Supporting information

Co doping modulates the electronic structure of nickel diselenide and promotes the simultaneous occurrence of glycerol oxidation and hydrogen evolution reactions

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Experimental Section

Raw materials

Selenium powder is purchased from McLean, nickel nitrate is produced by Shanghai Zhongqin Chemical Reagent Co., Ltd., cobalt nitrate is supplied by Adamas Beta (Shanghai) Chemical Reagent Co., Ltd., potassium hydroxide is provided by Shanghai Wokai Biotechnology Co., Ltd., sodium hydroxide and isopropanol are obtained from China National Pharmaceutical Group Chemical Reagent Co., Ltd., glycerin is sourced from Aladdin Reagents (Shanghai) Co., Ltd., and Nafion solution is produced by Alfa Aesar Chemical Co.

Synthesis of Co-$NiSe_2$

Weigh nickel nitrate (1-x mmol) and cobalt nitrate (x mmol) in the ratios of x = 0, 0.05, 0.1, 0.15, 0.2 mmol, ensuring the total molar amount is 1 mmol. Dissolve the metal salts in 25 mL of deionized water to prepare Solution 1. Weigh 4 g of NaOH and 2 mmol of selenium powder, and dissolve them in 5 mL of deionized water to create Solution 2. Combine Solutions 1 and 2, and stir the mixture for 30 min. Transfer the resulting solution to a 50 mL reaction vessel and conduct a hydrothermal reaction at 200 °C for 10 h. After cooling, wash the product with deionized water and anhydrous ethanol, then filter it. Dry the product under vacuum at 50 °C overnight to obtain cobalt-doped nickel selenide catalysts with varying compositions[1, 2].

Material characterization

The phase and structural testing of the experimental samples was conducted using a D8 ADVANCE X-ray diffractometer from Bruker, Germany. The testing conditions were as follows: scanning speed of 10°/min; scanning range from 10° to 80°; and X-ray source of Cu Kα (λ = 1.5418 Å). For morphological analysis of the prepared

samples, an ULTRA plus field emission scanning electron microscope (FE SEM) from Carl Zeiss, USA, was utilized. The microstructure of the prepared materials was examined using a TF20 transmission electron microscope from FEI, USA. The specific testing process involved taking a small amount of the sample and placing it in a centrifuge tube, adding an appropriate volume of ethanol solvent, and ultrasonically dispersing it for 10 min. Once the sample was evenly dispersed, a suitable amount was pipetted and deposited onto a microgrid, which was then dried prior to testing and observation[3].Using the ESCALABXI^{+}X-ray photoelectron spectrometer (XPS) from Thermo Fisher Scientific, we analyzed the valence states and composition of the surface elements of the samples. The XPS spectra were calibrated using the C 1s peak at 284.8 eV[4].

Preparation of catalyst electrodes

Weigh 5 mg of catalyst into a sample tube. Add 20 μL of Nafion and 980 μL of DMF solution, then sonicate for 1 h to create a homogeneous solution. Next, use a pipette to transfer 25 μL of the solution and coat it onto the surface of carbon paper. Allow the coated carbon paper to air dry naturally before testing. The carbon paper is treated with 0.5 mol L^{-1} hydrochloric acid, acetone, alcohol, and deionized water, with each treatment sonicated for 15 min and then dried at 60 °C before use. The dimensions of the carbon paper are 1 × 1 cm^2, resulting in a catalyst loading of 0.2 mg cm^{-2}.

Electrochemical performance testing

All electrochemical measurements were conducted on the Autolab PGSTA T128N electrochemical workstation using a three-electrode system,. The 10% Co-$NiSe_2$ sample served as the working electrode, with Hg/HgO functioning as the reference electrode and a platinum sheet as the counter electrode. The experimental potential was converted to the RHE using the equation E = E(Hg/HgO) + 0.059 pH + 0.098[5]. The electrocatalytic HER performance of the catalyst in 1 mol L^{-1} KOH electrolyte was tested using LSV or CV[6]. Electrochemical impedance spectroscopy measurements are

performed over a frequency range of 50 kHz to 0.01 Hz, under the open-circuit voltage corresponding to the electrodes. The charge transfer resistance (R_{ct}) is calculated from the diameter of the semicircle in the Nyquist plot. The double-layer capacitance (C_{dl}) is determined through CV at various scan rates. ECSA = 1*C_{dl}/C_s, in which the 12 is geometric area of the electrode, $C_s$represents the average specific capacitance of flat surfaces and its value in alkaline media is 0.040 mF cm^{-2}[7] The stability of the catalyst is assessed by analyzing the polarization curves before and after continuous CV cycling, as well as monitoring the change in test potential over time at a constant current density[8]. All of the above electrochemical tests were conducted without iR compensation.

Product Testing and Analysis

To determine the oxidation products of glycerol and calculate the corresponding Faradaic efficiency, experiments were conducted in an H-type electrolysis cell, utilizing 10% Co-$NiSe_2$ self-supporting electrodes as both the anode and cathode working electrodes. The cathode underwent a steady-state constant current test at a current density of 100 mA cm^{-2}, and hydrogen gas production was collected using a drainage method to calculate the Faradaic efficiency of hydrogen. Similarly, the anode was operated at a fixed current density of 100 mA cm^{-2}. After 2 h, a specific volume of the electrolyte solution was collected and analyzed using a nuclear magnetic resonance (NMR) spectrometer. In preparation for NMR analysis, 200 μL of the electrolyte solution, and 6 mL of DMSO were sequentially added to the NMR tube and sonicated for 10 min. The Faradaic efficiency (%) for the production of H_2 and formate was estimated using the following equations: FE (%) = 100% × V (H_2 production) / (QVs/αF) and FE (%) = 100% × n (formate production) / (Q/αF), where Q represents the total charge consumed during electrolysis, Vs is the standard molar volume (22.4 L mol^{-1}), F is Faraday's constant (96,485 C mol^{-1}), and α is the number of electrons required to produce H_2 molecules (α = 2) and for formate (α = 8/3)[9-13]. The formula for calculating the stability decay rate is: Decay Rate = [(Initial Voltage - Final Voltage)

/ Initial Voltage] * 100%.

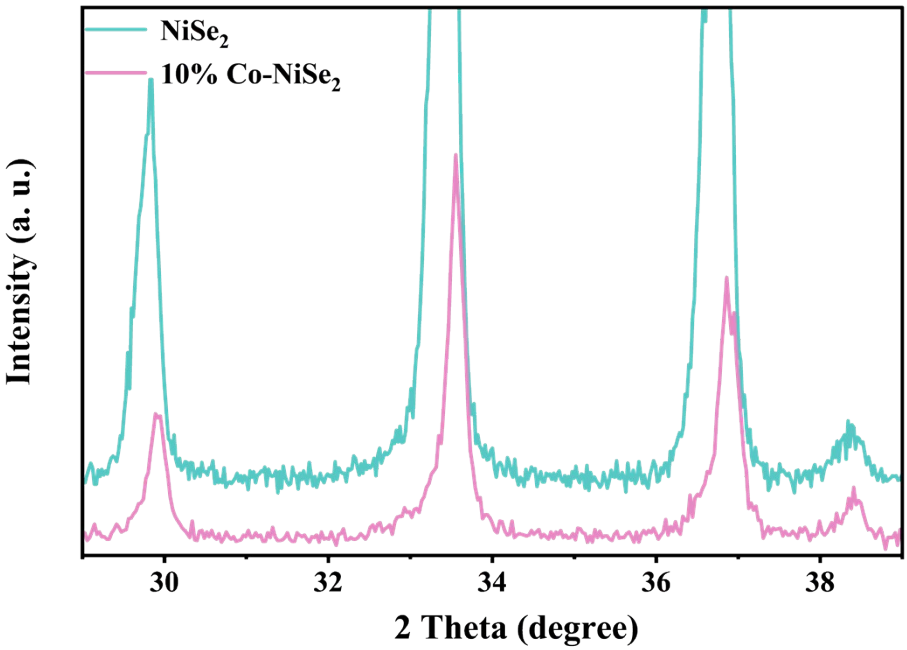

Figure S1 Local magnification of XRD.

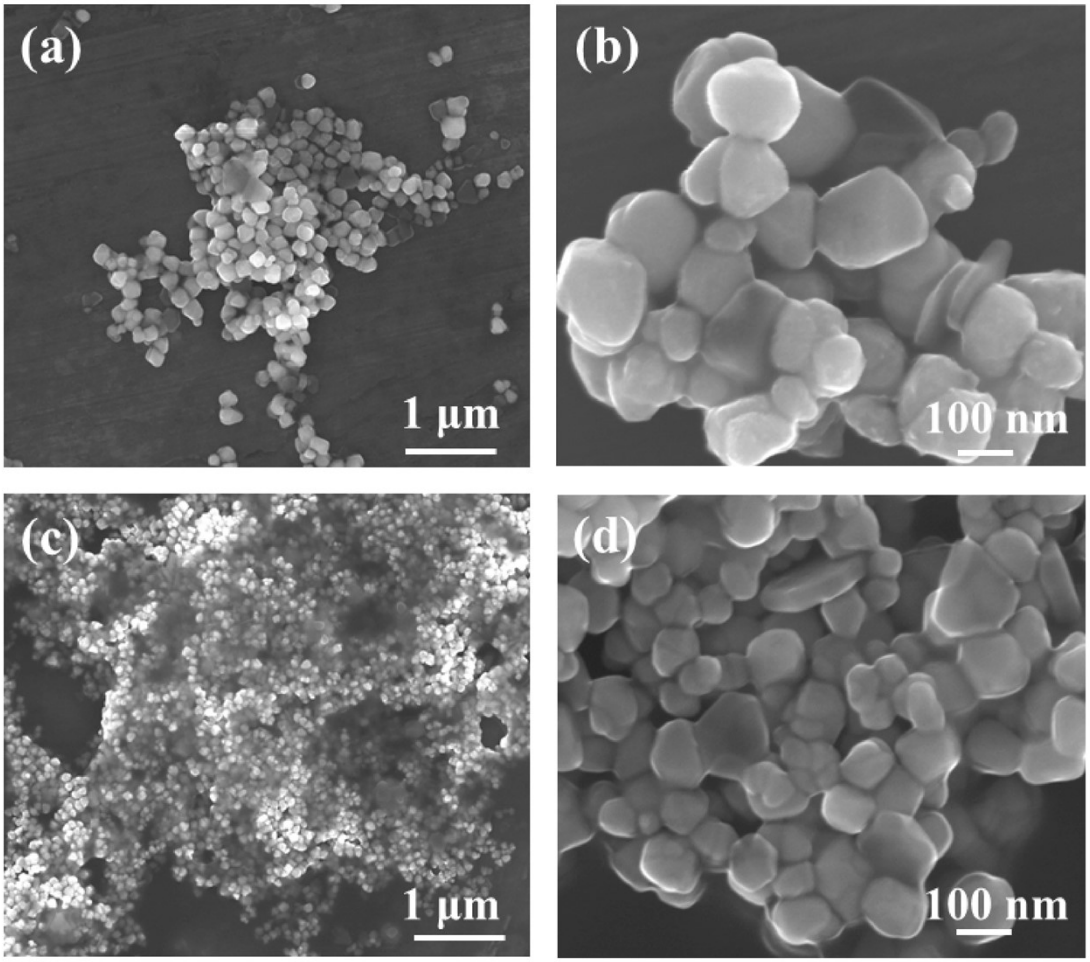

Figure S2 (a, b) SEM images of $NiSe_2$ at different resolutions. (c, d) SEM images of 10% Co-$NiSe_2$ at different resolutions.

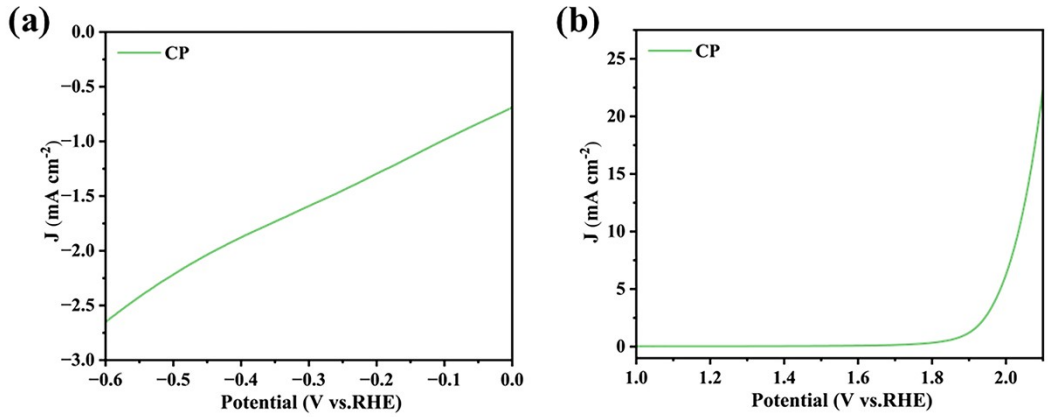

Figure S3 Electrochemical Performance Testing of Carbon Paper. (a) HER; (b)GOR.

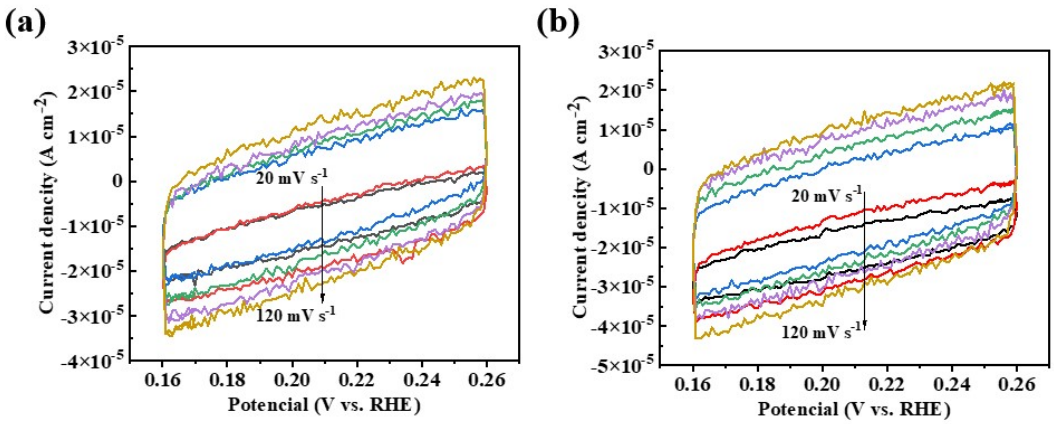

Figure S3 CV curves at different scan rates in the non-faraday range during the hydrogen evolution reaction: (a) $NiSe_2$ and (b) 10% Co-$NiSe_2$.

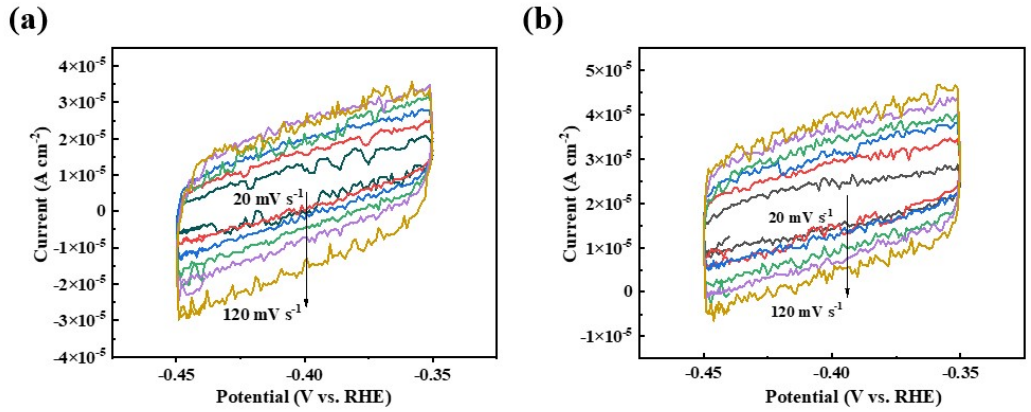

Figure S4 CV curves at different scan rates in the non-faraday range during the GOR: (a) $NiSe_2$ and (b) 10% Co-$NiSe_2$.

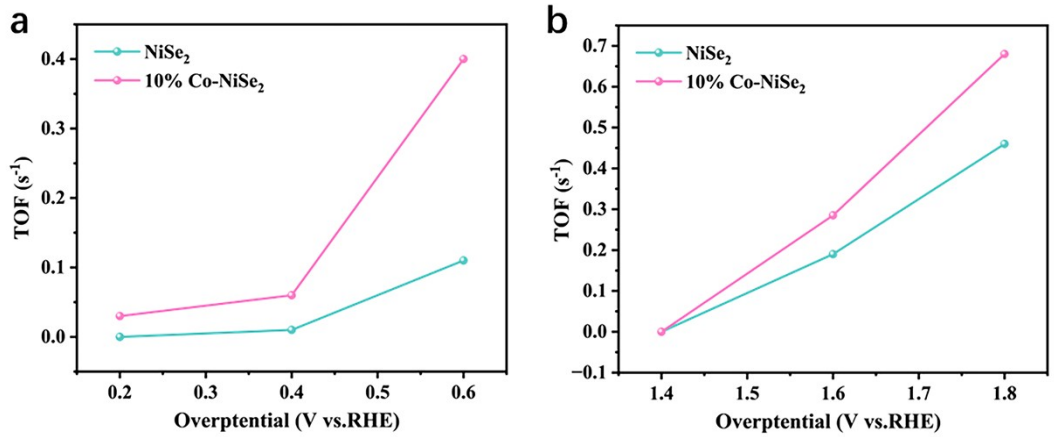

Figure S5 (a) TOF calculation of 10% Co-$NiSe_2$ and $NiSe_2$ in HER, (b)TOF calculation of 10% Co-$NiSe_2$ and $NiSe_2$ in GOR.

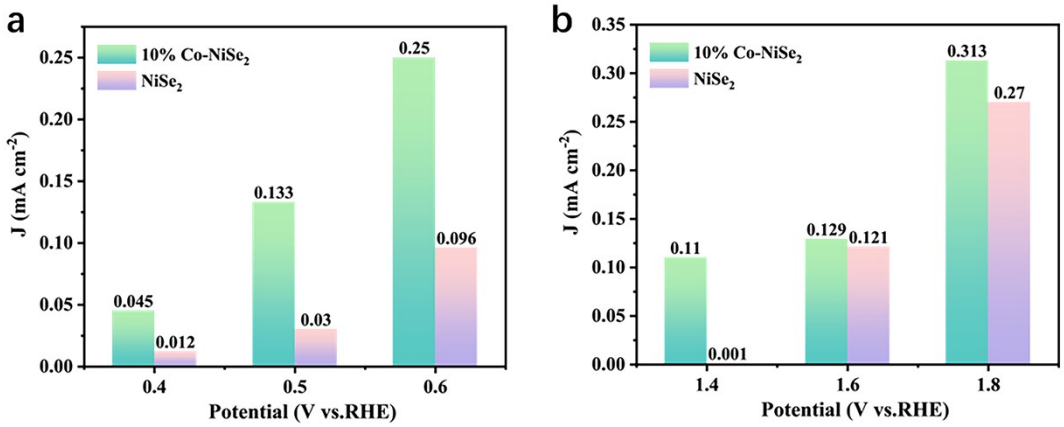

Figure S6 The electrochemical surface area normalized current densities of 10% Co-$NiSe_2$ and $NiSe_2$.(a) HER,(b) GOR.

Table S1: Comparison of the performance of 10%Co-$NiSe_2$ with other catalysts.

Catalyst	Electrolyte	Value-added products	J (mA cm^{-2})	Voltage (V)	Ref
10%Co-NiSe2	1 M KOH +0.1 M Gly	fromate	10	1.45	This work
NC@$CuCo_2N_x$/CF	1 M KOH +0.15 M BA	benzyl alcohol	10	1.62	[14]
Ni-Mo-N/CFC	1.0 M KOH +0.1 M Gly	fromate	10	1.36	[15]
LMOS-4	1 M KOH	O_2	10	1.58	[16]
Eu_3O_4/WO_x	1.0 M KOH +0.1 M Gly	fromate	10	1.52	[17]
Co-Rh_2	1 M KOH +1 M CH_3OH	HCOH	10	1.54	[18]

Referance

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