Supporting Information

Constructing CoO/Co₄N heterostructure with optimized electronic structure to

boost alkaline hydrogen evolution electrocatalysis

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Experiment

Materials

All chemicals are analytical grade without further purification. Deionized water was used as the the solvent. Cobalt nitrate hexahydrate (Co(NO₃)₂•6H₂O), urea, ammonium fluoride (NH₄F), were all purchased from Sinopharm Chemical Reagent Co., Ltd. Carbon cloth (CC) was purchased from CeTech Co., Ltd. Pt–C (Johnson Matthey Hispec 3600) was purchased from Shanghai Hesen Electric Co., Ltd.

Synthesis of Co(OH)F precursor

The precursor was directly grown on the carbon cloth by hydrothermal method. First, 1 mmol Co(NO₃)₂·6H₂O, 5 mmol urea, and 5 mmol NH₄F were dissolved in 12 mL deionized water, and then the solution was transferred to the 15 mL reactor and 1×2 cm² carbon cloth was subsequently immersed into the solution. After being sealed, Teflon-lined stainless-steel autoclave was put into the oven and remained at 120 °C for 6 hours. Furthermore, the obtained Co(OH)F precursor was washed with deionized water and ethanol, and dried in vacuum drying oven.

Synthesis of CoO/Co₄N and Co₄N

The precursor obtained in the first step synthesis was placed in the quartz tube. After being connected to another quartz tube containing 0.5 g urea, it was set in the middle of the tube furnace and heated to 550 °C for 2 hours with the rate of 2 °C/min in N₂ atmosphere. Moreover, the obtained sample, named as CoO/Co₄N, was taken out and washed with deionized water and ethanol three times and put into a vacuum drying oven. Through changing the heating temperature to 450 °C, 500 °C and 600 °C, a series of samples were obtained and named as CoO/Co₄N-450, CoO/Co₄N-500 and Co₄N, respectively.

Synthesis of CoO

The Co(CO₃)_{0.5}(OH) precursor was directly grown on the carbon cloth by similar hydrothermal method. First, 0.81 mmol Co(NO₃)₂·6H₂O, 4.2 mmol urea, and 3 mmol NH₄F were dissolved in 15 mL deionized water, and then the solution was transferred to the reactor and 1×2 cm² carbon cloth was subsequently immersed into the solution. After being sealed, Teflon-lined stainless-steel autoclave was put into the oven and heated to 130 °C for 6 hours. The obtained precursor was washed with deionized water and ethanol, and dried in vacuum drying oven. Then, CoO was obtained by calcining the dried precursors with urea at the temperature of 450 °C.

Electrochemical characterizations:

All electrochemical tests in this subject were conducted on the CHI 760 electrochemical workstation. Since the catalyst grows directly on the carbon cloth, the electrochemical test was performed under the three-electrode system and the prepared sample (loaded carbon cloth 0.4×0.5 cm²) was used as the working electrode. In addition, the carbon

rod and Hg/HgO electrode were served as counter electrode and reference electrode.

In the linear sweep voltammetry (LSV) test, it is necessary to form an argon saturated atmosphere, and the sweep speed is set to 5 mV s⁻¹ in Ar saturated atmosphere. It was conducted in 1 M KOH in the potential range from -0.9 V to -1.3 V. The potential was calibrated to the reversible hydrogen electrode (RHE) according to the following formula: E (vs RHE) = E (vs Hg/HgO) + 0.059 × pH + 0.098. The exact value of the potential versus reversible hydrogen electrode (RHE) of the Hg/HgO electrode was calibrated by using 20 wt% Pt/C deposited onto the glassy carbon (GC) rotating disk electrode to get the hydrogen oxidation polarization curve at 5 mV s⁻¹ under hydrogen atmosphere.

Faraday efficiency (FE) was determined by a drainage gas collecting method. The volume of generated H₂ was measured by a graduated tube, and converted to mole by ideal gas law. The theoretical amount of H₂ was then calculated based on the Faraday's law assuming that all charges that passed through the working electrode were 2e⁻. The Faraday efficiency is calculated based the following equation: $FE(\%) = \frac{2FV_{02}}{ItV_m} \times 100$, where Faraday constant (96485 C mol⁻¹), V₀₂ is the volume of gas (24 1 L mol⁻¹ at 20 ° C). Lis the

of the produced H₂ (L), V_m is the molar volume of gas (24.1 L mol⁻¹ at 20 $^{\circ}$ C), I is the current (A), t is the times (s).

DFT calculation

The DFT calculations were performed with generalized gradient approximation and Perdew–Burke–Ernzerhof (PBE) functional for exchange correlation energy and ultrasoft pseudo-potentials to account for core-valance interaction on CASTEP code of

the Materials Studio package of Accelrys Inc. The cutoff energy of 400 eV was set and the self-consistent field (SCF) tolerance was 1×10^{-6} eV. The three-layers Co₄N (111) surface (Figure S15) was selected with repeated in 4x4x3 unit cell and a vacuum width of 15 Å was used. The bottom one layer was fixed, while the top two layers and the adsorbates were allowed to relax. The 7*7*1 Monkhorst-Pack mesh k-points was sampled for all surface calculation. And all energy difference of all planes does not exceed 0.01 eV. DFT calculation results reveal that the Co₄N (111) surface is more stable than the (001), (010), (101), (110), (100) and (011) surface (with the lowest surface energy). In our calculation, the most stable H adsorption sites are the Co1-Co2-Co3 hollow sites and the most stable H₂O adsorption sites are the Co1 sites as shown in Figure S15. To investigate the effect of CoO for HER, we placed the CoO (001) on Co_4N (111), as shown in Figure S16. The hydrogen adsorption free energy ΔG_{*H} = $E_{(M-H)} - E_{(M)} - 1/2E_{(H2)} + \Delta E_{(ZPE)} - T\Delta S$ ($\Delta E_{(ZPE)}$ and ΔS are the zero-point energy and entropy). At 300 K, the $\Delta G_{*H} = E_{(M-H)} - E_{(M)} - 1/2E_{(H2)} + 0.24$ eV. Additionally, the water adsorption free energy $\Delta G_{*H2O} = E_{(M-H2O)} - E_{(M)} - E_{(H2O)} + \Delta E(ZPE) - T\Delta S$.



Figure S1. XRD patterns of Co(OH)F.



Figure S2. SEM image of Co(OH)F precursor.



Figure S3. Size distribution of CoO nanoparticles.



Figure S4. XRD patterns of CoO/Co₄N-x (x= 450-600) with different temperatures.



Figure S5. SEM images of CoO/Co_4N -x (x= 450-600).



Figure S6. The SEM image of CoO/Co₄N without carbon cloth.



Figure S7. (a) LSV curves of CoO/Co₄N-x (x= 450-600 in 1M KOH and (b) Scatter plot of corresponding LSV curve under current density of 10 mA cm⁻².



Figure S8. (a) XRD pattern and (b) SEM image of CoO.



Figure S9. Cyclic voltammertries with for capacitive currents at -0.5 V as a function of scan rate in 1M KOH (a) Co_4N ; (b) CoO/Co_4N ; (c) CoO; and (d) the C_{dl} of them.



Figure S10. (a) SEM image; (b) TEM image of CoO/Co₄N after HER test in 1M KOH

solution.



Figure S11. XRD patterns of CoO/Co₄N after HER test in 1M KOH solution.



Figure S12. XPS spectra of CoO/Co₄N after HER test in 1M KOH solution (a) Co 2p;

(b) N 1s; (c) O 1s.



Figure S13. The Faraday efficient of CoO/Co₄N in 1M KOH.



Figure S14. The LSV curves of $CoO/Co_4N/CC$ and CoO/Co_4N power/CC in 1.0 M KOH.



Figure S15. The unit cell structures of Co₄N and CoO.



Figure S16. The geometric configurations of CoO/Co₄N.



Figure S17. The calculated Mulliken charges for Co1, Co2, Co3, Co4 in Co₄N (111) and Co1', Co2', Co3', Co4', Co5 in CoO/Co₄N. The inset is the geometric configuration of Co₄N (111) surface and CoO/Co₄N heterostructure surface.



Figure S18. The Gibbs adsorption free energies of water on Co_4N and CoO/Co_4N surface.



Figure S19. The most stable geometric configuration of adsorption structure on Co_4N surface with top view(a) *H₂O; (b) *H+*OH; (c) *H.



Figure S20. The most stable geometric configuration of adsorption structure on CoO/Co_4N surface with top view(a) *H₂O; (b) *H+*OH; (c) *H.



Figure S21. (a-c) The structures of water adsorption on CoO/Co_4N (111) surface with different CoO density. (d) The corresponding water adsorption free energies for different CoO density.

Catalyst	j (mA cm ⁻²)	η (mV)	Reference
CoO/Co ₄ N	10	27	This work
Ni ₃ N-Co ₃ N PNAs/NF	10	43	1
Cu ₃ N/NF	100	150	2
Ni/NiMoN/CF	10	37	3
NC–NiCu–NiCuN	10	93	4
NiCoN/CC	10	68	5
MoS ₂ /NiFe-LDH	10	110	6
MoN	1	100	7
V-Co ₄ N	10	37	8
Co-Mo ₅ N ₆	10	19	9
M-Ti ₄ N ₃ T _x	10	330	10
NiCoN/C	10	103	11
Ni ₃ N@VN–NF	10	56	12

 Table S1 Comparison of representative HER catalysts in 1M KOH electrolyte.

Table S2. Values of components in R_{ct} electrical equivalent circuit.

	Co ₄ N	СоО	CoO/Co ₄ N
$R_{ct}(\Omega)$	6.11	10.61	32.47
Rs	3.26	3.17	3.08
CPE1	0.60	0.74	0.80

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