Supporting Information

Rational design of a low-cost, simple technology and high-performance CoNi/Co_3O_4 as a catalyst in sodium borohydride electro-oxidation reaction

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1.Characterization and electrochemical measurements

The composition of the catalysts was investigated using X-ray diffraction (XRD) (Cu-Kα). The composition of the catalyst surface was investigated using X-ray photoelectron spectroscopy (XPS), with the C1s peak (284.8 eV) as the calibration peak. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to analyze and study the morphology of the electrodes. The distribution of Co and Ni elements on the catalyst surface was analyzed using energy spectrometry (EDS).

The electrochemical tests were all carried out in a typical three-electrode system, which consists of a working electrode, an Ag/AgCl reference electrode (the filling solution is a saturated KCl solution), and a graphite counter electrode. The electrochemical testing methods were cyclic voltammetry (CV), chronoamperometry (CA), and linear sweep voltammetry (LSV).

2. Calculation formula

The diffusion coefficient D of $NaBH_4$ was calculated using the expression proposed by Wang et al[1], which is mainly related to the concentration of NaOH solution, 2 mol L^{-1} NaOH was used in this experiment.

$$D_{BH_4^-} = 2.01 \times 10^{-5} - 3.65 \times 10^{-6}x + 2.25 \times 10^{-7}x^2 \quad (Eq.\ S1)$$

where x is the concentration of NaOH, and D was calculated to be 1.37×10^{-5} in 2 mol L^{-1} NaOH concentration.

The electrooxidation of $NaBH_4$ at the electrode can be evaluated in terms of the reaction order β, which is calculated as follows:

$$j_p = zC_{NaBH_4}^{\beta} \quad (Eq.\ S2)$$

where j_p is the peak current density (A cm^{-2}), z is the A constant, and C is the $NaBH_4$ concentration (mol cm^{-3}).

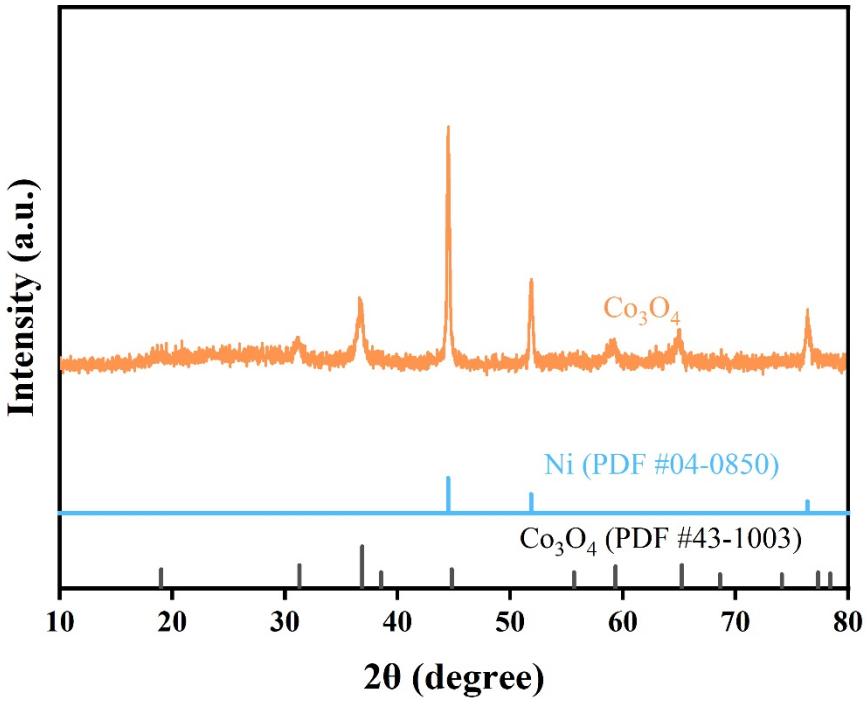

Fig. S1 XRD spectra of Co_3O_4.

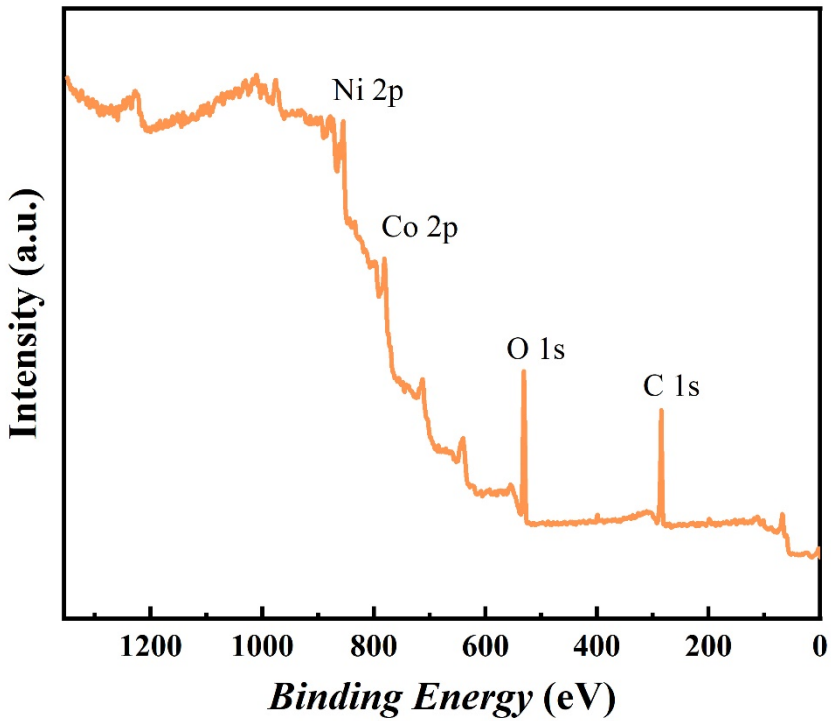

Fig. S2 XPS spectra of CoNi/Co_3O_4 electrodes.

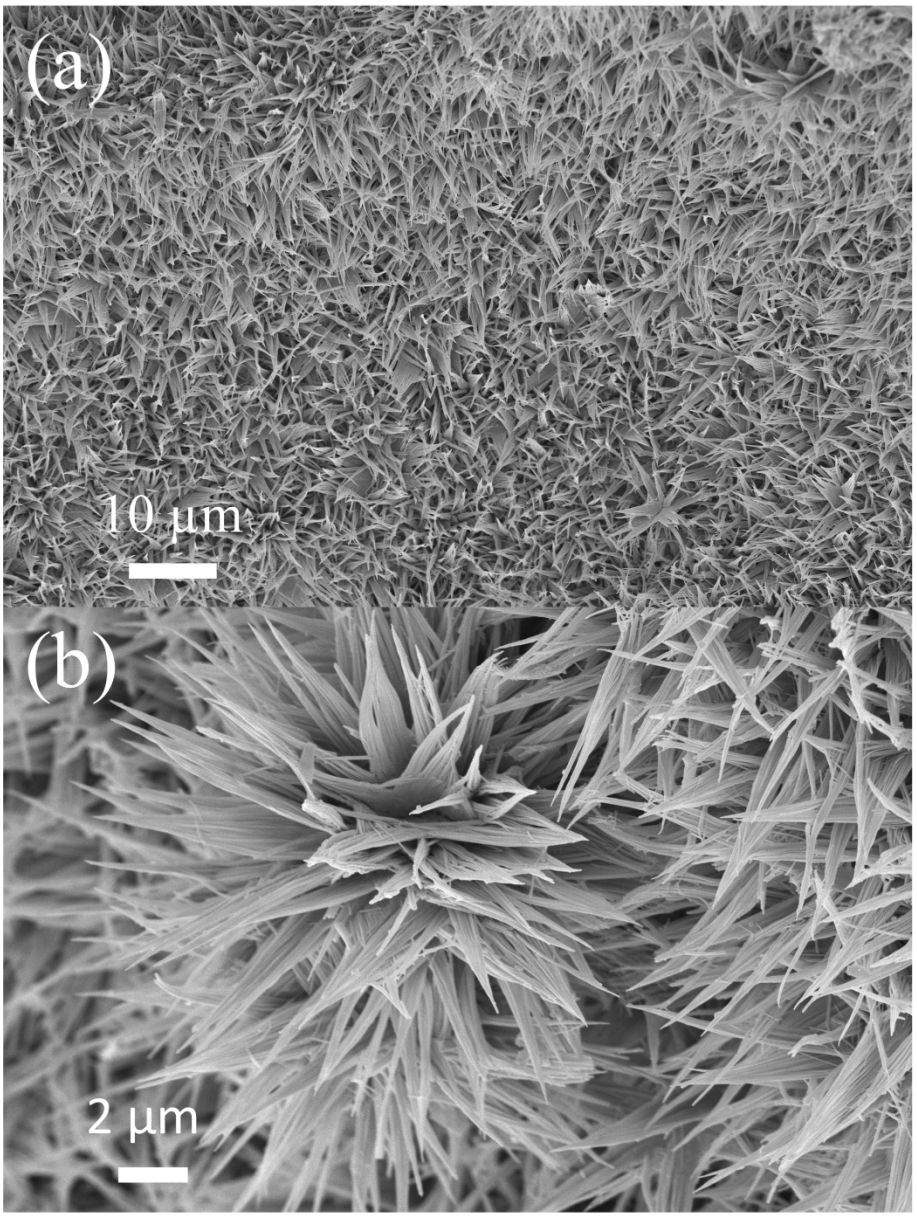

Fig. S3 SEM image of Co_3O_4.

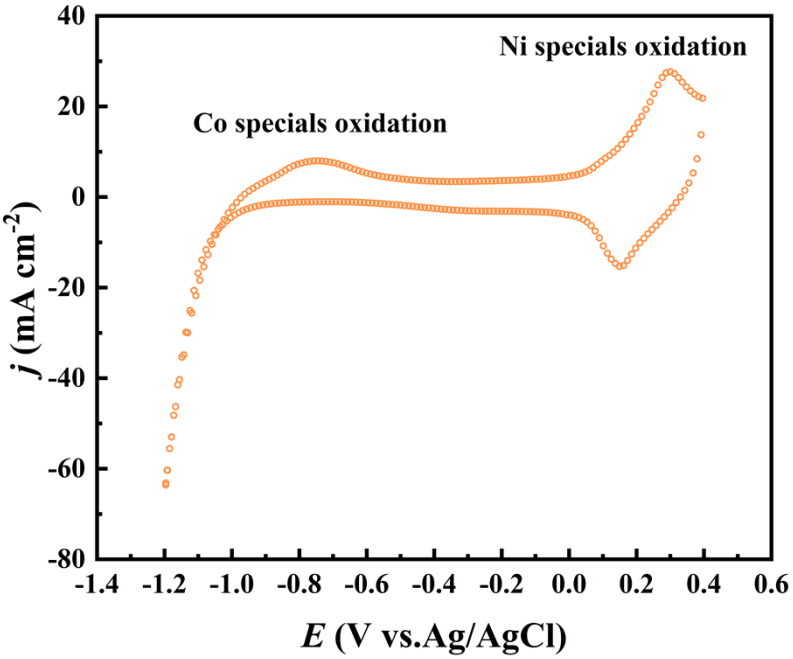

Fig. S4 CV curves for $CoNi/Co_3O_4$ catalysts (1:1 concentration ratio of Ni and Co in the deposition solution) at 2 mol L^{-1} NaOH.

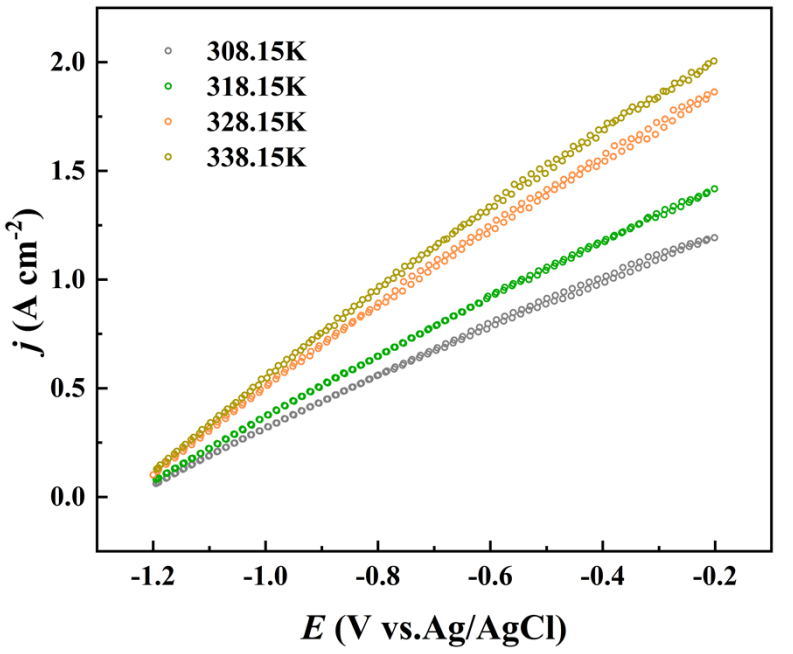

Fig. S5 CV curves of $CoNi/Co_3O_4$ catalysts were tested in 2 mol L^{-1} NaOH and 0.2 mol L^{-1} $NaBH_4$ at different temperatures (Ni:Co=1:1).

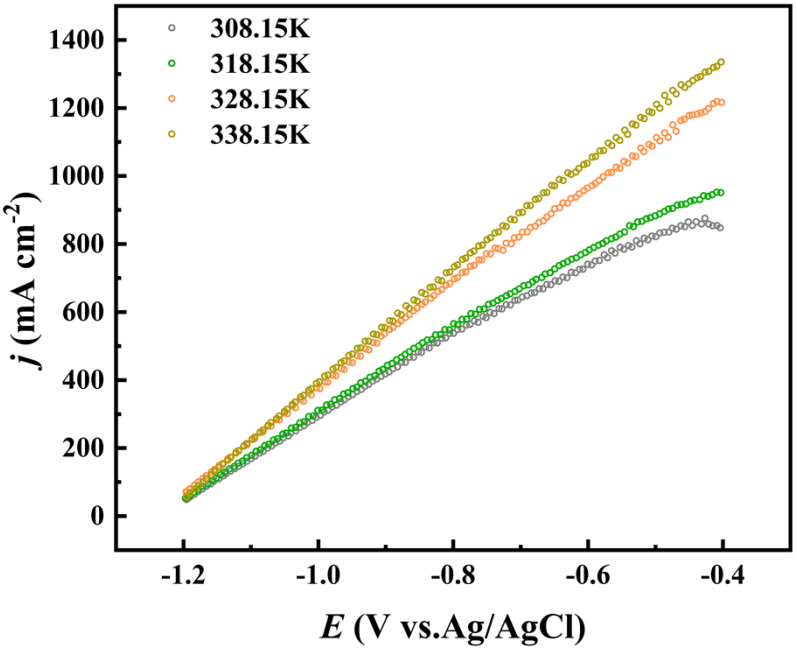

Fig. S6 CV curves of CoN/Co_3O_4 catalysts were tested in 2 mol L^{-1} NaOH and 0.2 mol L^{-1} $NaBH_4$ at different temperatures (Ni:Co =1:2).

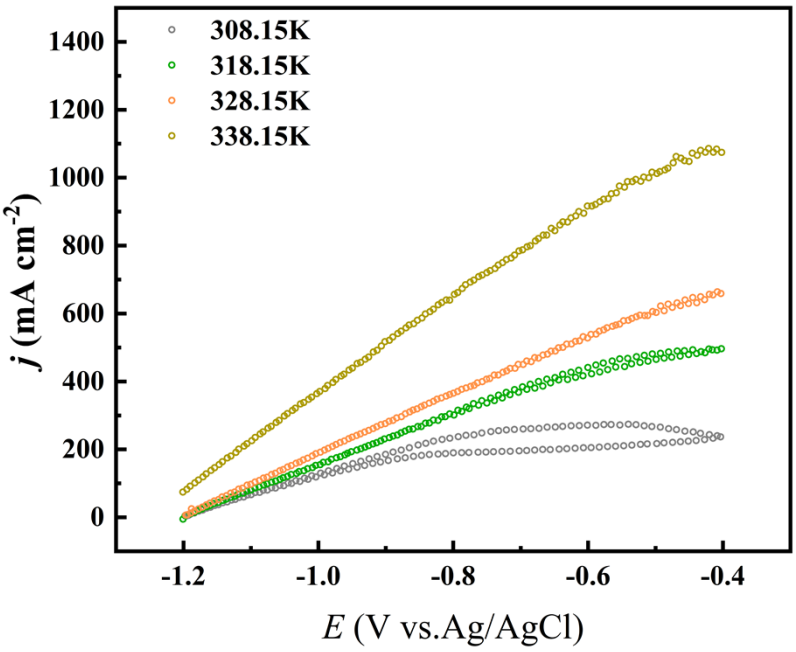

Fig. S7 CV curves of $CoNi/Co_3O_4$ catalysts were tested in 2 mol L^{-1} NaOH and 0.2 mol L^{-1} $NaBH_4$ at different temperatures (Ni:Co =3:1).

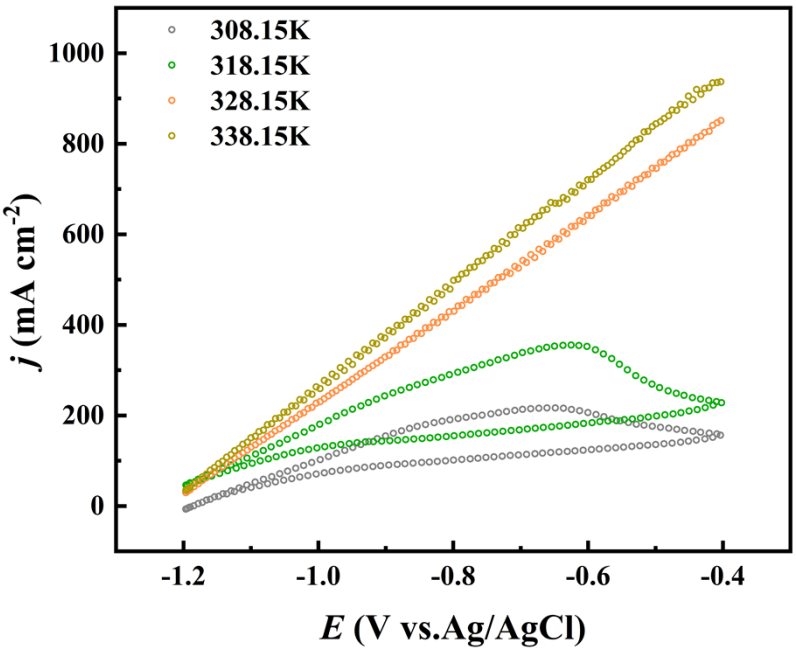

Fig. S8 CV curves of $CoNi/Co_3O_4$ catalysts were tested in 2 mol L^{-1} NaOH and 0.2 mol L^{-1} $NaBH_4$ at different temperatures (Ni:Co =2:1).

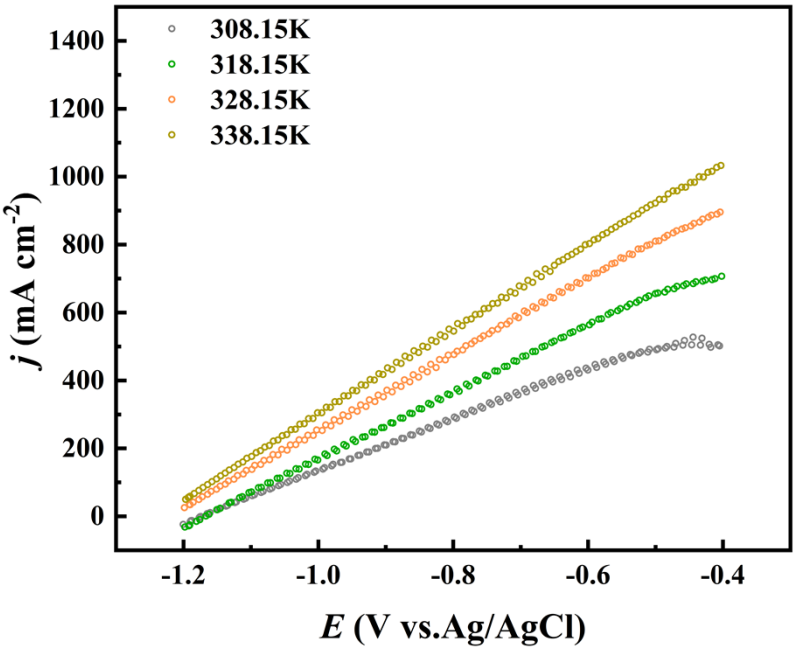

Fig. S9 CV curves of $CoNi/Co_3O_4$ catalysts were tested in 2 mol L^{-1} NaOH and 0.2 mol L^{-1} $NaBH_4$ at different temperatures (Ni:Co =1:3).

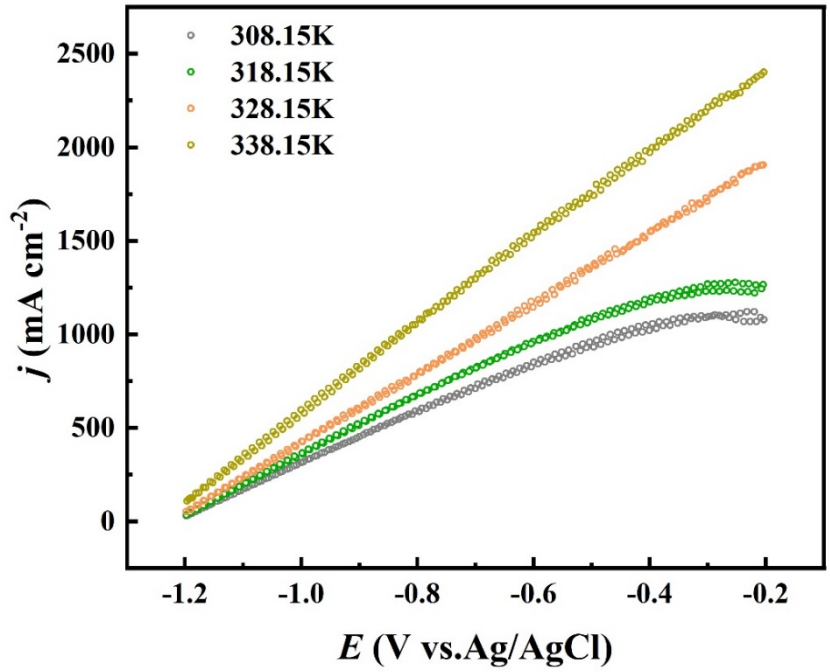

Fig. S10 CV curves of Co_3O_4 catalysts were tested in 2 mol L^{-1} NaOH and 0.2 mol L^{-1} $NaBH_4$ at different temperatures.

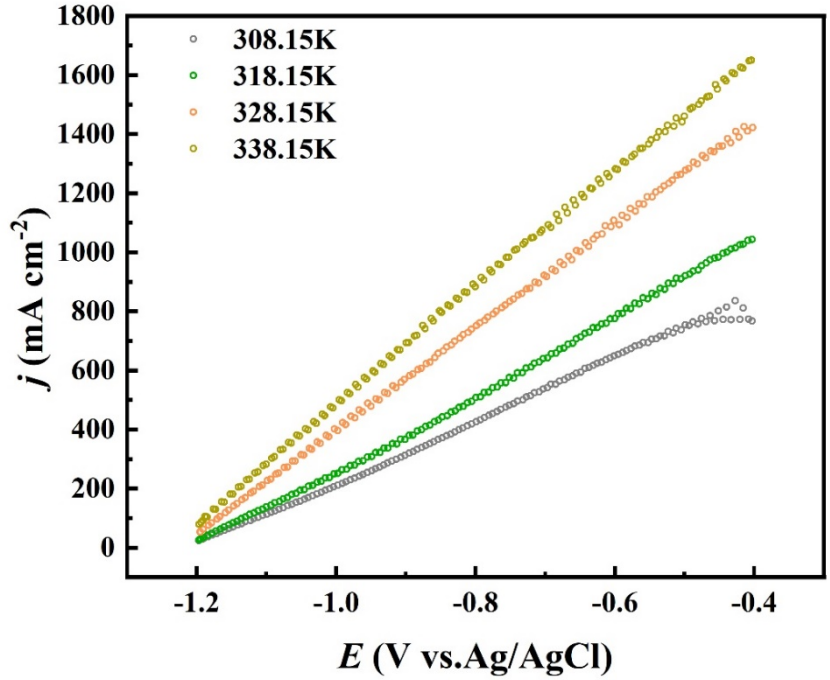

Fig. S11 CV curves of CoNi catalysts were tested in 2 mol L^{-1} NaOH and 0.2 mol L^{-1} $NaBH_4$ at different temperatures.

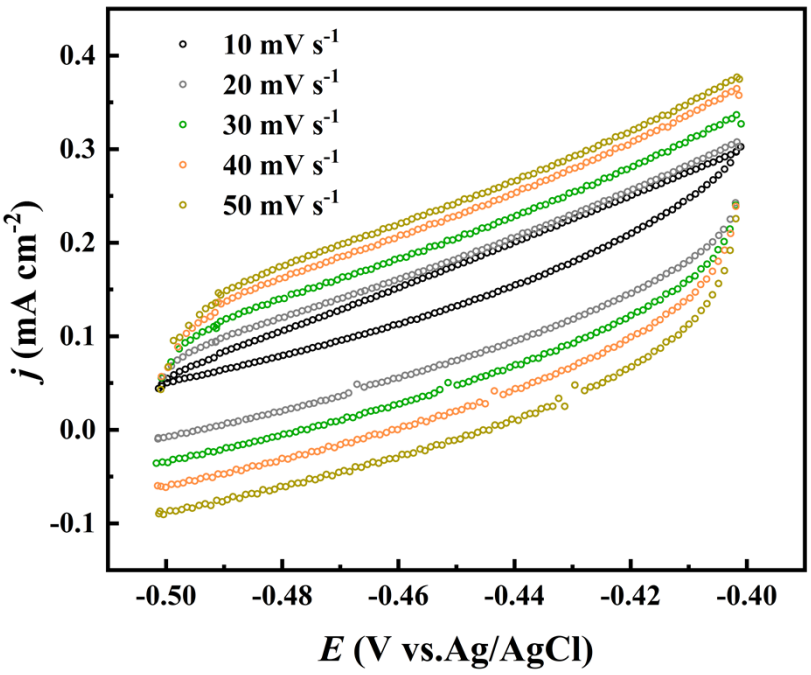

Fig. S12 CV curves of NF electrode at different scan rates (10-50 mV s^{-1}) in 2 mol L^{-1} NaOH.

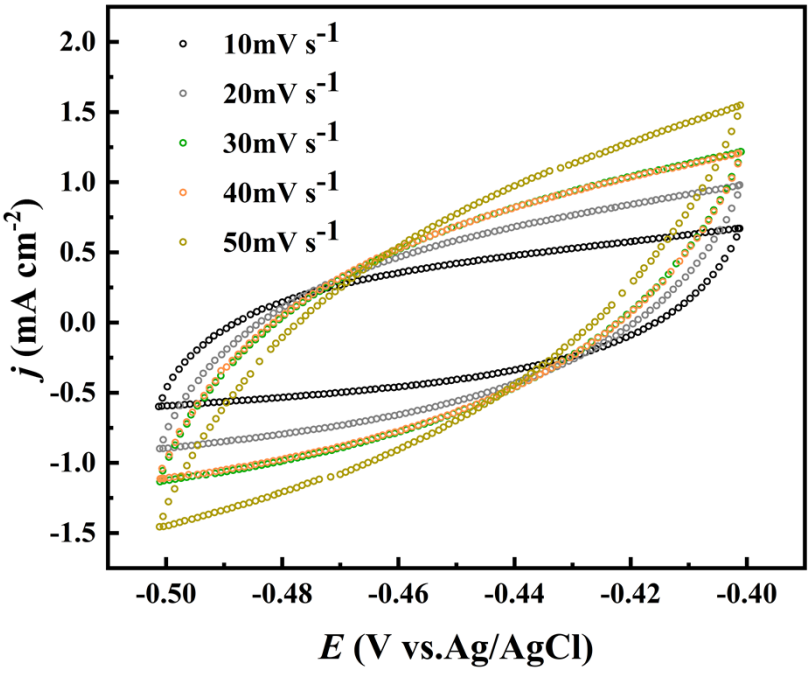

Fig. S13 CV curves of Co_3O_4 electrode at different scan rates (10-50 mV s^{-1}) in 2 mol L^{-1} NaOH.

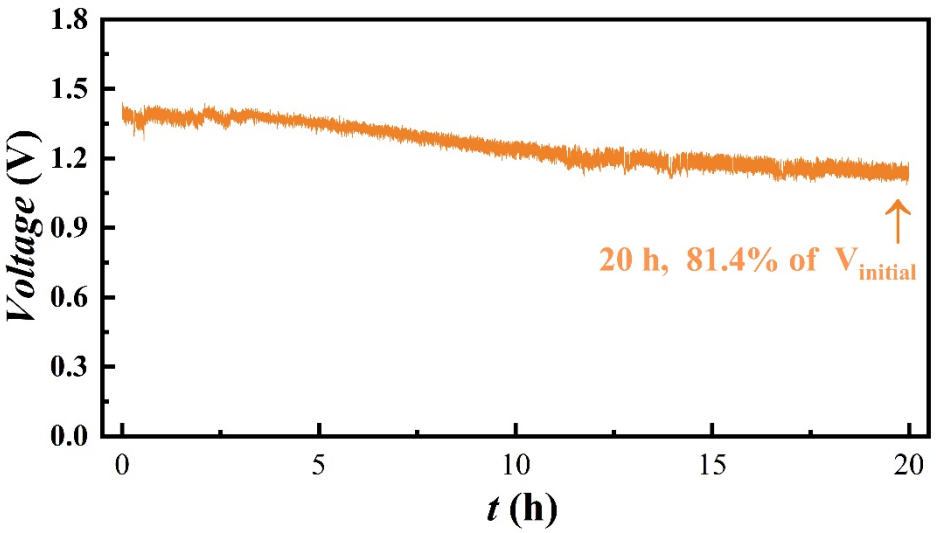

Fig. S14 Constant discharge current test at 60 mA cm^{-2}.

Table. S1 Comparison of different electrodes regarding current density in a three-electrode system.

Electrode	Composition of electrolyte	*j* (mA cm^{-2})	Ref.
$CoNi/Co_3O_4$	2 M NaOH+0.1 M $NaBH_4$	650	This work
NiMoN@NC-600	1 M NaOH+0.135 M $NaBH_4$	~ 100	2
AuCo@rGO	2 M NaOH+0.12 M $NaBH_4$	~ 450	3
CoNi@rGO	2 M NaOH+0.1 M $NaBH_4$	~ 190	4
Ni@Zn	2 M NaOH+0.135 M $NaBH_4$	~ 270	5
CuNiPd	2 M NaOH+0.1 M $NaBH_4$	~ 630	6
Ni@NiP	2 M NaOH+0.135 M $NaBH_4$	~ 255	7

Table. S2 A comparison of DBHPFC performance.

Anode	Cathode	Anolyte	Catholyte	T(K)	Power (mW cm^{-2})	Ref.
$CoNi/Co_3O_4$	Pt/C	2 M NaOH+ 0.3 M $NaBH_4$	1M H_2SO_4 + 1.2 M H_2O_2	313.15	108.5	This work
CoNi-NS/Ni	Pd/Ti	4 M NaOH+ 0.5 M $NaBH_4$	2M H_2SO_4 + 0.8 M H_2O_2	303.15	80.6	4
CoNi-NS/rGO	Pd/Ti	4 M NaOH+ 0.5 M $NaBH_4$	2M H_2SO_4 + 0.8 M H_2O_2	333.15	140	4
Ni@Zn	Pt/C	3 M NaOH+ 2 M $NaBH_4$	1 M H_2SO_4 + 4 M H_2O_2	298.15	180.3	5
Pd/C + Ni (0.5)	Pt/C	3 M NaOH+ 1.5 M $NaBH_4$	1.5 M H_2SO_4 +15 wt% H_2O_2	353.15	50	8
Pd@N/C-8	Pd@N/C-8	2 M NaOH+ 0.3 M $NaBH_4$	2 M H_2SO_4 + 1.6 M H_2O_2	333.15	137	9

References

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