

Electronic Supplementary Information (ESI) for Chem. Comm.

Space-confined construction of two-dimensional nitrogen-doped carbon with encapsulated bimetallic nanoparticles as oxygen electrocatalysts

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1. Experimental section

1.1 Materials

CoCl₂·6H₂O (AR, 99%), NiCl₂·6H₂O (AR, 99%), 2-methylimidazole (AR, 99%), TEOS (AR, 99%), CTAB (AR, 99%) and Terephthalic acid (AR, 99%) were purchased from the Energy Chemical. Zn(NO₃)₂·6H₂O (AR, 99%), NaOH (AR, 99%), N, N-dimethylformamide (DMF) (99.5%), Methanol (AR, 99.5%) and Ethanol (AR, 99.7%) were purchased from Sinopharm Group Chemical Reagent Co., Ltd.. All chemicals were used without further purification.

1.2 Preparation of NiCo-MOF nanosheets Materials

DMF (32 mL), ethanol (2 mL) and water (2 mL) were mixed in a beaker. Then, 0.75 mmol of BDC was added to dissolve under ultrasound. Then 0.375 mmol of CoCl₂·6H₂O and 0.375 mmol of NiCl₂·6H₂O were added to the above solution for ultrasonic dissolution. 8 mL of TEA was injected quickly under stirring and kept stirring to obtain a uniform colloidal suspension. Then, the colloidal solution was continuously sonicated for 8 h (99 kHz) under airtight conditions. The obtained solid was washed with ethanol (3 times) and then dried at room temperature.

1.3 Synthesis of two-dimensional NiCo-MOF@ZIF-L(Zn)

16 mmol of 2-methylimidazole (1.314 g) was dissolved in 40 mL of DI water and stirred for 5 min. Next, 5 mg of the synthetic NiCo-MOF nanosheets was added and sonicated several minutes, to form A solution. Then, 2 mmol of Zn(NO₃)₂·6H₂O was separately dissolved in 40 mL water, to form solution B. In the case of continuous agitation of A solution, B solution was quickly poured in. The mixed solution was stirred at room temperature for 3 h. The obtained precipitates were collected by centrifugation (8000 rpm, 5 min), washed with DI water for 3 times, and dried in vacuum freeze dryer for further application.

1.4 Synthesis of three-dimensional precursor NiCo-MOF@ZIF-L(Zn)@SiO₂

The preparation of CTAB solution: 250 mg of CTAB is dissolved in 10 mL of deionized water. Preparation of NaOH solution: 150 mg of NaOH was dissolved in 25 mL of DI water. Preparation of TEOS solution: 4 mL of TEOS was dissolved in 20 mL of methanol. Next, 600 mg of NiCo-MOF@ZIF-L(Zn) was dissolved in 240 mL of distilled water, and 6 mL of CTAB solution, 9.6 mL of NaOH solution, and 7.2 mL of TEOS in methanol were added in sequence, and then stir at room temperature for 24 h. Finally, the obtained light purple precipitates were collected by centrifugation (6000 rpm, 5 min), washed with methanol for 3-5 times, and dried in vacuum freeze dryer for further application.

1.5 Synthesis of NiCo-NC@SiO₂

The 200 mg of precursor NiCo-MOF@ZIF-L(Zn)@SiO₂ powder was weighed in a quartz boat and carbonized in a tubular furnace. Ar flow was introduced into the furnace. The air in the furnace was exhausted at the initial 40 minutes without heating, then heated to 900 °C at the heating rate of 5 °C·min⁻¹. After calcination for 2 h, the temperature was reduced to room temperature at the cooling rate of 5 °C·min⁻¹. Finally, NiCo-NC@SiO₂ were obtained.

1.6 Synthesis of NiCo-NC

First, prepare an aqueous solution of NaOH. Preparation of NaOH solution: 12 g of NaOH was dissolved in 300 mL of deionized water.

Add 50 mg of NiCo-NC@SiO₂ powder to 30 mL of NaOH solution and stir for 4 h at 30 °C. The reaction solution was centrifuged (13000 rpm, 10 min), washed with deionized water 3 times, and the resulting black precipitate was dried in a freeze dryer for 12 hours. The 20 mg of dried black sample powder was weighed in a quartz boat and carbonized in a tubular furnace. Ar flow was introduced into the furnace. The air in the furnace was exhausted at the initial 40 minutes without heating, then heated to 900 °C at the heating rate of 5 °C·min⁻¹. After calcination for 2 h, the temperature was reduced to room temperature at the cooling rate of 5 °C·min⁻¹. Finally, NiCo-NC were obtained.

Ni-NC, Co-NC, and NiCo-NC without using SiO₂ coating were chosen as references. The corresponding precursor material is replaced with Ni-MOF nanosheets, and the Co-MOF nanosheets are processed in the same way to obtain Ni-NC and Co-NC materials. And NiCo-MOF@ZIF-L(Zn) were pyrolyzed in the same way (900 °C, 5 °C·min⁻¹, 2 h) to obtain NiCo-NC-1 materials.

1.7 Characterization

Powder X-ray diffraction (PXRD) patterns were obtained on a X-ray diffractometer (Bruker, D8 Advance, Cu K α , $\lambda = 1.5406 \text{ \AA}$, 40 kV/40 mA). Scanning electron microscopy (SEM) was performed on a Hitachi SU8020 SEM at an accelerating voltage of 5 kV. Transmission electron microscope (TEM) was conducted on a JEOL JEM-2100 TEM with a field emission gun operating at 200 kV. EDS analysis was conducted on an AMETEK Materials Analysis EDX equipped on the TEM. All X-ray photoelectron spectroscopic (XPS) spectra were collected by a Kratos AXIS ULTRA XPS. Brunauer-Emmett-Teller (BET) specific surface area was measured in Micromeritics ASAP 2020. Thermogravimetric analysis (TGA) was applied by heating the as-prepared sample at a rate of 10 °C min⁻¹ with N₂ and air from 20 °C to 1000 °C in a TA Instruments SDT Q600. The Raman spectrum were measured with a Raman Spectrometer (Renishaw, in Via Reflex). Elemental analyzer (Vario EL III, Elementar Analysensysteme GmbH) was applied to measure the content of C, H, and N.

1.8 Electrochemical measurement

All electrochemical tests are performed on the CHI 660E electrochemical workstation at 30 °C. All ORR and OER performance tests are evaluated by a three-electrode system. The working electrode is a rotating disk electrode (RDE) with a diameter of 5 mm (0.196 cm²) or a rotating ring disk electrode (RRDE) with a diameter of 5.61 mm (0.247 cm²). The counter electrode is a graphite rod, and the reference electrode is a saturated Ag/AgCl electrode. The cyclic voltammetry (CV) test is carried out in 0.1 M KOH filled with Ar or O₂ (scan rate is 50 mV·s⁻¹). The linear sweep voltammetry (LSV) test is carried out in 0.1 M KOH filled with O₂ at a speed range of 400 to 1600 rpm (scan rate is 5 mV·s⁻¹). Current time chrono current response measured at 0.66 V (relative to RHE). In the OER test, the working electrode is a glassy carbon (GC) electrode with a diameter of 3 mm (0.07 cm²). The counter electrode is a graphite rod, and the reference electrode is a saturated Ag/AgCl electrode. The LSV test is tested in 0.1 M KOH (scan rate of 5 mV·s⁻¹).

The catalyst used for the ORR test was prepared as follows: 2 mg of the catalyst was dispersed in a mixed solution containing 333 μL of deionized water, 166 μL of ethanol, and 10 μL of Nafion solution (5 wt%). The mixed solution was sonicated for 1 hour to form a uniform suspension. Then, take out 20 μL of the catalyst solution from the pipette and drop it evenly on the rotating disk electrode (RDE) electrode. After natural drying, a uniform film is formed.

The catalyst used for the OER test was prepared as follows: 2 mg of the catalyst is dispersed in a mixed solution containing 333 μL of deionized water, 166 μL of ethanol, and 10 μL of Nafion solution (5 wt%), and then sonicated for 1 hour to obtain a uniform solution. Drop 5 μL of catalyst ink on the GC electrode, and then slowly dry at room temperature. The final mass load of the catalyst on the electrode is about 0.28 mg cm⁻².

The potentials corresponding to the reversible hydrogen electrode (RHE) electrode was calculated with the following equation:

$$E_{RHE} = E_{Ag/AgCl} + (0.197 + 0.0591 \times pH)$$

The number of electron transfers (n) is calculated using the Koutecky-Levich (K-L) formula:

$$1/j = 1/j_l + 1/j_k = 1/B\omega^{1/2} + 1/j_k$$

j is the measured current density; j_l is the diffusion current density; j_k is the dynamic current density; ω is the speed (rpm); B can be confirmed by the Koutecky-Levich (K-L) formula:

$$B = 0.2nFC_0(D_0)^{2/3}v^{-1/6}$$

Where n is the number of transferred electrons; F is the Faraday constant (96485 C mol⁻¹); C_0 is the concentration of O₂ in 0.1 M KOH (1.2×10^{-6} mol cm⁻³); D_0 is the O₂ concentration in 0.1 M KOH (1.9×10^{-5} cm² s⁻¹) the diffusion coefficient; v is the

viscosity of 0.1 M KOH ($0.1 \text{ cm}^2 \text{ s}^{-1}$).

OER measurement: Calculate the potential corresponding to the reversible hydrogen electrode (RHE) electrode by the following formula:

$$E_{RHE} = E_{Ag/AgCl} + (0.197 + 0.059 \times pH)$$

The overpotential (η) is calculated by the following formula:

$$\eta = E_{RHE} - 1.23$$

Zn-air battery performance test: All zinc-air battery tests are performed on CHI 660E electrochemical workstation at room temperature, each charge and discharge cycle is 20 minutes, and the current density is 2 mA cm^{-2} . LSV is used to record the dynamic charge and discharge polarization curve on the CHI 660E electrochemical workstation, and the scan rate is 10 mV s^{-1} . The discharge characteristic curve is obtained by testing at a current density of 20 mA cm^{-2} . The battery consists of a zinc foil with a diameter of 15 mm and a thickness of 0.25 mm, 6.0 M KOH and 0.2 M ZnCl_2 electrolytes, and a catalyst-coated carbon cloth/gas diffusion layer air electrode.

Preparation of the air cathode: A carbon cloth ($1.5 \times 1.5 \text{ cm}^2$) is attached to the gas diffusion layer ($1.8 \times 1.8 \text{ cm}^2$) by hot pressing. 5 mg of the catalyst was dissolved in 950 μL of ethanol, then dropped into 50 μL of Nafion aqueous solution (5 wt%), and sonicated for 30 minutes to form a uniform suspension. Spread 400 μL of the catalyst suspension evenly on the carbon cloth with a load of about 2 mg cm^{-2} . After the catalyst solvent has evaporated, the cathode can be prepared for Zn-air battery assembly and further testing.

Table S1. The electron transfer numbers under different conditions.

Catalysts	0.7 V	0.6 V	0.5 V	0.4 V	0.3 V	0.2 V
NiCo-NC	3.79	3.80	3.80	3.82	3.82	3.83
Pt/C	3.83	3.87	3.90	3.92	3.95	3.96

Table S2. Electrochemical ORR activities of catalysts in this work and other reported works.

Catalyst	Electrolyte	$E_{1/2}$ vs RHE	Ref.
NiCo-NC	0.1M KOH	856 mV	This work
Co/NC	0.1M KOH	830 mV	Angew. Chem. Int. Ed., 2016, 55 , 4087. ¹
Co/N-C-800	0.5 M H ₂ SO ₄	863 mV	ChemElectroChem, 2019, 6 , 2546. ²
Co@Co ₃ O ₄ /NC	0.1M KOH	850 mV	Angew. Chem. Int. Ed., 2016, 55 , 4087. ¹
Co/HNCP	0.1M KOH	845 mV	ACS Catal., 2018, 8 , 7879. ³
CoZn-NC-700	0.1M KOH	840 mV	Adv. Funct. Mater., 2017, 27 , 1700795. ⁴
NC-Co ₃ O ₄ -90	0.1M KOH	870 mV	Adv. Mater., 2017, 29 , 1704117. ⁵
CuCo@NC	0.1M KOH	866 mV	Chem. Euro. J., 2019, 25 , 12780. ⁶
Co-C ₃ N ₄ /CNT	0.1M KOH	840 mV	J. Am. Chem. Soc., 2017, 139 , 3336. ⁷
Co ₃ O ₄ -NP/N-rGO	0.1M KOH	750 mV	Adv. Energy Mater., 2018, 8 , 1702222. ⁸
Co-CoO/N-rGO	0.1M KOH	780 mV	Adv. Funct. Mater., 2015, 25 , 5799. ⁹
N-Co ₃ O ₄ @NC-2	0.1M KOH	770 mV	Adv. Funct. Mater., 2019, 29 , 1902875. ¹⁰

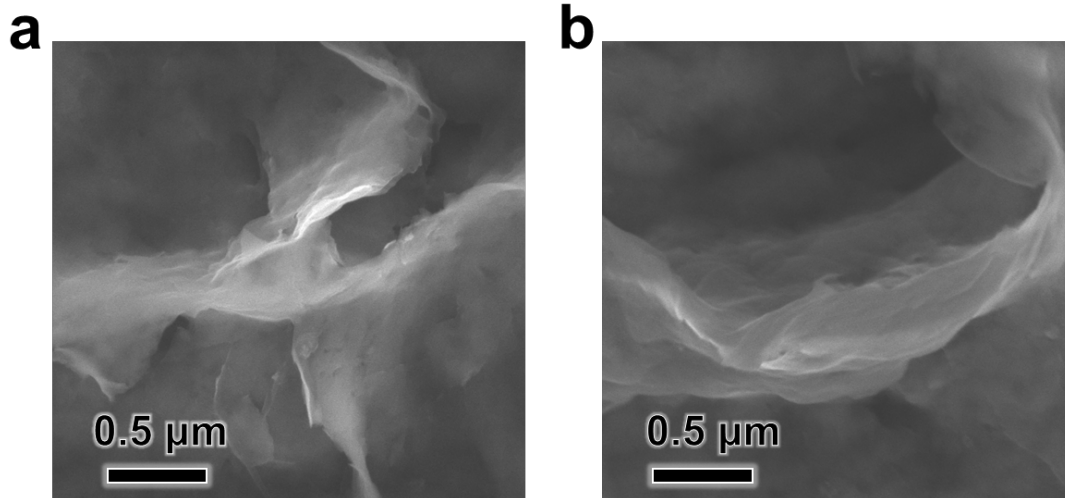


Fig. S1. SEM image of 2D NiCo-MOF.

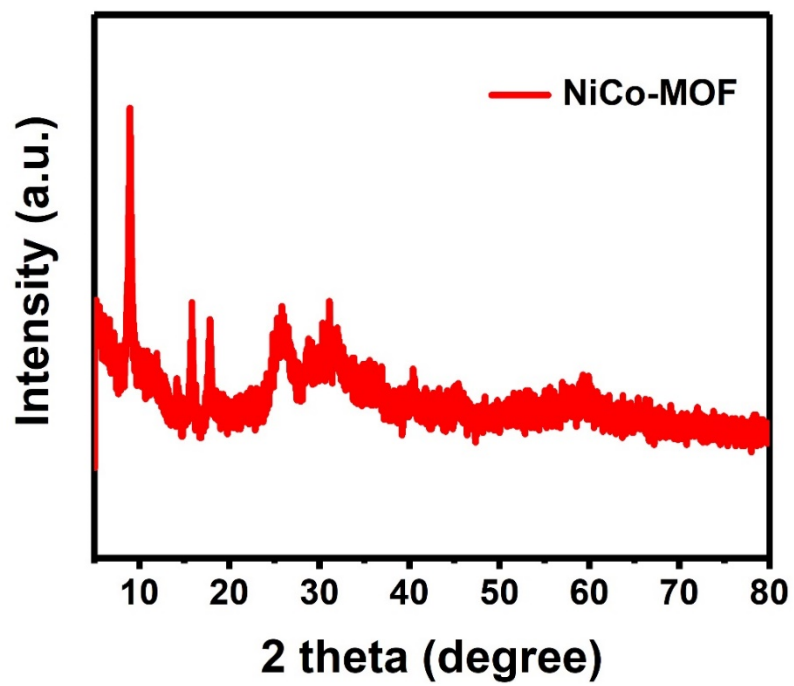


Fig. S2. PXRD patterns of 2D NiCo-MOF.

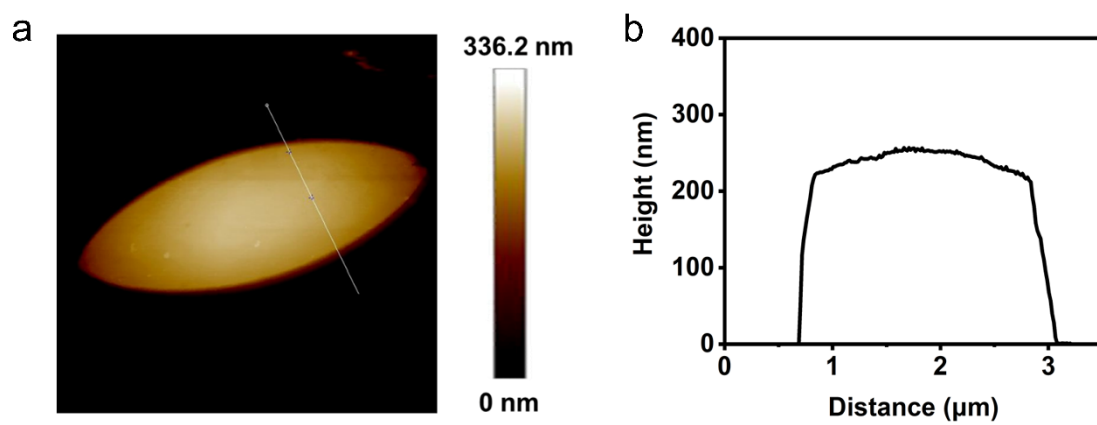


Fig. S3. The AFM image and corresponding height measurement of NiCo-MOF@ZIF-L(Zn).

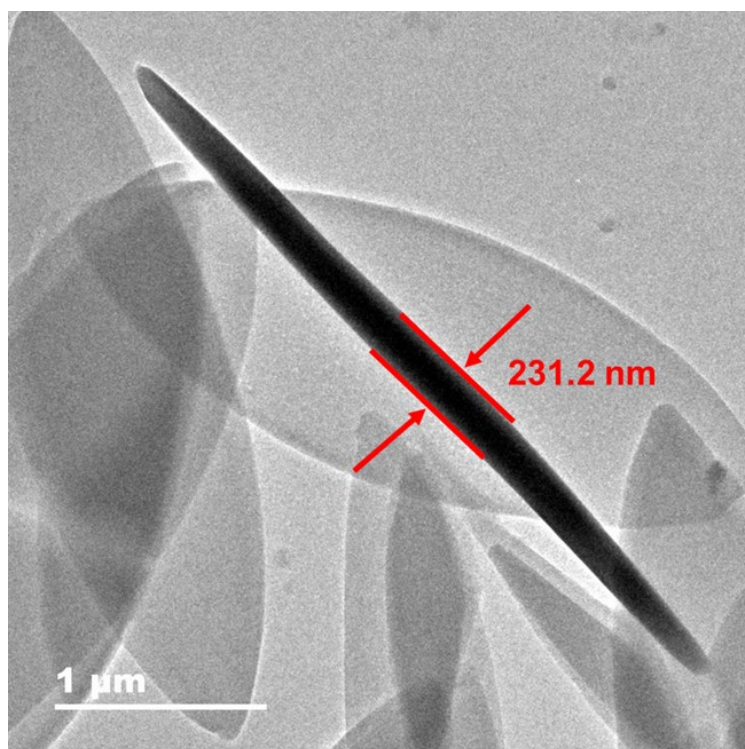


Fig. S4. TEM image of NiCo-MOF@ZIF-L(Zn).

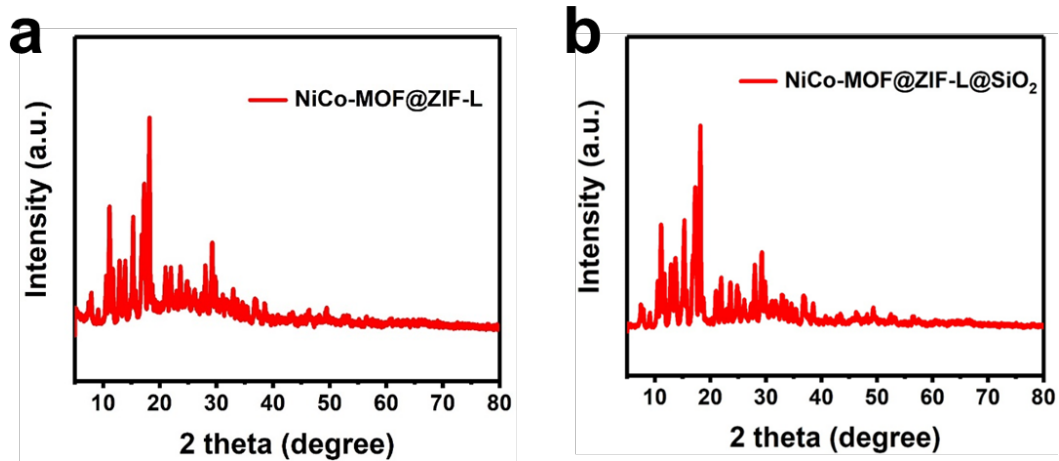


Fig. S5. PXRD patterns of NiCo-MOF@ZIF-L(Zn) and NiCo-MOF@ZIF-L(Zn)@SiO₂.

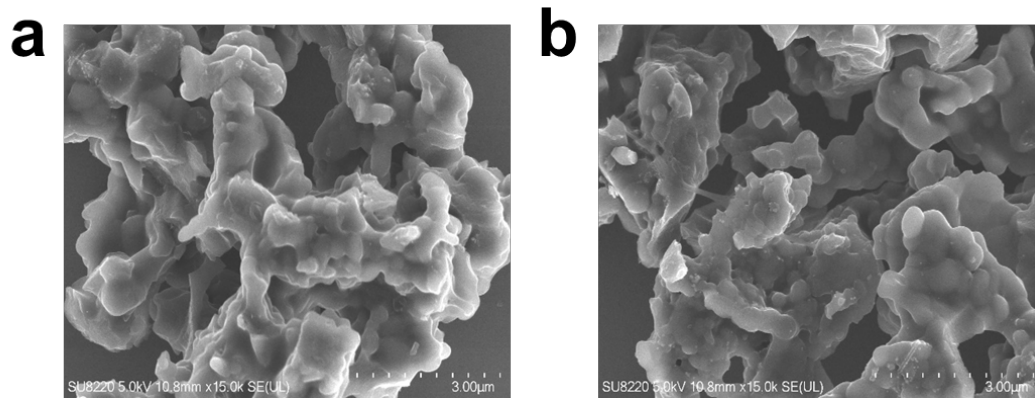


Fig. S6. SEM image of NiCo-NC-1.

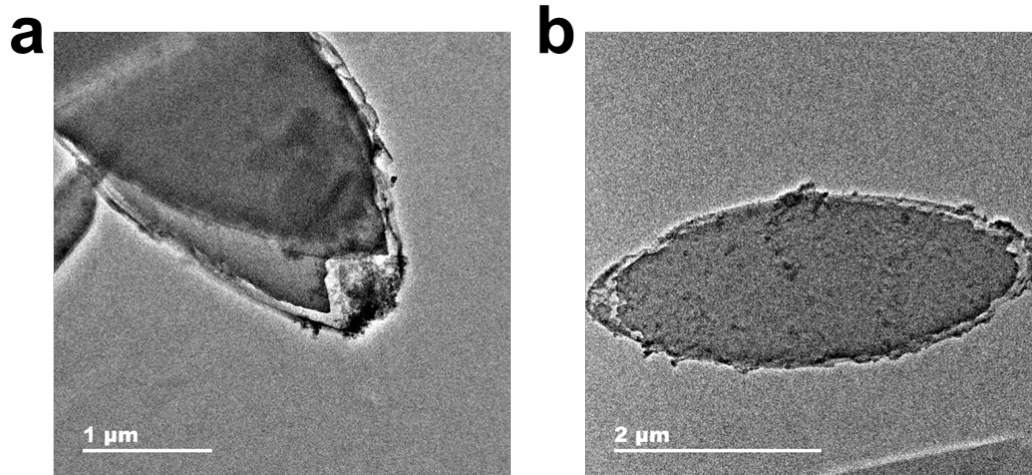


Fig. S7. TEM image of NiCo-NC@SiO₂.

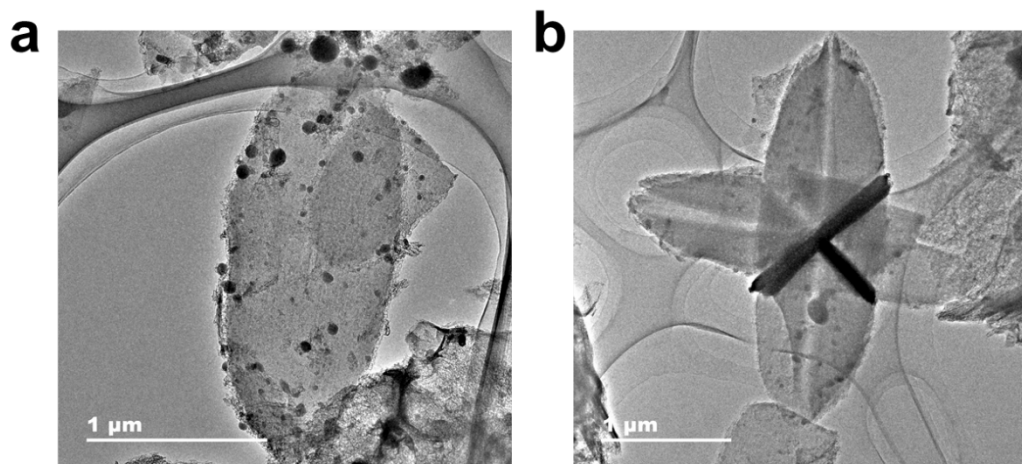


Fig. S8. TEM image of NiCo-NC.

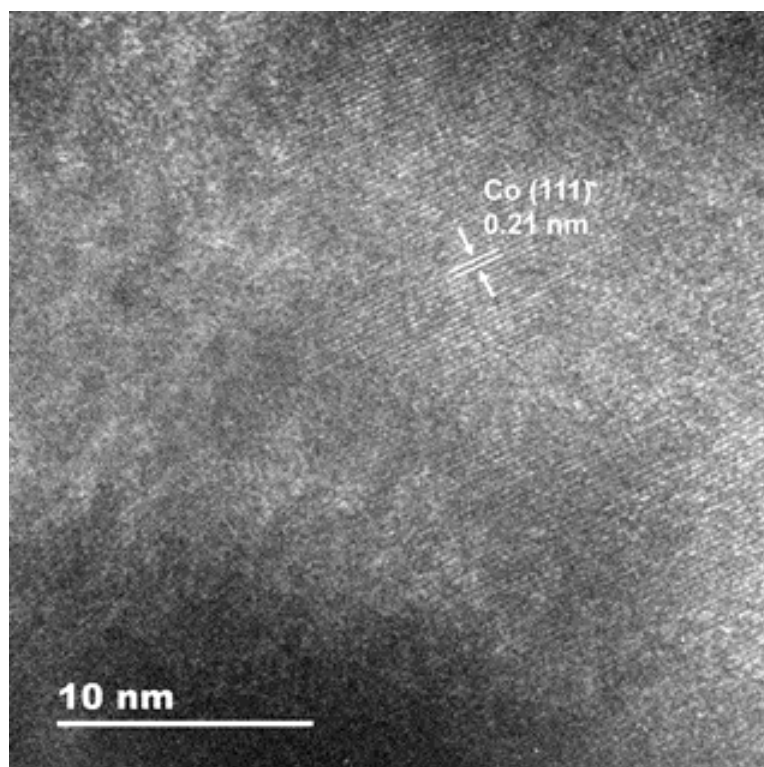


Fig. S9. HRTEM image of NiCo-NC.

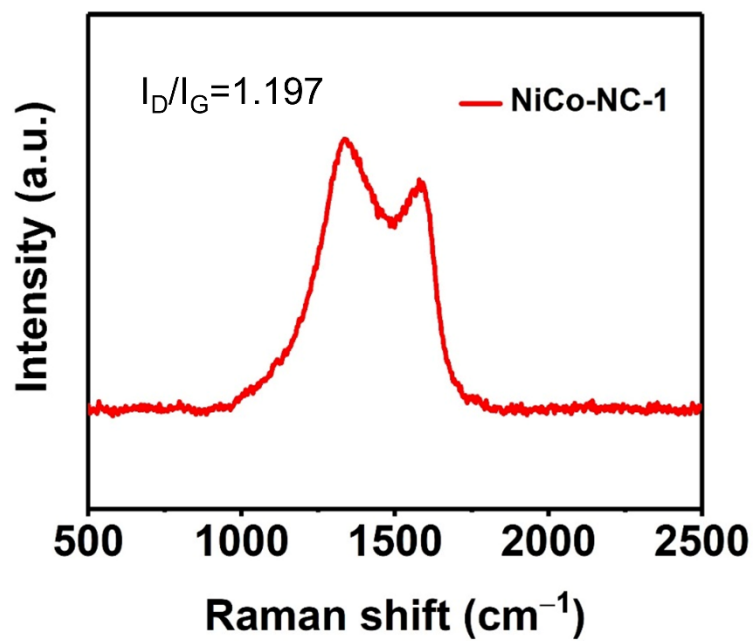


Fig. S10. Raman spectra of NiCo-NC-1.

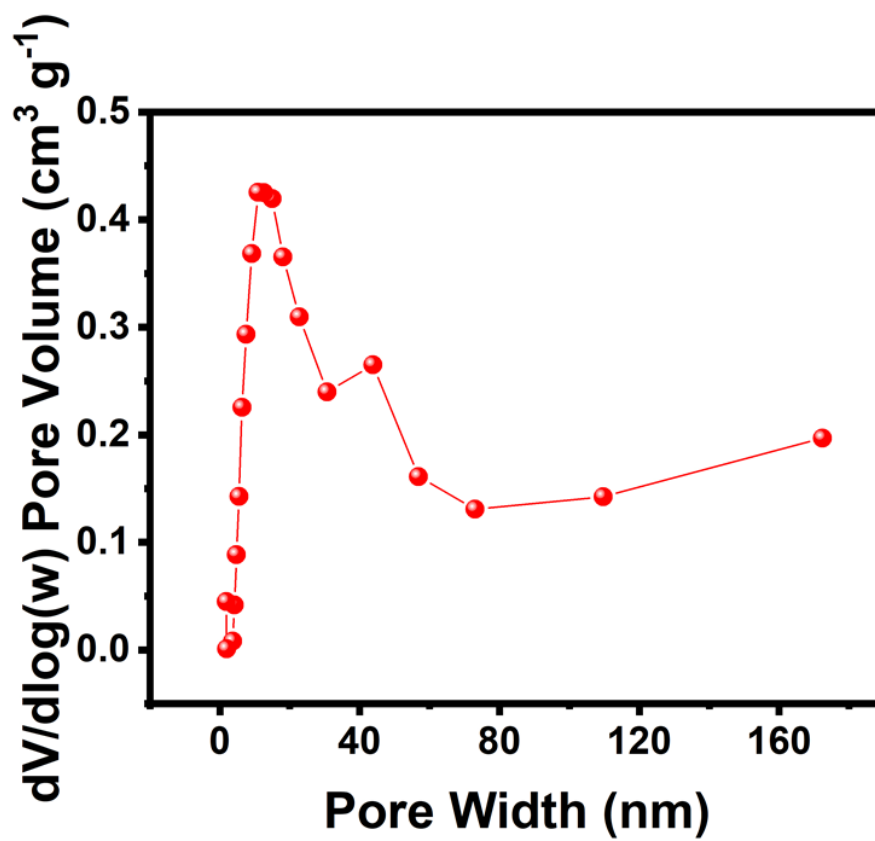


Fig. S11. Pore size distribution of NiCo-NC distribution.

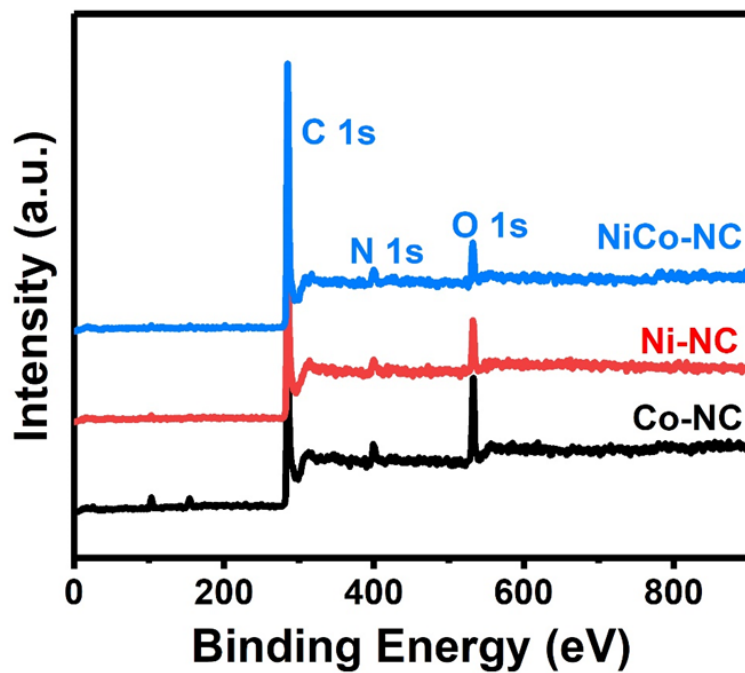


Fig. S12. XPS survey spectra of NiCo-NC, Ni-NC, and Co-NC.

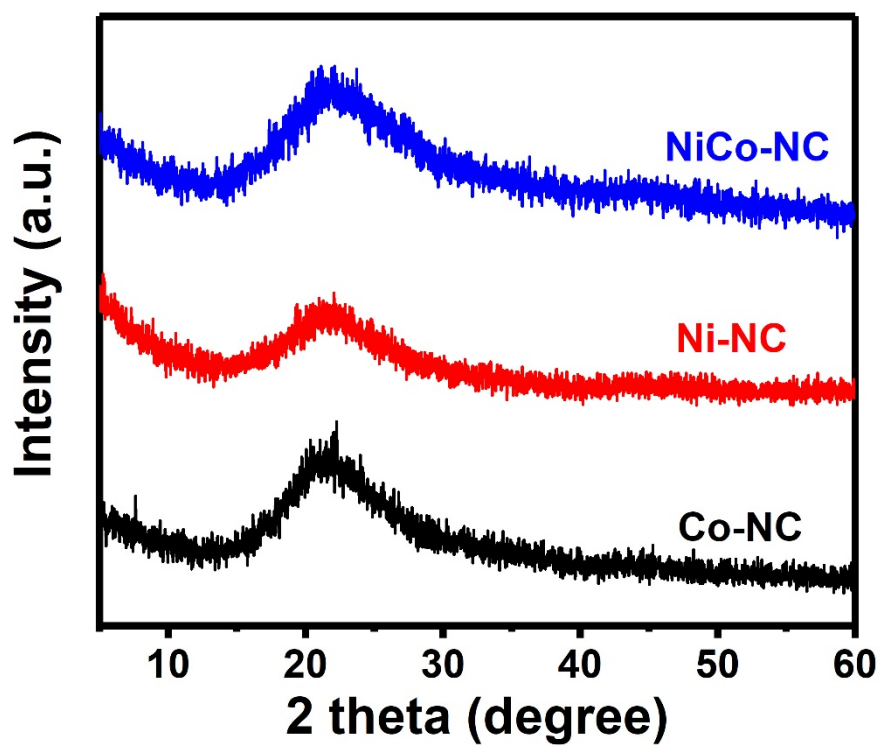


Fig. S13. PXRD patterns of NiCo-NC, Ni-NC, and Co-NC.

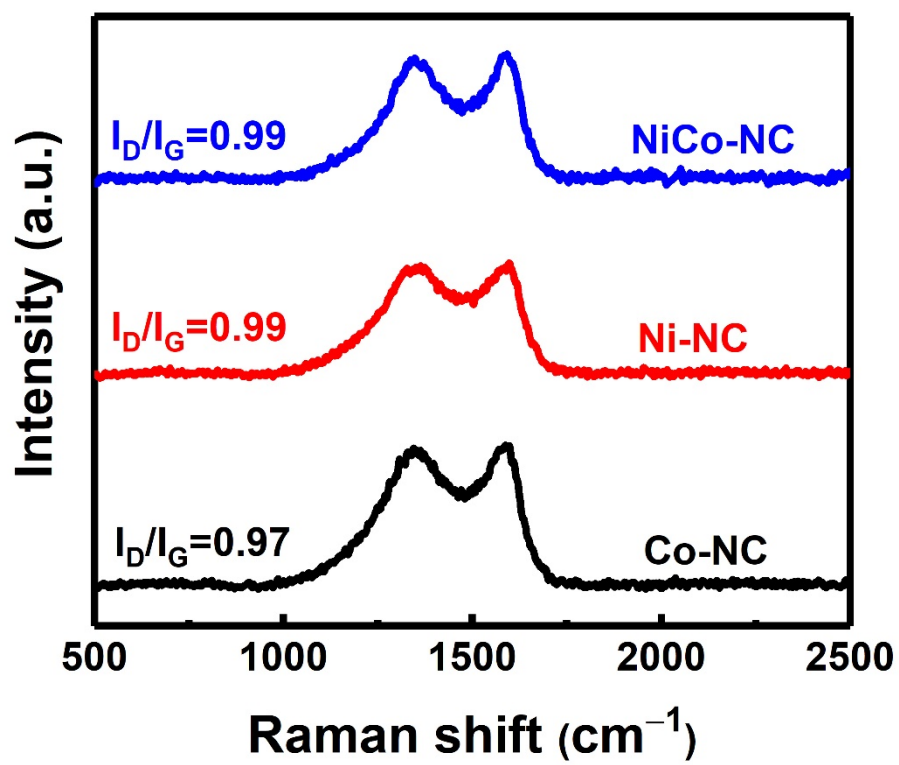


Fig. S14. Raman spectra of NiCo-NC, Ni-NC, and Co-NC.

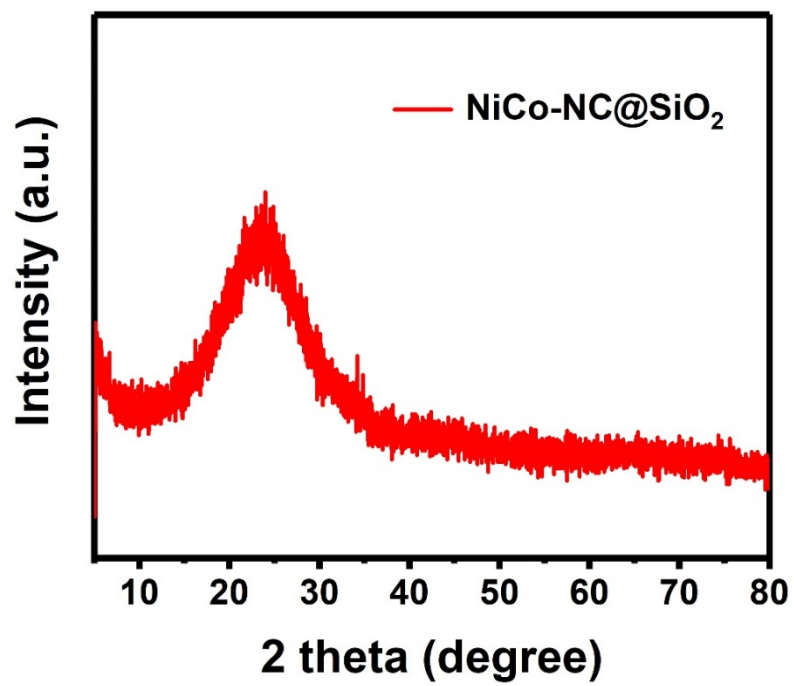


Fig. S15. PXRD patterns of NiCo-NC@SiO₂.

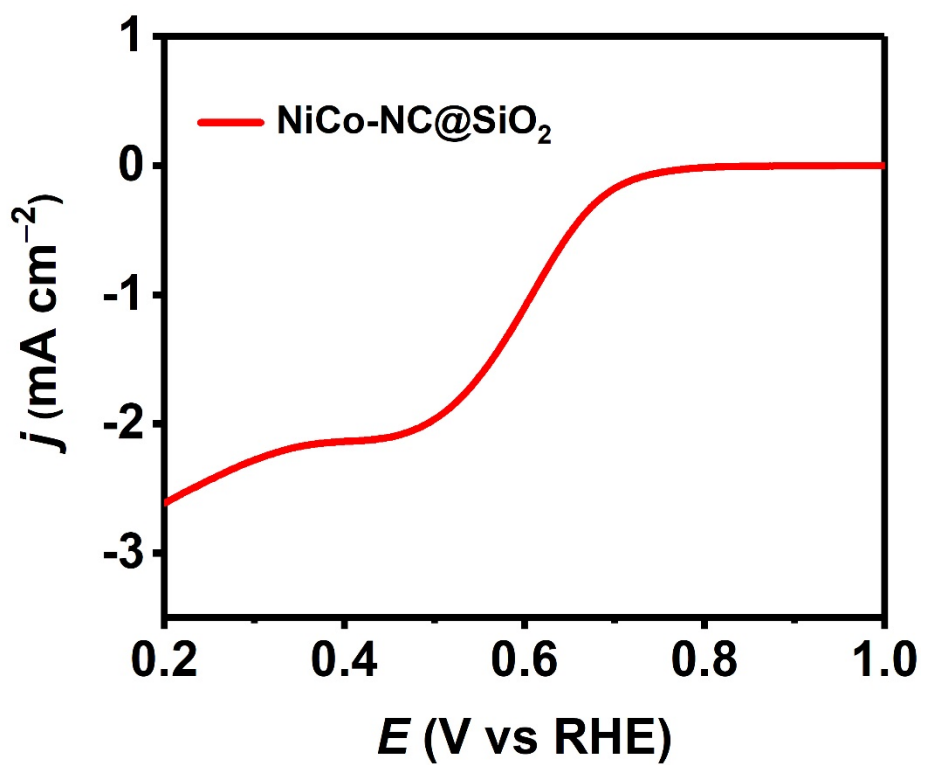


Fig. S16. LSV curves from NiCo-NC@SiO₂ in O₂-saturated 0.1 M KOH.

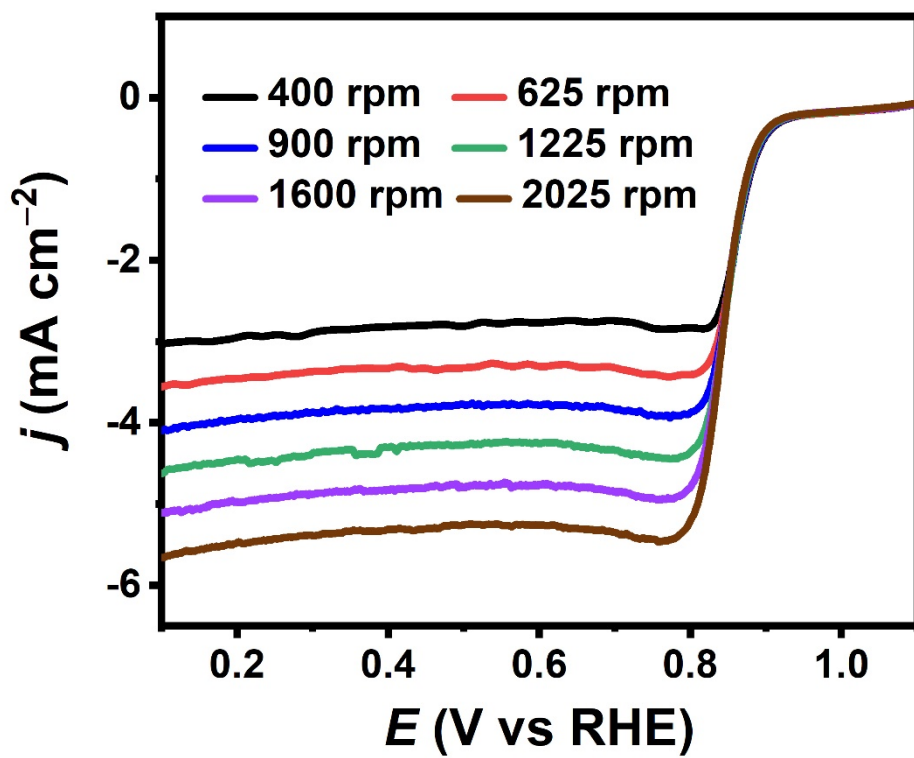


Fig. S17. The LSV curves of NiCo-NC at various rotational speeds.

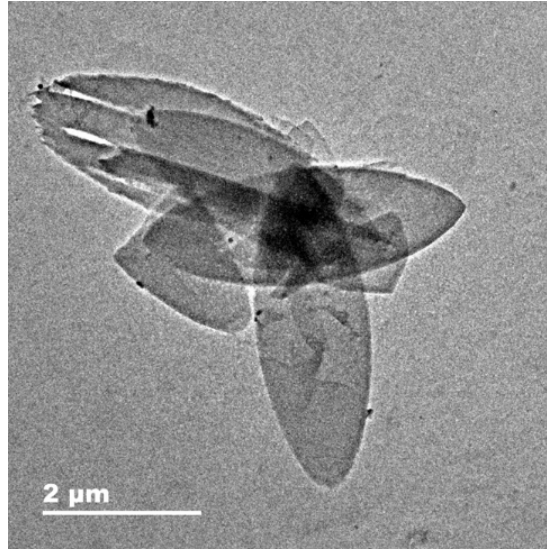


Fig. S18. TEM images of NiCo-NC after long-term ORR test.

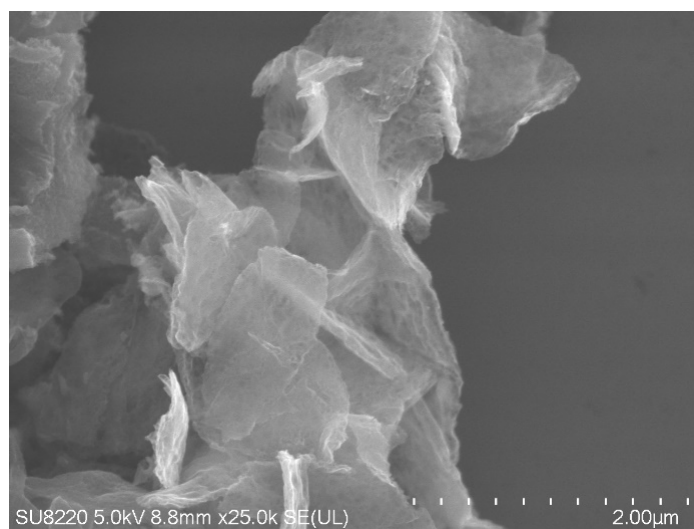


Fig. S19. SEM image of NiCo-NC after long-term ORR test.

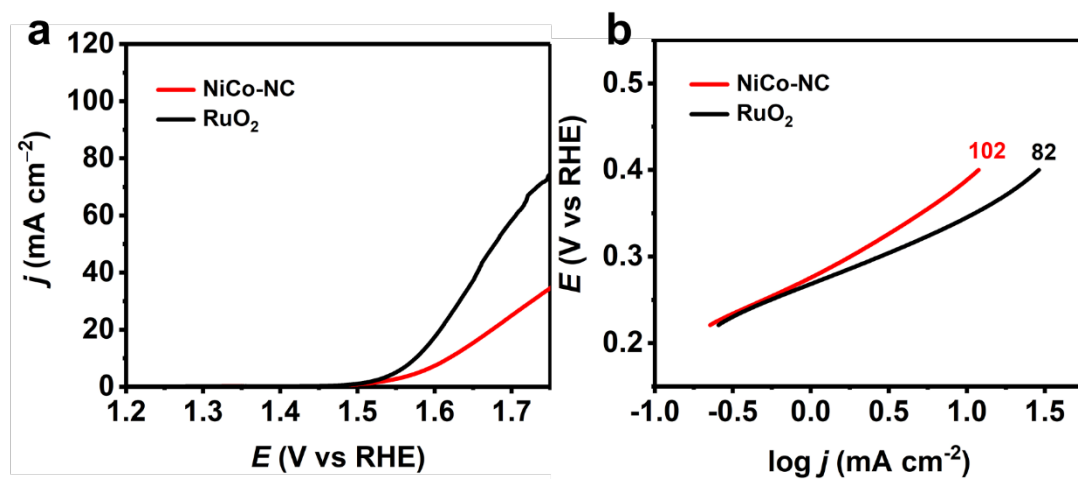


Fig. S20. LSV curves and Tafel plots of NiCo-NC catalysts and RuO₂ in 1.0 M KOH.

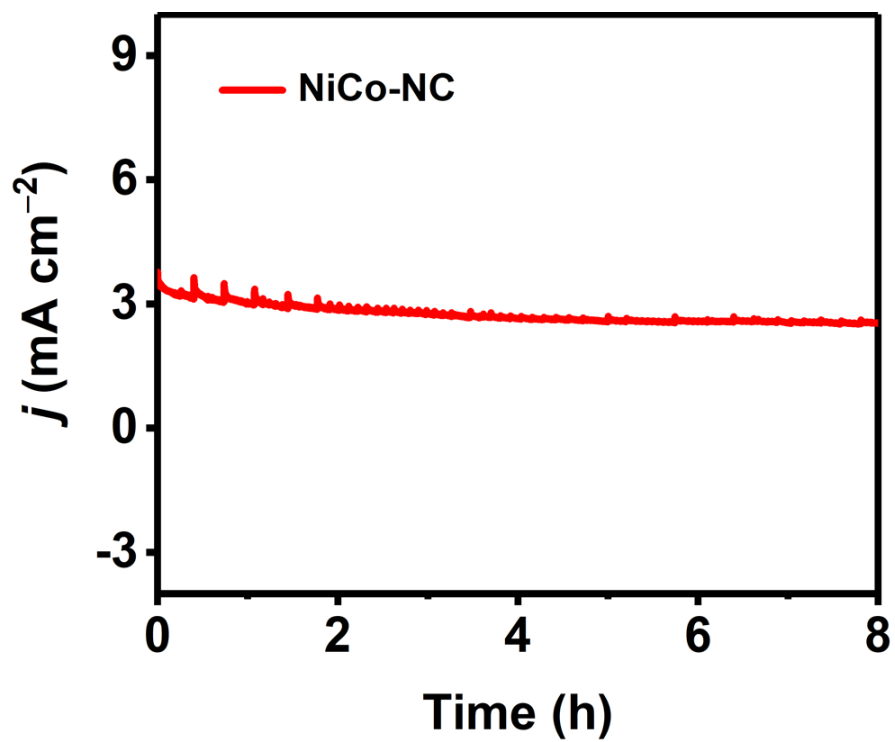


Fig. S21. j - t measurements for the NiCo-NC catalyst at 0.65 V (vs. RHE) in 1.0 M KOH.

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