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Supporting Information

Understanding Electrocatalytic Mechanism of Self-Template Formation of Hierarchical Co₉S₈/Ni₃S₂ Heterojunctions for Highly Selective Electroreduction of Nitrobenzene[†]

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1. Experimental Section

1.1 Chemical Reagents and Materials. Nitrobenzene was obtained from Macklin. Azobenzene was obtained from TCI. Pchloronitrobenzene was obtained from Acros Organics. KOH, dichloromethane (DCM), methanol, ethyl acetate, acetone and HNO₃ (65%-68%) were purchased from Xilong Science Co., Ltd (China). Ni foam (200 mm×300 mm×1.0 mm) was obtained from Kunshan Guangjiayuan Electronics, Jiangsu, and Ti mesh (100 mm×100 mm×1.0 mm) was obtained from Qirui Metal Materials, Hebei. Other reagents, unless otherwise stated, were obtained from commercial sources (Aladdin, Innochem) and were used without further purification.

1.2 Pretreatment of Ni foam. Firstly, in order to remove the surface oxidized layer, a piece of Ni foam (2.0 cm \times 3.0 cm \times 1.0 mm) was cleaned by sonication consecutively in acetone solution for 5 min, then dipped in 1.0 M HCl solution for 10 min, finally washed with ethanol and distilled water (5 min each), respectively. As-obtained nickel foam was dried in a vacuum oven 50 °C, sealed and stored for later use.

1.3 Synthesis of Co-Ni layered-double-hydroxide (LDH) Precursors. All reagents and analytical grades were used without any further purification. In a typical procedure, $Co(NO_3)_2 \cdot 6H_2O$ and urea were dissolved in 60 mL distilled water to form a clear solution, and added in a 100 mL Teflon-lined stainless steel autoclave, then, a piece of Ni foam (2.0 cm × 3.0 cm) was immersed in the solution, and heated at 120 °C. In order to optimize the morphology of precursor, various amounts $Co(NO_3)_2 \cdot 6H_2O$ (n = 0.024 mol, 0.022 mol, 0.020 mol, 0.018 mol, 0.016 mol or 0.014 mol) were heated at 8 hours (h), Co-Ni layered-double-hydroxide (LDH) precursors with smooth surface was perpendicular and uniformly grown on Ni foam was constructed by 0.018 mol Co salts. At the same time, different hydrothermal time (n = 10 h, 8 h, 6 h, 4 h or 2 h) were taken with 0.018 mmol Co salts, which can further verify the most optimal morphology at 8 h. After heating at 120 °C for 8 h, the Ni foam with fuchsia substance was taken out and cleaned by distilled water and ethanol to remove any possible contamination on the surface, and finally dried at 50 °C for 12 h in a vacuum oven.

1.4 Synthesis of Co₉S₈/Ni₃S₂-NF, Ni₃S₂/NF, Co₉S₈/Ti. In the typical process, 0.2 mol/L Na₂S aqueous solution was transferred into a 100 mL Teflon-lined stainless steel autoclave and as-obtained Co-Ni layered-double-hydroxide (LDH) precursor was added into the reaction system. Subsequently, the reaction system was heated to 160 °C for 8 h. The assynthesized black compounds were then washed with distilled water and absolute ethanol, and the final products were dried at 50 °C for 12 h in a vacuum oven. By contrast, Ni₃S₂/NF was synthesized by replacing 0.018 mol Co(NO₃)₂·6H₂O with Ni(NO₃)₂·6H₂O, other conditions remain unchanged. Co₉S₈/Ti was synthesized by Titanium mesh as the supporter, other conditions remain unchanged.

1.5 Materials Characterizations. SEM measurements were performed via a Quanta 200F scanning electron microscope (JEOL, JSM-6380LV). TEM images, HRTEM images, SAED patterns and EDS were performed by a scanning transmission electron microscope (JEOL, JEM-2100F). The N₂ adsorption-desorption measurements were performed on an Autosorb iQ (Anton-Paar China), and the specific surface areas were obtained by the BET model. XRD patterns were obtained by a Bruker D8 Advance X-ray diffractometer. XPS and UPS spectra were recorded on a Shimadzu AXIS Supra. FTIR spectra were recorded on a Thermo Nicolet 6700. Raman spectroscopy was performed on a HORIBA Scientific LabRAM HR Raman spectrometer system. The gas chromatograph (GC) was measured on Agilent 7890A with thermal conductivity (TCD) and flame ionization detector (FID). The injection temperature was set at 350 °C. Nitrogen was used as the carrier gas at 0.5 Mpa, high purity air was used as the carrier gas at 0.5 Mpa, hydrogen was used as the carrier gas at 0.4 Mpa. All reported data are averages of experiments performed at least thrice.

2. Electrochemical measurements

Before tests, the Nafion 117 membrane was pretreated by heating it in H_2O_2 (5%) aqueous solution at 80 °C for 1 h and ultrapure water at 80 °C for another 1 h, respectively, followed by treatment in 0.05 M H_2SO_4 for 1 h and ultrapure water for another 3 h. All the purchased chemicals were used directly without further purification. All instruments and electrodes were from Tianjin Gaoshiruilian Technology Co., Ltd. Electrochemical measurements were carried out in a divided three-compartment with a H-Cell consisting of a working electrode, a Pt plate counter electrode, and a Hg/HgO reference electrode, which was separated into cathode cell (30 mL) and anode cell (30 mL) by the anion membrane (Dupont N117, thickness:183 μ m). The potential measured in this study were aligned to reversible hydrogen electrode (RHE) scale by using the Nernst equation from Hg/HgO using equation (1).

 $E_{\text{RHE}} = E_{(\text{Hg/HgO})} + 0.059 pH + E_{(\text{Hg/HgO})}^{\theta}$

where $E_{(Ha/HaO)}$ was the measured potential using Hg/HgO, and $E_{(Ha/HaO)}^{\theta}$ is the standard potential of Hg/HgO of 0.095 V.

The exposed surface area of the working electrodes was 1.0 cm². Linear sweep voltammetry (LSV), chronoamperometry was performed using an electrochemical workstation (CS Studio 5). The solution of 1.0 M KOH (pH = 14.0) was employed as electrolyte with 1,4-dioxane (Diox) and H₂O (10:25 v/v, 35.0 mL) as the co-solvent unless otherwise stated. Gas chromatograph (GC) yields were reported.

3. Estimate the electrochemical active surface area (ECSA).

The electrochemical double-layer capacitance (C_{dl}) was calculated to estimate the electrochemical surface area (ECSA) through cyclic voltammetry (CV) measurement.¹⁻³ First, this measurement was performed on the same working electrode, the CV was swept in a potential window with no faradic processes between 0.25 to 0.35 V vs RHE with different scan rates (5, 10, 20, 40, 60, 80, and 100 mV s⁻¹). By plotting the difference in current density (j) between the anodic and cathodic sweeps 0.5(j_{anodic} -j_{cathodic}) at 0.30 V vs RHE against the scan rate. ECSA was calculated using ECSA=R_f/m_{loading}, where mloading is the loading mass of catalyst per geometrical area of the electrode. R_f = C_{dl}/40 μ F cm⁻² (the average specific capacitance of a flat standard electrode with 1 cm² of real surface area is 40 μ F cm⁻²).

4. Quantitative analysis of reduction products

To analyze the conversion (con.) of nitroarenes, calculate the corresponding selectivity (sel.) and Faraday efficiency (FE) of aminoarenes, 35 mL of the electrolyte solution was extracted with dichloromethane (DCM) or ethyl acetate after chronoamperometry testing. The extracted products were confirmed by the comparisons of their GC retention time. Yields were determined by GC analysis. The con. (%) of the nitroarenes, sel. (%) and FE (%)of aminoarenes were calculated using the following equations,⁴⁻⁶ respectively.

The nitroarenes conversion (%) and the selectivity (%) of oxidation products were calculated using equations (2)	and (3):
Nitroarenes conversion - mol of nitroarenes consumed 100%	(2)
mol of initial nitroarenes	
Product selectivity – mol of nitroarenes formed	(3)
mol of initial nitroarenes	
The Faradaic efficiency (%) of product formation was calculated using the equation (4):	
Faradaic efficiency = $\frac{mol \ of \ product \ formed}{total \ charged \ passed} \times 100\%$	(4)

where F is the Faraday constant (96,485C mol⁻¹) and n is the electron transfer number.

5. Computational Details

Density function theory calculation were performed by using the CP2K package.⁷ PBE functional⁸ with Grimme D3 correction⁹ was used to describe the system. Unrestricted Kohn-Sham DFT had been used as the electronic structure method in the framework of the Gaussian and plane waves method.^{10, 11} The Goedecker-Teter-Hutter (GTH) pseudopotentials,^{12, 13} DZVP-MOLOPT-GTH basis sets¹⁰ were utilized to describe the molecules. A plane-wave energy cut-off of 500 Ry has been employed.

The Co₉S₈ (440) layer and Ni₃S₂ (110) layer were chosen as the surface slab supercell to decrease the complexity of calculation. Population analysis was performed by the Mulliken scheme, and a kinetic-energy cutoff of 500 eV was used for the plane-wave expansion. Geometry optimization was repeated until the total energy tolerance was converged to 2×10^{-5} eV and the changes of the force on the atoms less than 0.05 eV/Å. The exact number and location of atoms are shown:

$$\Delta G = E_{DFT} + \Delta E_{ZPE} - T\Delta S$$
(5)
where G is Gibbs free energy E is the electronic energy from DET calculations. ZPE is zero-point-energy. T is temperature

where G is Gibbs free energy, E_{DFT} is the electronic energy from DFT calculations, ZPE is zero-point-energy, T is temperature of 298 K.

The adsorption energy was calculated by using the equation (6):

The Gibbs free energy was calculated using the equation (5):

$$\Delta E_{ads} = E_{total} - (E_{surface} + E_{absorbate})$$
(6)
Where E_{total} , $E_{surface}$ and $E_{substrate}$ are the total energy of the adsorption state system, the total energy of the pure surface and

Where E_{total} , $E_{surface}$ and $E_{substrate}$ are the total energy of the adsorption state system, the total energy of the pure surface and the total energy of absorbate, respectively. According to the definition, a more negative value of ΔE_{ads} suggests a more energetically favorable (exothermic) reaction.

6. Supporting Figures



Fig. S1 (a) SEM images, (b) and its corresponding EDS elemental mapping images of Co, Ni and O of CoNi-LDH/NF.



Fig. S2 SEM image and its corresponding EDS elemental mapping images of Ni, Co and S of Co₉S₈/Ni₃S₂-NF.



Fig. S3 (a, b) SEM images and (c) and its corresponding EDS elemental mapping images of Co, S and O of Co₉S₈/Ti.



Fig. S4 (a, b) SEM images and (c) and its corresponding EDS elemental mapping images of Ni, S and O of Ni₃S₂/NF.



Fig. S5 SEM images of different content of Co salts of Co_9S_8/Ni_3S_2-NF at 8 h hydrothermal time are (a, b) 0.024 mol, (c, d) 0.022 mol, (e, f) 0.020 mol, (g, h) 0.016 mol, (i, j) 0.014 mol.



Fig. S6 SEM images of different hydrothermal time of Co_9S_8/Ni_3S_2 -NF at 0.018 mmol Co salts are (a, b) 10 h, (c, d) 6 h, (e, f) 4 h, (g, h) 2 h.



Fig. S7 XRD patterns of Co_9S_8/Ni_3S_2 -NF and Co_9S_8 powder.



Fig. S8 XRD patterns of different content of Co salts of Co_9S_8/Ni_3S_2 -NF at 8 h hydrothermal time.



Fig. S9 XRD patterns of (a) Co_9S_8/Ti and (b) Ni_3S_2/NF .



Fig. S10 Co_9S_8/Ni_3S_2 -NF, Co_9S_8/Ti and Ni_3S_2/NF , (b) the proportions of Co and Ni in various Co_9S_8/Ni_3S_2 -NF with different content of Co salts for CoNi-LDH/NF production at 8 h hydrothermal time.



Fig. S11 High-resolution XPS S 2p spectra of (a) Co_9S_8/Ni_3S_2 -NF, (b) Co_9S_8/Ti and (c) Ni_3S_2/NF .



Fig. S12 High-resolution XPS Co 2p spectra of (a) Co_9S_8/Ti , (b-f) different content of Co salts of Co_9S_8/Ni_3S_2 -NF at 8 h hydrothermal time are 0.024 mol, 0.022 mol, 0.020 mol, 0.016 mol, 0.014 mol.



Fig. S13 High-resolution XPS Ni 2p spectra of (a) Ni_3S_2/NF , (b-f) different content of Co salts of Co_9S_8/Ni_3S_2-NF at 8 h hydrothermal time are 0.024 mol, 0.022 mol, 0.020 mol, 0.016 mol, 0.014 mol.



Fig. S14 High-resolution XPS S 2p spectra of (a-e) different content Co salts of Co_9S_8/Ni_3S_2 -NF at 8 h hydrothermal time are 0.024 mol, 0.022 mol, 0.020 mol, 0.016 mol, 0.014 mol.



Fig. S15 FTIR spectra of CoNi-LDH/NF.



Fig. S16 Raman spectra of CoNi-LDH/NF.



Fig. S17 The corresponding pore-size distribution profiles of CoNi-LDH/NF, Ni_3S_2/NF and Co_9S_8/Ni_3S_2-NF .



Fig. S18 The photograph of the electrolytic apparatus.



Fig. S19 (a, c) LSV curves of Co_9S_8/Ni_3S_2 -NF and control samples in 1.0 M KOH aqueous solution ($Diox/H_2O$, 2:5 v/v). (b, d) LSV curves of Co_9S_8/Ni_3S_2 -NF and control samples in 1.0 M KOH aqueous solution ($Diox/H_2O$, 2:5 v/v) with 0.8 mmol PhNO₂.



Fig. S20 (a, b) Nyquist plots of Co_9S_8/Ni_3S_2 -NF and catalysts during optimization process.



Fig. S21 CV curves of (a) Co_9S_8/Ni_3S_2 -NF, (b) Ni_3S_2/NF , and (c) Co_9S_8/Ti acquired at scan rates of 5,10, 20, 40, 60, 80, 100 mV s⁻¹. (d) Plots of the current density at 0.30 (vs. RHE) vs scan rate for the Co_9S_8/Ni_3S_2 -NF, Ni_3S_2/NF , and Co_9S_8/Ti . (e)The LSV curves from Fig. S21d normalized to the electrochemical active surface area (ECSA).



Fig. S22 GC curves of (a)nitrobenzene (PhNO₂), (b) aniline (PhNH₂), (c) azobenzene, (d) azoxybenzene, and (e) GC curves mixed in 0.01M concentration.



Fig. S23 The corresponding calibration curves by GC of (a)nitrobenzene (PhNO₂), (b) aniline (PhNH₂), (c) azobenzene, and (d) azoxybenzene.



Fig. S24 (a, b) Conversion (Con.) of PhNO₂, selectivity (Sel.) and FE of PhNH₂ over Co_9S_8/Ni_3S_2 -NF and control samples in 1.0 M KOH aqueous solution (Diox/H₂O, 2:5 v/v).



Fig. S25 (a) Polarization curves (inset: SEM images), (b) Nyquist plots of first test and after 8 cycles (8h per cycle) test.



Fig. S26 (a, b) SEM images, (c) TEM image and (d) corresponding EDS elemental mapping of Co_9S_8/Ni_3S_2 -NF after 8 cycle tests within 8 cycles (8 h per cycle) at 0.121 V (vs. RHE).



Fig. S27 XRD patterns of before and after reaction of Co_9S_8/Ni_3S_2 -NF.



Fig. S28 (a) The XPS survey spectra of before and after reaction of Co_9S_8/Ni_3S_2 -NF, and the high-resolution XPS spectra of (b) Co 2p, (c) Ni 2p, (d) S 2p.



Fig. S29 Compositions and geometries of lattice planes of the models the (a) Co_9S_8 (440)/Ni₃S₂ (110) heterojunction, (b) Co_9S_8 (440) and (c) Ni₃S₂ (110), and OH adsorption on one Co atom at (d) Co_9S_8 (440)/Ni₃S₂ (110) heterojunction, (e) Co_9S_8 (440) and (f) Ni₃S₂ (110) surface. The fuchsia, caeseous, yellow, red, and white spheres represent the Co, Ni, S, O and H atoms, respectively.



Fig. S30 The catalytic pathway of the optimized intermediates (a) on (440) model facet of Co_9S_8 and (b) on (110) model facet of Ni_3S_2 . The fuchsia, caeseous, yellow, gray, blue, red, and white spheres represent the Co, Ni, S, C, N, O and H atoms, respectively.



Fig. S31 UPS plots of Co_9S_8/Ni_3S_2 -NF, Co_9S_8/Ti and Ni_3S_2/NF .

7. Supporting Tables

Catalyst	Hydrogen Source	Con. (%)	Sel. (%)	Y. (%)	Ref.
Pd-PIL-Tf ₂ N	Ethanol	100.0	98.0	98.0	14
Pt/HS-C	H_2	98.6	99.2	97.8	15
Cu-CoOx-MgO-500	H ₂	-	99.0	-	16
Pt/Al ₂ O ₃	Propane	100.0	-	-	17
$Mo_4O_4N_3$	$N_2H_4 \cdot H_2O$	-	-	99.0	18
mpg-C ₃ N ₄	H ₂	>99.0	-	-	19
PdNi/SM-CN	NaBH ₄	100.0	68.8	68.8	20
Fe ₁ /N-C	Isopropanol	>99.0	>99.0	>99.0	21
10%Ni/r-SiO ₂ -CIS	H ₂	99.9	>99.9	>99.8	22
Fe ₃ S ₂ (CO) ₉	$N_2H_4 \cdot H_2O$	-	-	85.0	23
Ru@NPC-1	$N_2H_4 \cdot H_2O$	35	>99.0	>34.7	24
N-doped CNTs	H ₂	60.0	90.0	-	25
oCNT	Hydrazine hydrate	99.3	89.8	-	26
Au-PAFs	NaBH ₄	-	100.0	-	27
AuNP@PPh ₂ -PIILP	NaBH ₄	99.0	100.0	-	28
Ru-morin@ N_2	NaBH ₄	-	-	91.0	29
NiNPs/DNA	NaBH ₄	-	-	>99.0	30
Pt ₁ /PO ₄ -CeO ₂ -500	H_2	100.0	100.0	-	31
Pt/C	H ₂	100.0	>99.0	-	32
Pd-6Ni-N-C60	H ₂	98.0	98.2	-	33
Co ₁ /G	NaBH ₄	99.0	98.0	-	34
Co@mesoNC	H ₂	-	>99.0	-	35
Co@g-C/N-800	H ₂	100.0	100.0	-	36
Ni phen@SiO ₂ - 1000	H ₂	85.0	-	-	37
Co@CN-600-AT	Formic acid	43.1	93.3	-	38

Table S1 The performance of $PhNO_2$ reduction toward $PhNH_2$ by thermocatalytic method based on various catalysts reported in literatures.

Catalyst	PhNO₂ Substrate	Condition	Hydrogen Source	Operating Potential	Reaction Time / h	Con. (%)	Sel. (%)	FE (%)	Ref.
(FeCoNiCuZn) -G	400 µM	1.0 M KOH	H ₂ O	- 1.0 V (vs. Ag/AgCl)	4	-	97.0	-	39
CuCo ₂ O ₄ /NF	0.5 mmol	1.0 M KOH	H ₂ O	-1.0 V (vs. SHE	(300 C)	95.8	97.2	89.0	6
CuPd	0.03 M	0.25 M NaH ₂ PO ₄	H ₂ O	-0.8 V (vs. Ag/AgCl)	12	>99.0	71.1	72.9	40
Cu ₃ Pt/C	5.0 mM	1.0 M KOH	H ₂ O	-0.3 V (vs. RHE)	-	100.0	99.0	-	41
Co ₃ S _{4-x} NS	0.5 mmol	1.0 M KOH /anhydrous acetonitrile (24:1 v/v, 25mL)	H ₂ O	–1.0 V (vs. Hg/HgO)	6	>98.0	99.0	-	4
СоР	0.5 mmol	1.0 M KOH	H ₂ O	-1.2 V (vs. Ag/AgCl)	2.5	98.0	99.0	-	5
Cu-CTF	5 mM	0.1 M PBS	H ₂ O	–0.6 V (vs. Ag/AgCl)	2.5	-	-	65.0	42
Co₃Sଃ/Ni₃S₂- NF	0.8 mmol	1.0 M KOH (Diox/H₂O, 2:5 v/v, 35mL)	H₂O	–0.8 V (vs. Hg/HgO)	8	99.0	96.0	95.3	This Work

Table S2 The performance of PhNO₂ reduction toward PhNH₂ by electrocatalytic method based on various electrocatalyst reported in literatures.

 Table S3 Elemental contents of Ni, Co, C, S and O based on TEM analysis and energy dispersive X-ray spectroscopy (EDS) for

 the Co_9S_8/Ni_3S_2 -NF catalyst.

Sample —	Chemical composition						
	Ni	Со	S	С	0		
Atomic Fraction (at %)	3.63	12.62	10.60	20.45	52.70		
Mass Faction (wt %)	8.63	30.15	13.78	23.43	24.00		

Complex	Chemical composition (at %)						
Samples -	Ni	Со	S	С	0		
0.018mol Co ²⁺ Ni ₃ S ₂ /NF	14.54	-	0.89	24.06	60.52		
0.018mol Co ²⁺ Co ₉ S ₈ /Ti	-	12.06	9.55	20.61	57.78		
0.018mol Co ²⁺ CoNi-LDH/NF	3.78	6.66	-	34.30	52.04		
0.014mol Co ²⁺ Co ₉ S ₈ /Ni ₃ S ₂ -NF	6.26	9.54	7.14	17.89	59.17		
0.016mol Co ²⁺ Co ₉ S ₈ /Ni ₃ S ₂ -NF	9.04	5.19	7.97	20.49	57.32		
0.018mol Co ²⁺ Co ₉ S ₈ /Ni ₃ S ₂ NF	3.70	11.46	8.40	14.45	62.00		
0.020mol Co ²⁺ Co ₉ S ₈ /Ni ₃ S ₂ -NF	4.16	8.29	7.62	19.27	60.66		
0.022mol Co ²⁺ Co ₉ S ₈ /Ni ₃ S ₂ -NF	2.73	9.25	7.83	21.40	58.79		
0.024mol Co ²⁺ Co ₉ S ₈ /Ni ₃ S ₂ -NF	3.32	8.06	6.40	27.23	55.00		

Table S4 Elemental contents of Ni.	Co. S	. C and O based on XPS ana	vsis for the catal	vsts with 8 h h	drothermal time.
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 Table S5
 The Brunauer-Emmett-Teller (BET) surface area, total pore volume, and average pore diameter of catalysts.

Samples	BET surface area (m² g ⁻¹)	total pore volume (cm³ g⁻¹)	average pore diameter (nm)
CoNi-LDH/NF	15.563	0.037	9.455
Co_9S_8/Ni_3S_2-NF	7.368	0.026	14.320
Ni ₃ S ₂ /NF	5.606	0.006	4.297

Table S6 Three geometric values of the electronic elements extracted from this electrical equivalent circuit model.

	Rs	Ra	Rct
Samples ^a	(Ω cm²)	(Ω cm²)	(Ω cm²)
Co ₉ S ₈ /Ni ₃ S ₂ -NF	0.92	2.28	0.37
Ni ₃ S ₂ /NF	1.20	26.29	40.42
Co ₉ S ₈ /Ti	1.16	4.73	14.53

^a: Rs is related to the series resistance. Ra denotes the electrode resistance. Rct denotes the charge transfer resistance. CPE is the constant phase angle element, which represents the double layer capacitance of solid electrode in the real-world situation.

Samples	C _{dl} (mF cm ⁻²)	ECSA (cm ² g ⁻¹)
Co ₉ S ₈ /Ni ₃ S ₂ -NF	252.5	12.1
Ni ₃ S ₂ /NF	34.2	4.1
Co ₉ S ₈ /Ti	104.7	7.0

Table S7 The survey of double-layer capacitance (C_{dl}) and electrochemically active surface area (ECSA).

Charge (Q / C)		460.7	
Con. (%)		99.0	
	PhNH₂	Azoxybenzene	Azobenzene
Sel. (%)	96.0	1.6	2.4
Y. (%)	95.0	1.6	2.4
FE (%)	95.3	1.2	2.4

Table S8 Conversion (Con.) of PhNO₂, selectivity (Sel.) and FE of products of Co₉S₈/Ni₃S₂-NF within 8 h at 0.121 V (vs. RHE).

	-							
Cycles	1	2	3	4	5	6	7	8
Sel. (%)	98.1	98	97.5	96.4	96.1	95.5	95.3	94.6
Y. (%)	95	91.6	92.7	93.3	90.8	94.7	91.9	92.5
FE (%)	91.4	86.1	89.9	87	88.2	92.6	88.2	90.6

Table S9 Cycle-dependent performance of transforming $PhNO_2$ into $PhNH_2$ after 1 to 8 cycles (8 h per cycle) at 0.121 V (vs.RHE) over Co_9S_8/Ni_3S_2 -NF.

Complex		Chei	nical compos	ition	
Samples	Ni	Со	S	С	0
Atomic Fraction (at %)	3.47	12.95	10.25	21.38	51.95
Mass Faction (wt %)	8.79	30.58	14.21	22.56	23.86

Table S10 Elemental contents of Ni, Co, C, S and O based on TEM analysis and energy dispersive X-ray spectroscopy (EDS)for after reaction of Co_9S_8/Ni_3S_2 -NF after 8 cycles (8 h per cycle) reaction at 0.121 V (vs. RHE).

Samples –	Chemical composition (at %)				
	Ni	Со	S	С	0
Co_9S_8/Ni_3S_2-NF (initial)	3.70	11.46	8.40	14.45	62.00
Co_9S_8/Ni_3S_2 -NF (After 8-cycle test)	3.45	11.51	8.38	17.28	59.38

Table S11 Elemental contents of Ni, Co, S, C and O based on XPS analysis for before and after 8 cycles (8 h per cycle)reaction of Co_9S_8/Ni_3S_2 -NF at 0.121 V (vs. RHE).

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