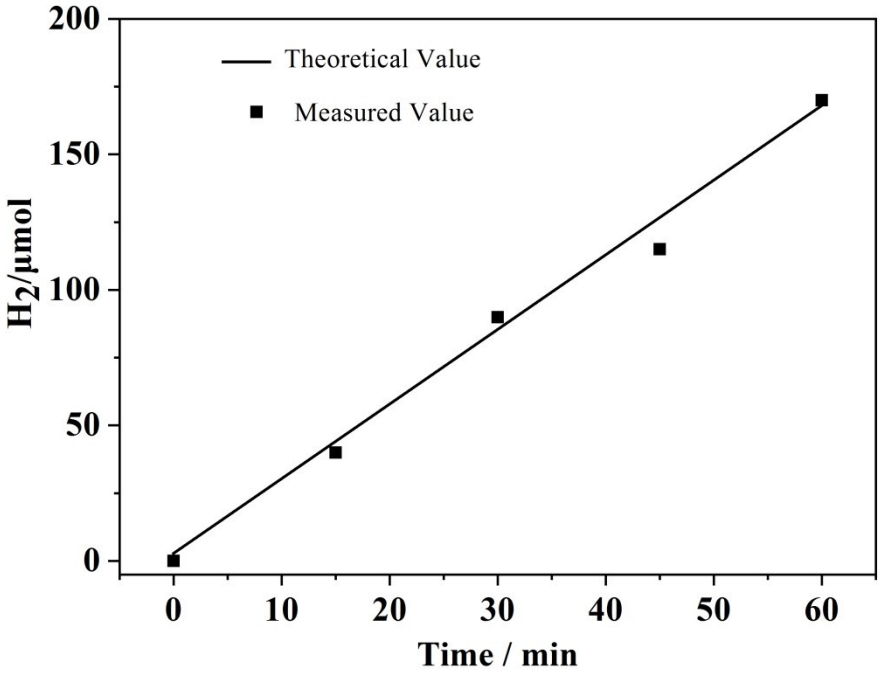

Fig. S6 Ectrocatalytic efficiency of H_2 production over Co-N-Ni_3S_2/NF.

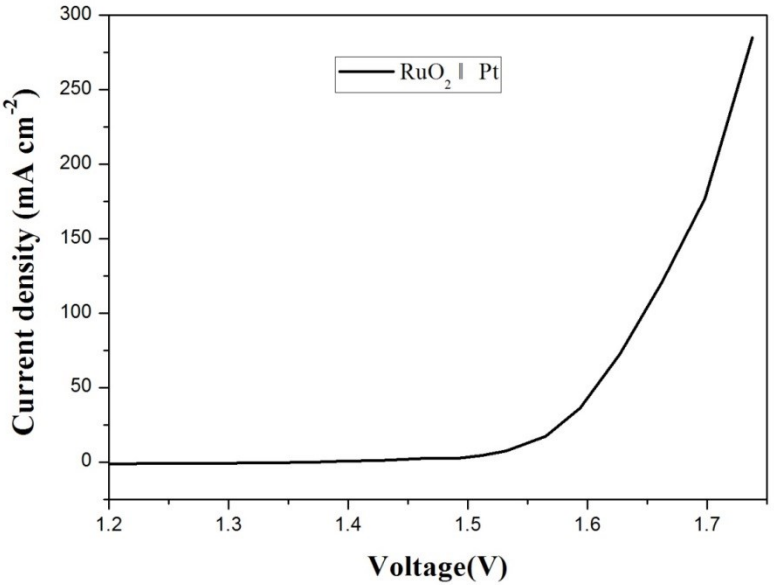

Fig. S7 Polarization curve of the RuO_2 and Pt for water splitting with a scan rate of 5 mV s^{-1} in 1 M KOH.

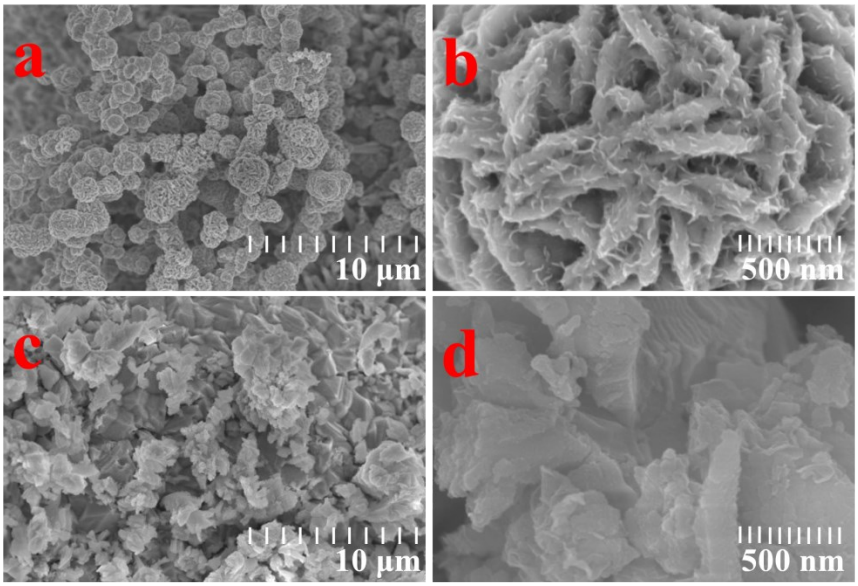

Fig. S8 SEM image of fresh(a,b) and recovered(c,d) Co-N-Ni_3S_2/NF (after 12 h tests).

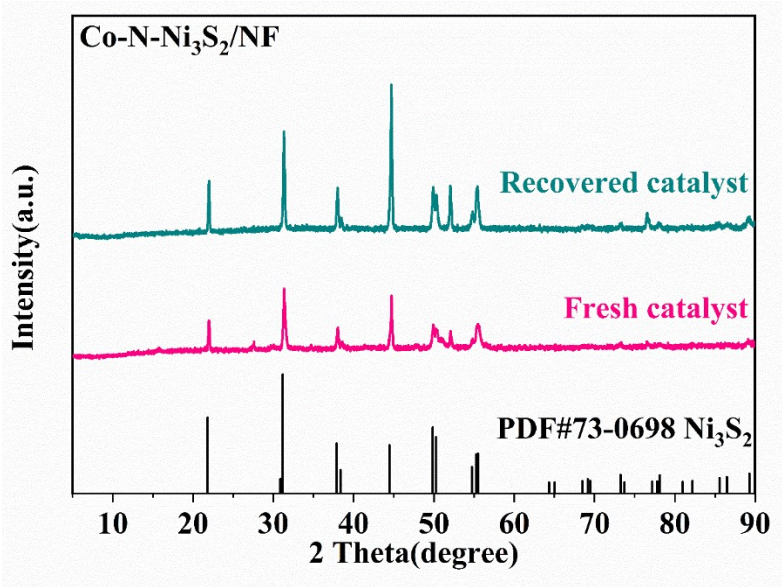

Fig. S9 XRD patterns of Co-N-Ni_3S_2/NF before and after stability test (after 12 h tests).

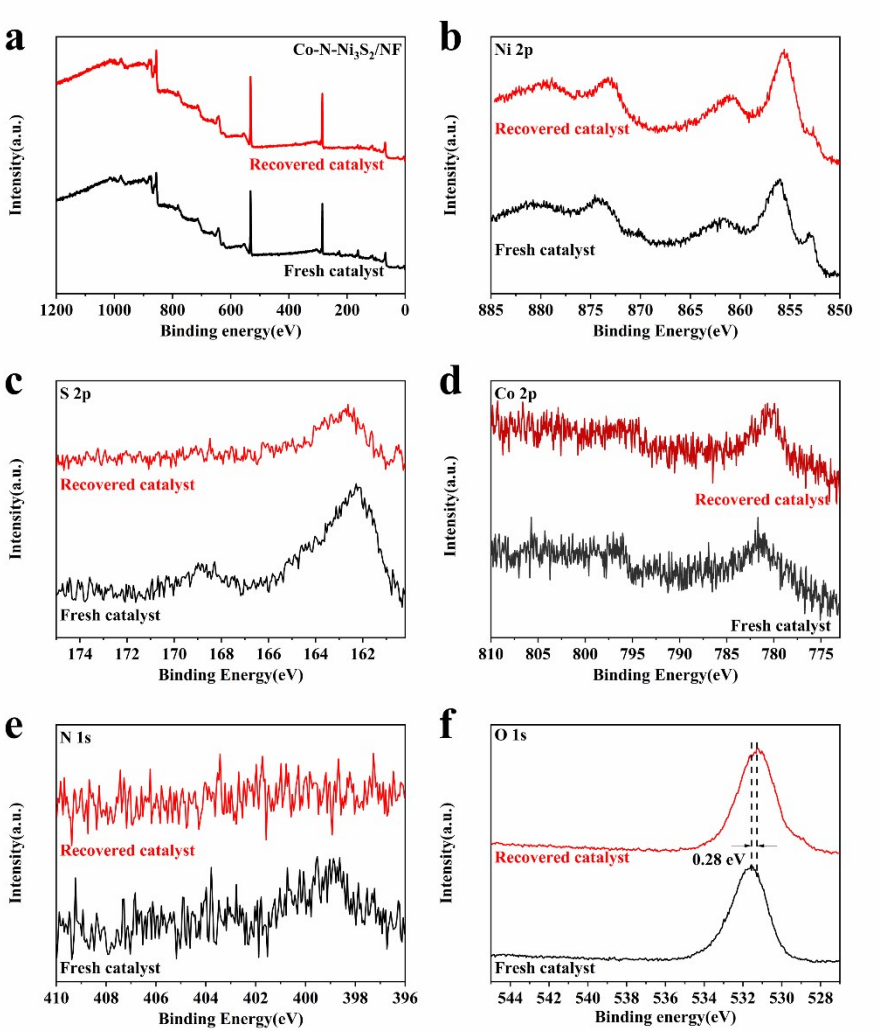

Fig. S10 (a) XPS survey spectra, (b) Ni 2p, (c) S 2p, (d) Co 2p,(e) N 1s and (f) O 1s high resolution XPS spectra of fresh and recovered Co-N-Ni_3S_2/NF, respectively (after 12 h tests).

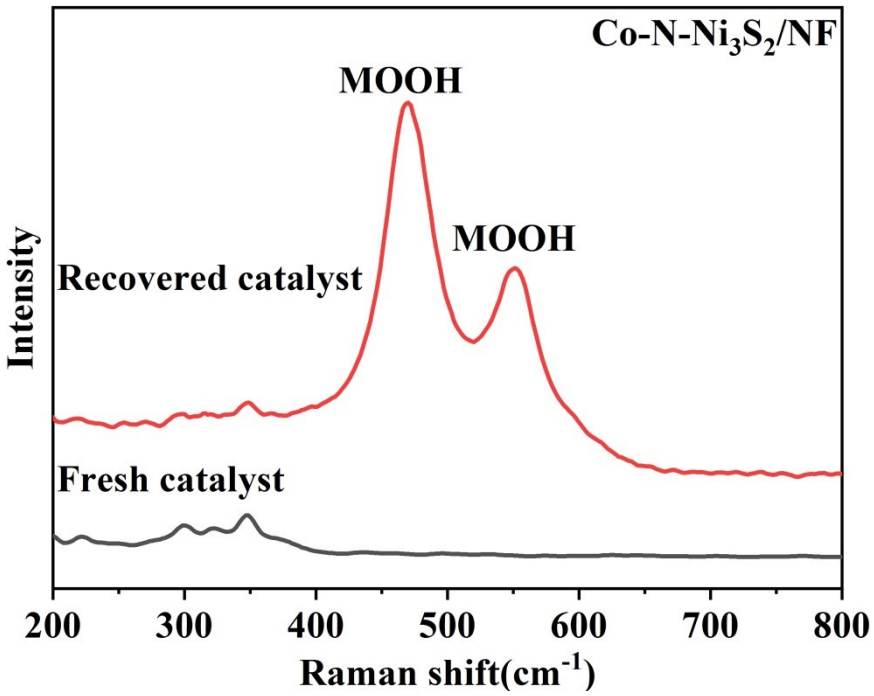

Fig. S11 Raman of fresh and recovered Co-N-Ni_3S_2/NF for OER reaction.

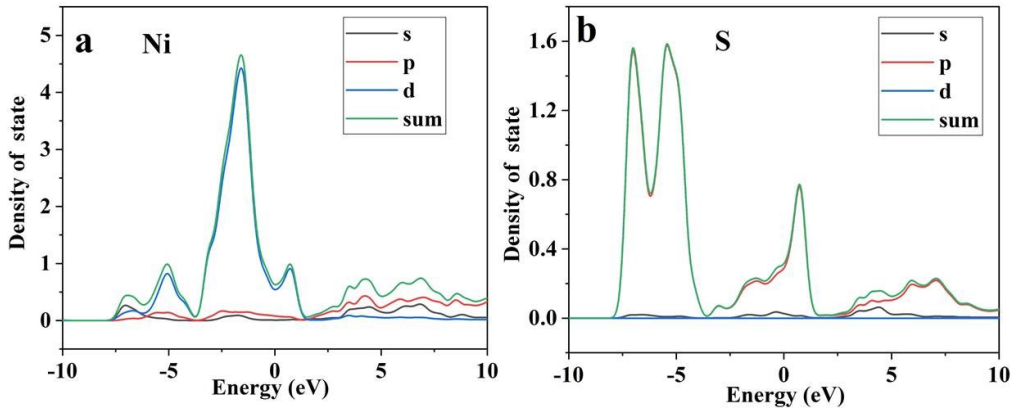

Fig. S12 Density of states for Ni_3S_2, (a) Ni and (b) S.

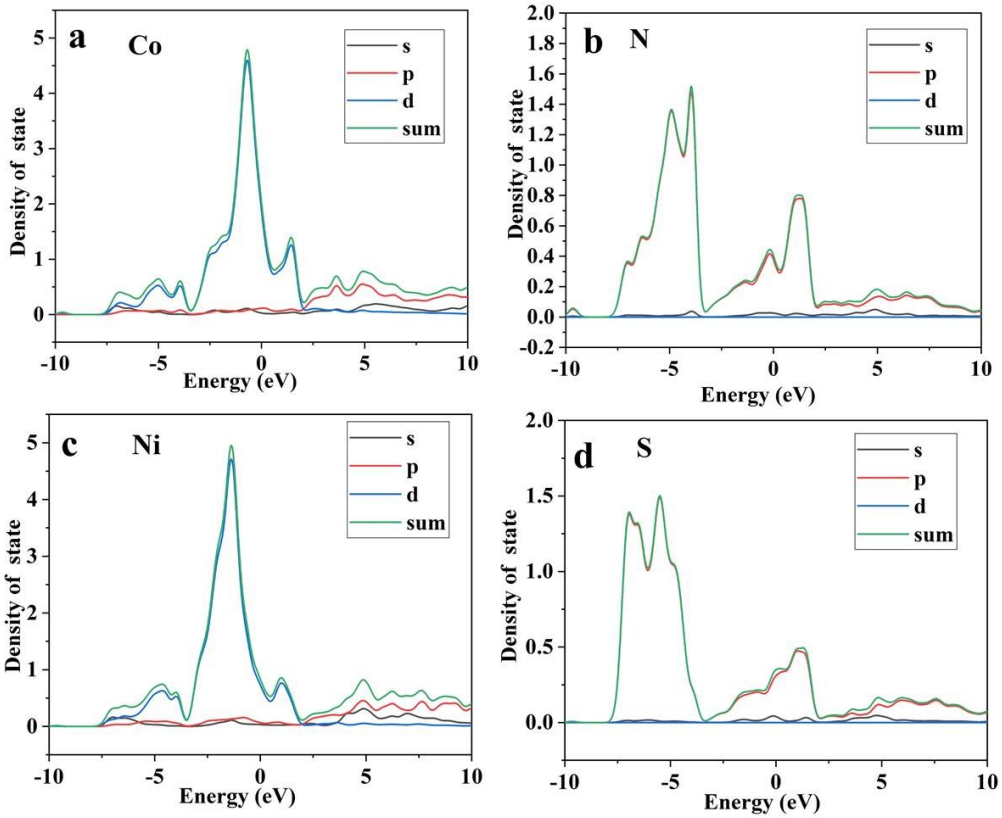

Fig. S13 Density of states for Co-N-Ni_3S_2, (a) Co, (b)N, (c) Ni and (d) S.

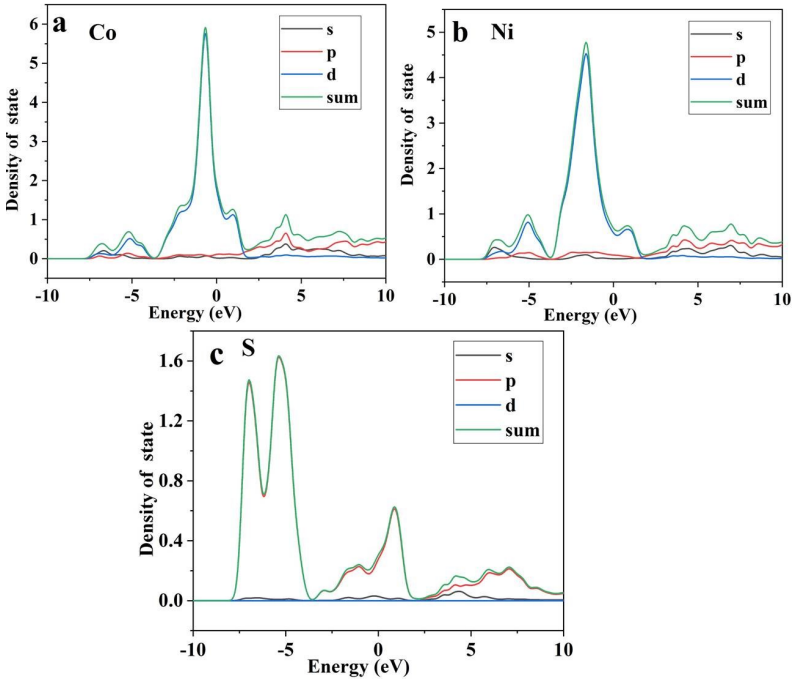

Fig. S14 Density of states for Co-Ni_3S_2, (a) Co, (b) Ni and (c) S.

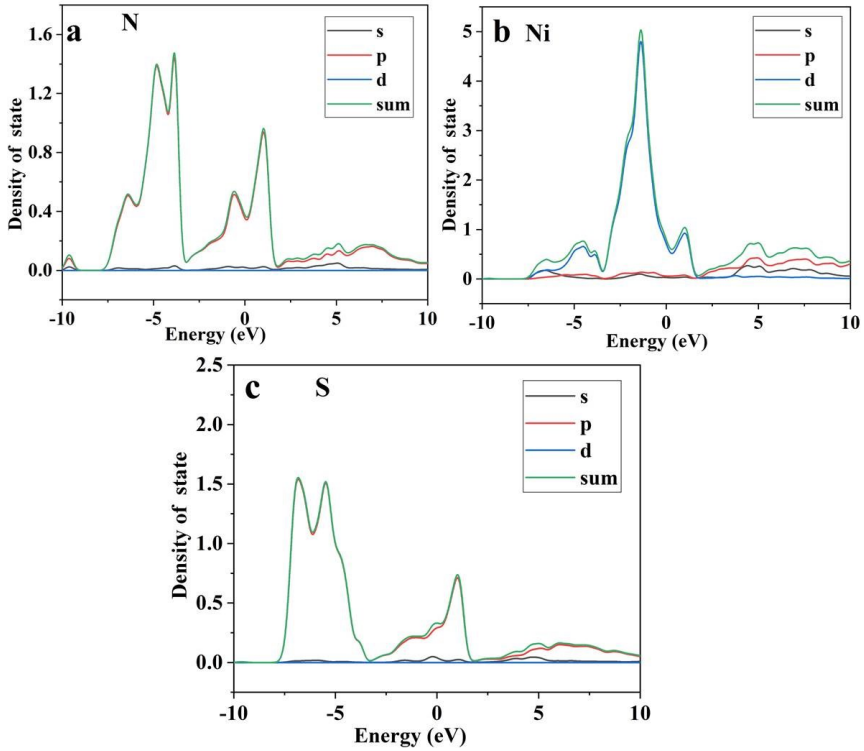

Fig. S15 Density of states for N-Ni_3S_2, (a) N, (b) Ni and (c) S.

Table S1. Overall water splitting performances of Co-N-Ni_3S_2/NF and other reported electrocatalysts in alkaline media. (1 M KOH).

Catalyst	η_{10} (j = -10 mA/cm^2)	electrolyte	Ref.
Co-N-Ni_3S_2/NF	1.50 V	1 M KOH	This work
$NiMoPO_x$	1.55 V	1 M KOH	[1]
$Co_{0.75}Ni_{0.25}Se$/NF	1.60 V	1 M KOH	[2]
Mo-Ni_3S_2	1.66 V	1 M KOH	[3]
Co_2P/EG	1.67 V	1 M KOH	[4]
CoSe	1.77 V	1 M KOH	[5]

Reference

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