Supporting Information

Self-Supported Co_3O_4@Zn-$CoNi_2S_4$/NF Core-Shell Nanoarrays as an Efficient Bifunctional Electrode for Overall Water Splitting

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Supplementary Figures and Tables

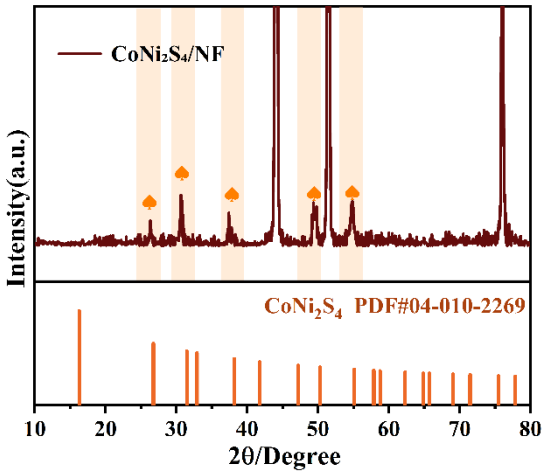

Fig S1. XRD pattern of the $CoNi_2S_4$/NF.

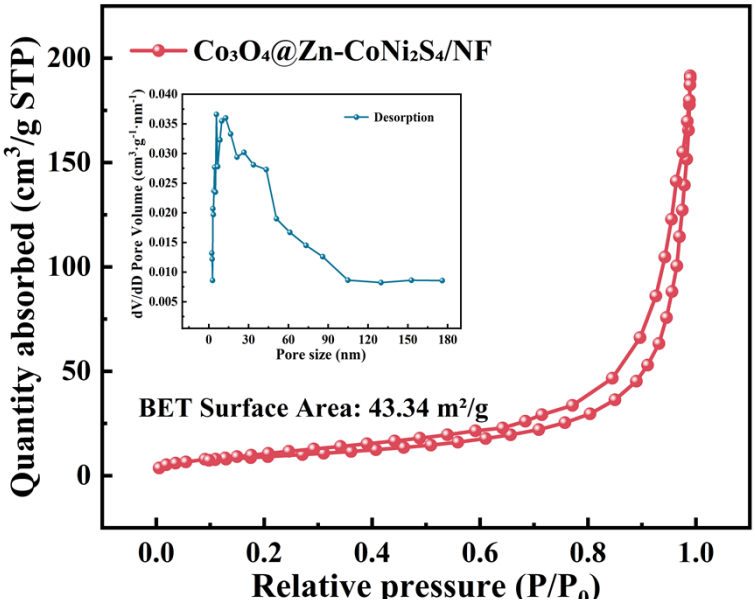

Fig.S2. N_2 adsorption-desorption isotherms and pore size distribution of Co_3O_4@Zn-$CoNi_2S_4$/NF.

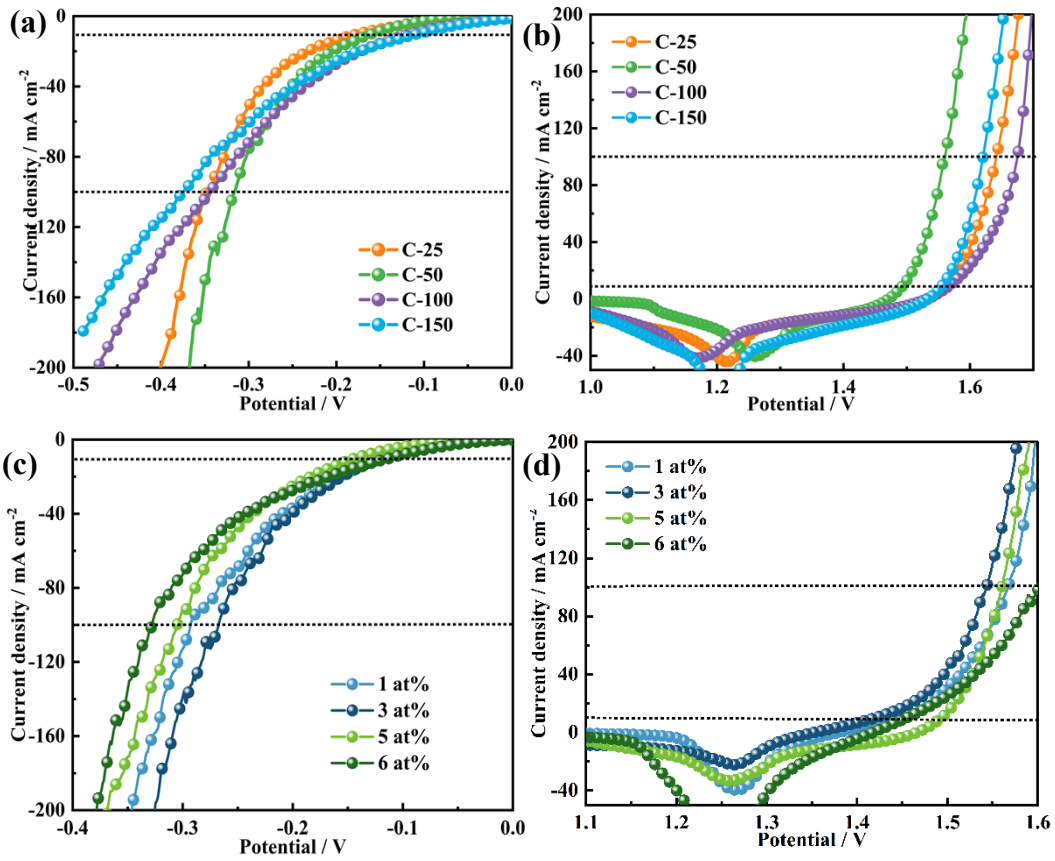

Fig. S3 (a) HER and (b) OER LSV curves of the C-25, C-50, C-100, and C-150. (c) HER and (d) OER LSV curves with varying Zn doping contents.

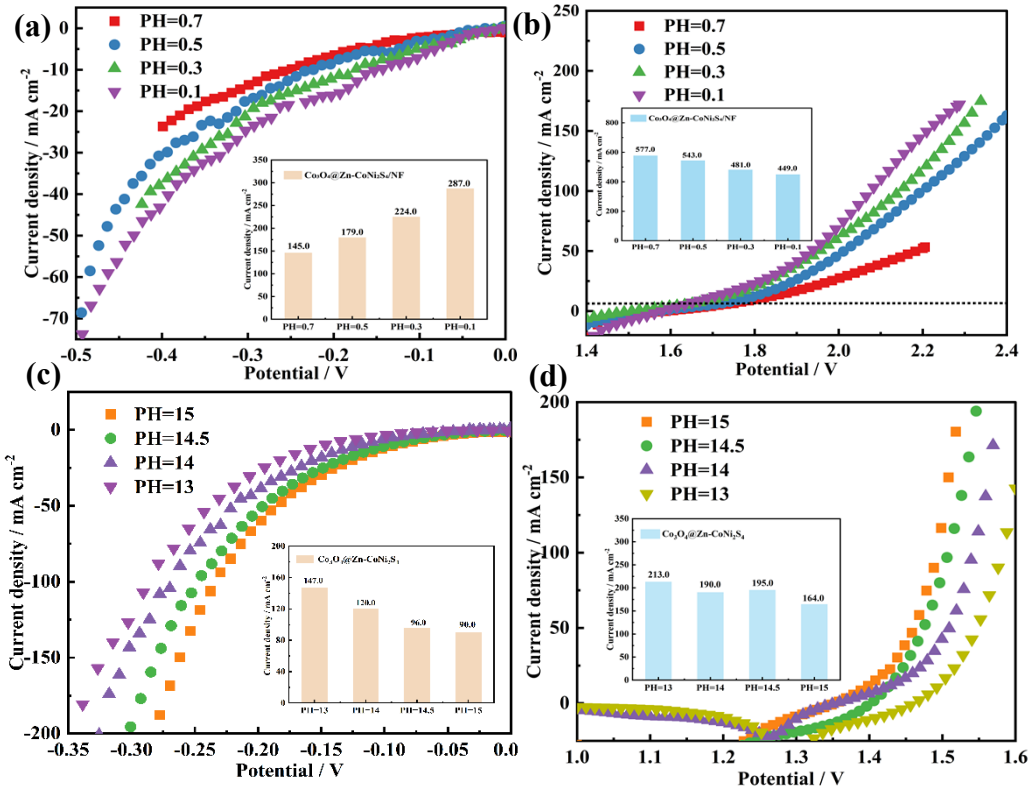

Fig. S4. LSV curves of Co_3O_4@Zn-$CoNi_2S_4$ for (a) HER and (b) OER measured in H_2SO_4 solutions (pH ≈ 0.7, 0.5, 0.3, and 0.0)；(c) HER and (d) OER measured in KOH solutions (pH ≈ 13.0, 14.0, 14.5, and ~15.0).

In response to these comments, LSV measurements are conducted in both acidic and alkaline electrolytes to evaluate the catalytic activity of Co_3O_4@Zn-$CoNi_2S_4$. For the acidic tests, 0.1 M, 0.3 M, 0.5 M and 1.0 M H_2SO_4 are employed, corresponding to a pH range of approximately 0.7–0.0. For the alkaline tests, 0.1 M, 1.0 M, 3.0 M and 5.0 M KOH are used, with a pH range of about 13.0–15.0.

Given that NF undergoes corrosion in acidic electrolytes, Co_3O_4@Zn-$CoNi_2S_4$ powder is uniformly coated onto carbon cloth using a mixture of Nafion and ethanol as the binder. Electrochemical performance tests are then carried out under the same conditions as those described in the main text. The results demonstrate that the catalyst exhibits excellent catalytic activity in alkaline media, which is consistent with the main conclusions of this paper. However, its performance decreases significantly in acidic electrolytes, as illustrated in Fig. S4 (a–d) (page 3 of the Supporting Information).

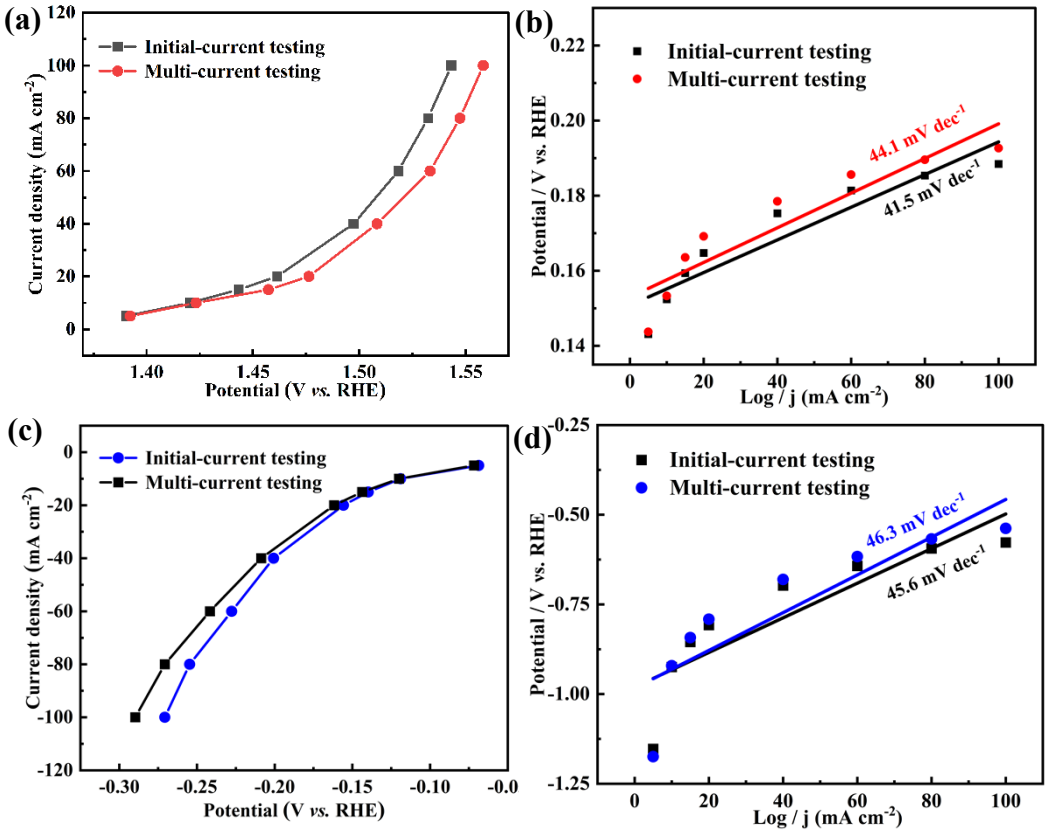

Fig. S5. Comparison of polarization curves and corresponding Tafel plots obtained from LSV and steady-state potentiostatic measurements for Co_3O_4@Zn-$CoNi_2S_4$/NF.

Table 1 The OER overpotentials and standard deviations

Sample	η @ 10 mA cm^{-2} (V)	Standard Deviation	Sample Size
Co_3O_4@Zn-$CoNi_2S_4$/NF	195mV	±2.63	3
Co_3O_4@$CoNi_2S_4$/NF	265mV	±2.71	3
Co_3O_4/NF	303mV	±2.94	3

Table 2 The HER overpotentials and standard deviations

Sample	η @ 10 mA cm^{-2} (V)	Standard Deviation	Sample Size
Co_3O_4@Zn-$CoNi_2S_4$/NF	120mV	±2.64	3
Co_3O_4@$CoNi_2S_4$/NF	160mV	±3.25	3
Co_3O_4/NF	168mV	±2.29	3

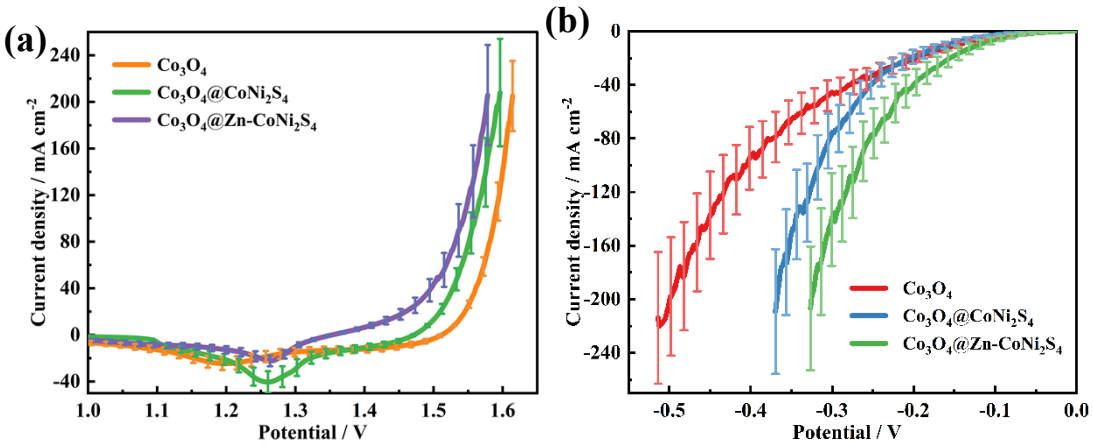

Fig. S6 Overpotential comparison at a current density of 10 mA cm^{-2} for (a) the OER and (b) the HER of Co_3O_4@Zn-$CoNi_2S_4$/NF.

Fig. S7 Schematic diagram of the faradaic efficiency measurement setup

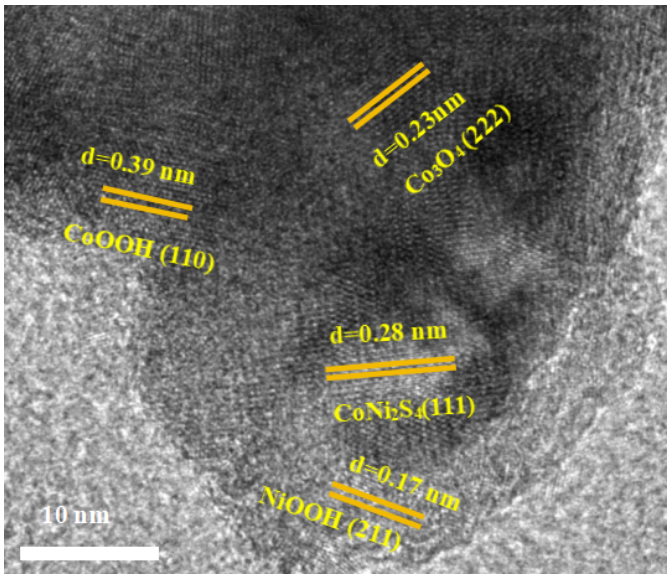

Fig. S8 HRTEM image of Co_3O_4@Zn-$CoNi_2S_4$/NF after cycling.

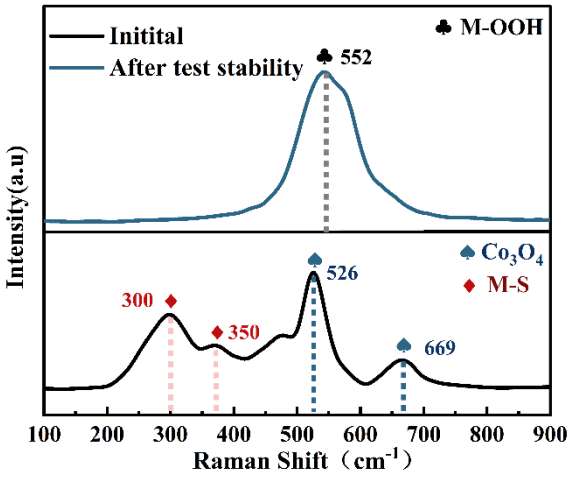

Fig. S9 Raman spectra of Co_3O_4@Zn-$CoNi_2S_4$/NF before and after cycling.