High-curvature Carbon Supported Ni Single Atom with Charge Polarization for High-efficient CO_2 Reduction

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Experimental section

Chemicals

Triethylamine (≥99.0%), *N,N*-dimethylformamide (DMF) was purchased from Shanghai Macklin Biochemical Co., LTD; $Ni(NO_3)_2$ $6H_2O$ (≥98.0%), Ethylenediaminetetraacetic acid (EDTA), isopropyl alcohol were purchased from Shanghai Chemical Reagent Co., Ltd.

All chemicals were used without further purification.

Material preparation

For the solution of A, Ethylenediaminetetraacetic acid (EDTA, 3.54g) and Triethylamine (10ml) were first dissolved in *N,N*-dimethylformamide (DMF, 150ml), then, string for twenty minutes at 50°C to get a homogeneous solution.

For the solution of B, $Ni(NO_3)_2$ $6H_2O$ (5.82g) was dissolved in *N,N*-dimethylformamide (DMF, 150ml), then string for 1 hour to get a homogeneous solution. After that, mix solution A and solution B, string for 3 hours. At the end of reaction, the product was collected by centrifugation, washed with DMF for five times, and finally dried in muffle oven at 80 °C. The samples were annealed at 800 °C, 900 °C and 1000 °C with a rate of 5 min for 2 hours in Ar atmosphere, which followed by naturally cooling to room temperature.

For the acid leaching treatment, the as prepared C-Ni-n precursor were leached in 3 M H_2SO_4 for 12 hours to almost remove unstable Ni nanoparticles and other species and washed with DI water till the pH approximate 7, these resultant catalysts were donated as C-NiN_4-800, C-NiN_4-900 and C-NiN_4-1000, respectively.

Structural characterizations

The samples were first characterized by XRD with a 9 KW advanced X-ray diffractometer equipped with Cu Kα radiation (λ =1.54178Å) at a scan rate of 5° min^{-1}. The morphology study was conducted by transmission electron microscopy (TEM, JEOL-F200) with an acceleration voltage of 200 KV and Energy-dispersive X-ray spectroscopy (EDS) mapping images were taken ender a scanning TEM model. Using X-ray photoemission spectroscopy (XPS, ESCALAB250Xi) to identified the chemical environment on the catalyst surface, the obtained spectra were calibrated with C *1s* binding energy (284.8 eV). Brunauer-Emmett-Teller (BET) specific surface areas were evaluated by N_2 adsorption/desorption test conducted on a physisorption analyzer. The Ni content of series C-NiN_4-n samples were obtained by Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) instrument from PerkinElmer Optima 7300DV. The HAADF-STEM images were collected by Titan Themis Z field emission transmission electron microscope with double spherical aberration corrector. The local chemical structure around Ni was characterized using Ni K-edge X-ray absorption fine structure (XAFS) measurements performed at the was conducted in National Synchrotron Radiation Laboratory (NSRL) by using soochow beamline for energy materials at the beamline MCD-A and MCD-B.

Electrochemical measurements

H-type electrolytic cell was used for CO_2 electrochemical reduction with a CHI66OE potentiostat. Nafion 117 membrane was inserted between the cathodic chamber and anodic chamber. Both chambers were filled with 25ml 0.5 M $KHCO_3$ and 16 ml headspace. For electrode preparation, 2 mg catalyst was dispersed in 300 μl isopropyl alcohol, 700 μl deionized water and 0.5 wt% Nafion solution, and sonicated 20 minutes to form a uniform ink. Drop 100 μl of the solution mentioned above onto the 1×2 cm^2 carbon paper (Toray TGP-H-060, loading amount: 0.2 mg cm^{-2}). A Pt mesh (1 cm^2) and a saturated Ag/AgCl electrode served as the counter electrode and reference electrode, respectively. The working electrode and the reference electrode were placed in the cathodic compartment, while the Pt electrode was placed in the anodic side. Before test, inject CO_2 into the $KHCO_3$ electrolyte continuously for at least 30 minutes to insure to remove residual air. All measured potentials were converted to RHE potentials by the following formula:

$$E_{RHE}=E_{Ag/AgCl}+0.0591V\ pH+0.197V$$

The scan rate of LSV and CV tests were 10 mV/s.

The electrochemical impedance spectroscopy (EIS) is collected from 100000 Hz to 0.1 Hz at 0.5 V (VS RHE) in CO_2 saturated 0.5 M $KHCO_3$. The poison resistance experiment is tested under 0.5 M $KHCO_3$ electrolyte containing 0.1 M KSCN to block the NiN_4 active sites.

CO_2 products analysis

Seal the cell after that the additional CO_2 bubbling for 10 minutes, and the electrochemical CO_2RR performance was evaluated by using Amperometric *i-t* Curve measurement at constant potential. Taking 2.5 ml of gas in the empty headspace with a microinjection needle, then the gas was injected into a gas chromatography (GC). The GC equipped with a thermal conductivity detector (TCD) for H_2 and a flame ionization detector (FID) for CO and quantification. The following formula gives the calculation method of Faradaic efficiency of the gas products.

$$\text{FE (\%)} = \frac{\alpha nF}{Q_{total}} \times 100$$

The number of electrons transferred of CO and H_2 is 2, and F is the Faraday's constant (96485 C mol-1). Qtotal is the amount of charge in the test time (measured by the potentiostat), n is the number of moles for a given product (detected by GC).

Theoretical Calculation Details

Spin-polarized density functional theory (DFT) calculations were performed by the Vienna Ab initio Simulation Package (VASP) plane-wave DFT code, with the generalized gradient approximation of Perdew–Burke–Ernzerhof to describe electron exchange and correlation.[1, 2] The plane-wave basis is cut off by 500 eV. The projector-augmented plane wave (PAW) was used to describe the electron–ion interactions.[3] A set of (5 × 5 × 1) k-points were carried out for geometric optimization, and the convergence threshold was set as 10^{-5} eV in energy and 0.02 eV $Å^{-1}$ in force.

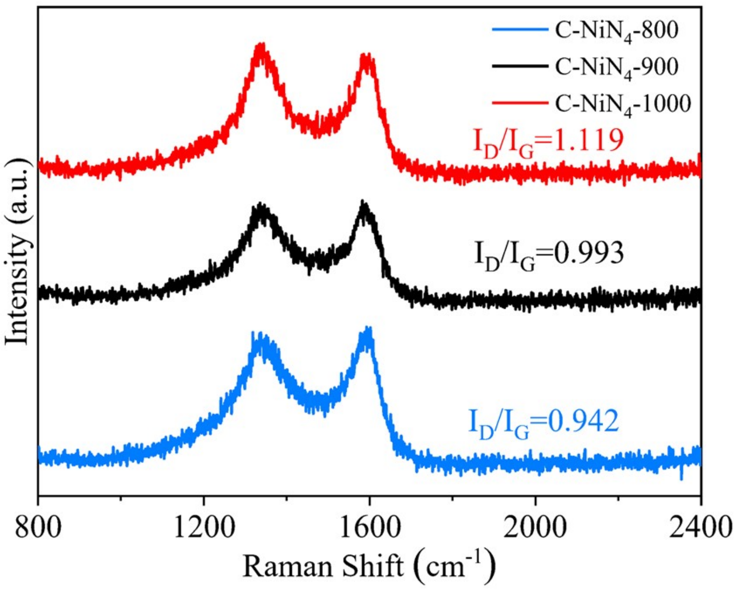

Figure S1. Raman measurements for C-NiN$_4$-800, C-NiN$_4$-900, and C-NiN$_4$-1000.

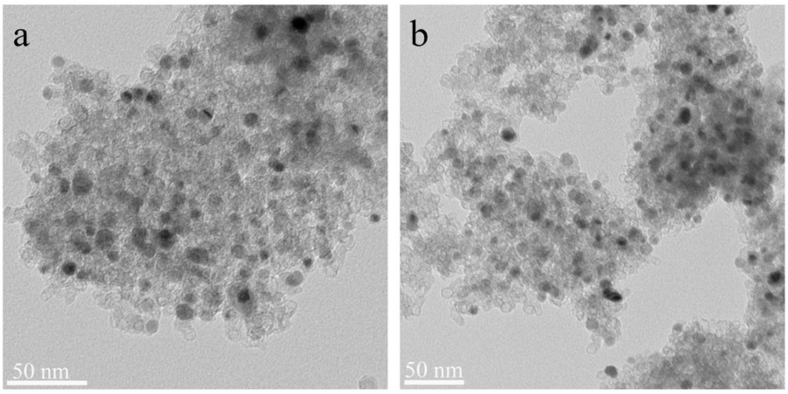

Figure S2. (a) TEM image of C-NiN$_4$-800; (b) TEM image of C-NiN$_4$-900.

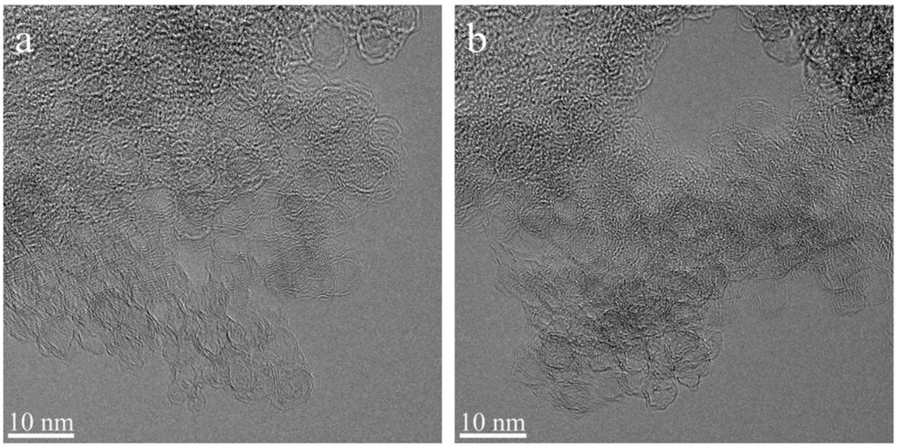

Figure S3. (a) and (b) The TEM images of C-NiN_4-1000.

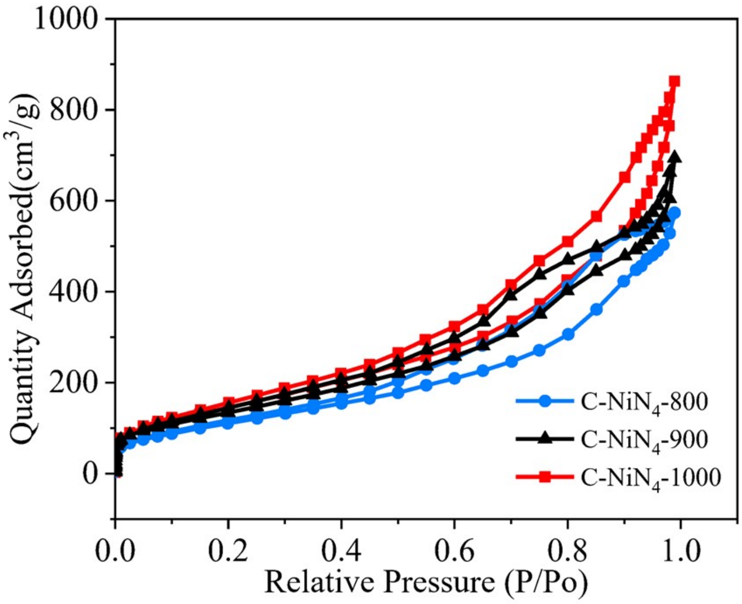

Figure S4. Nitrogen adsorption-desorption isotherms for C-NiN_4-1000, C-NiN_4-900, and C-NiN_4-800.

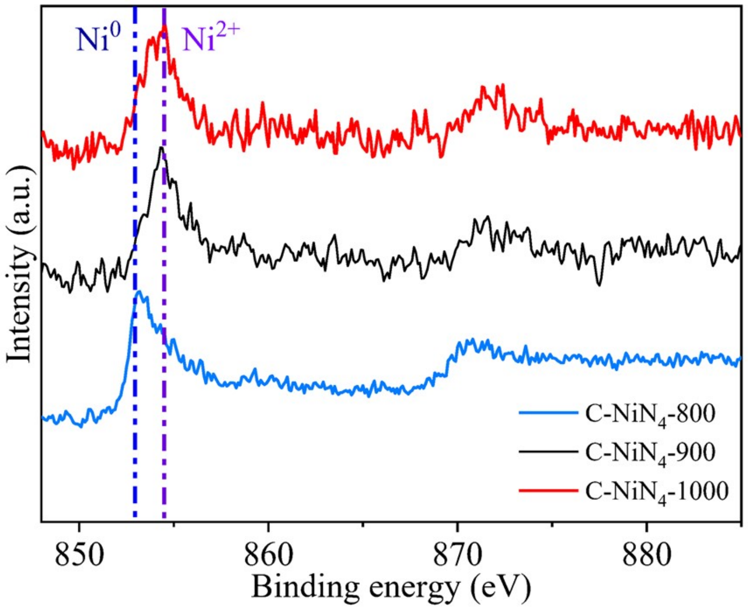

Figure S5. Ni 2p XPS spectrums for C-NiN$_4$-1000, C-NiN$_4$-900, C-NiN$_4$-800.

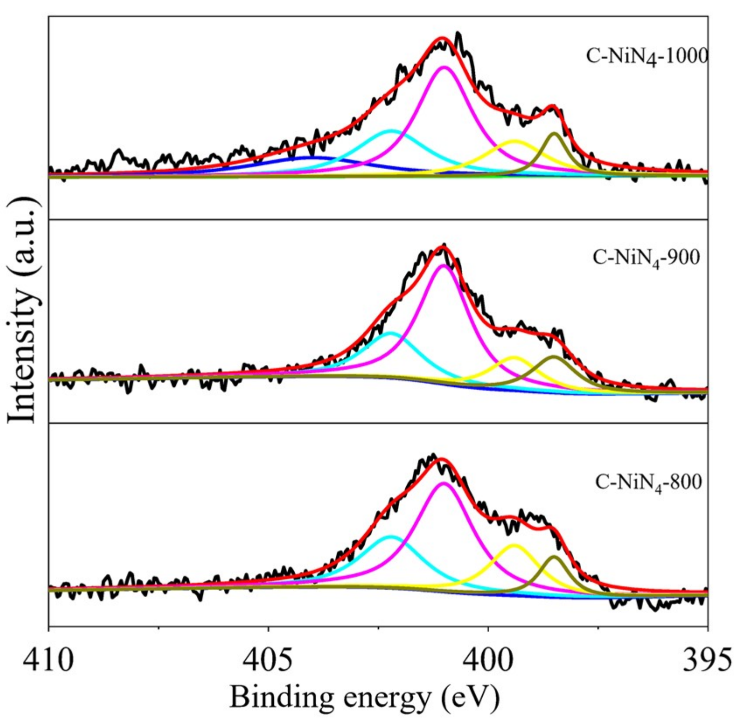

Figure S6. The N 1s XPS spectra of C-NiN$_4$-1000, C-NiN$_4$-900, C-NiN$_4$-800.

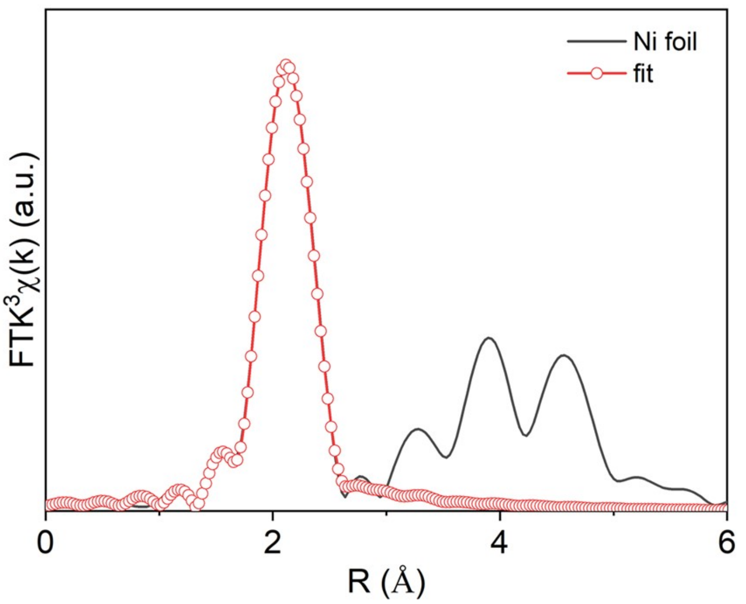

Figure S7. XAFS fitting curve of Ni foil.

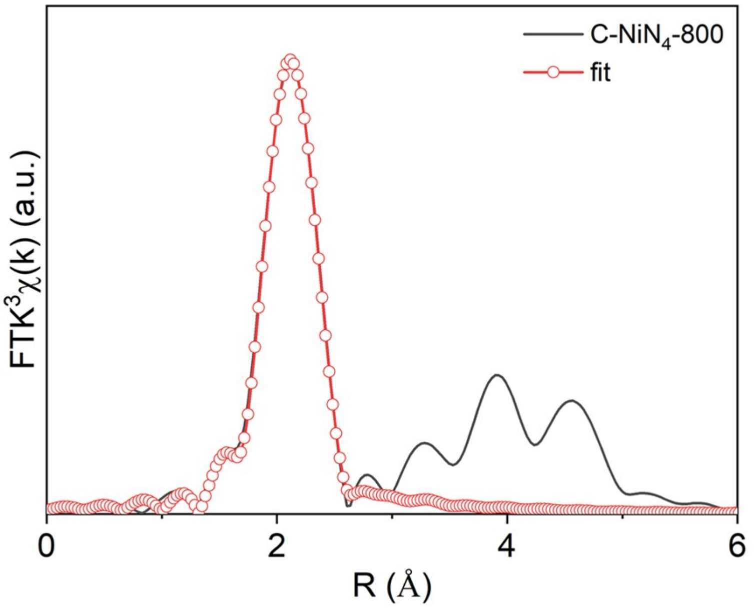

Figure S8. XAFS fitting curve of C-NiN$_4$-800.

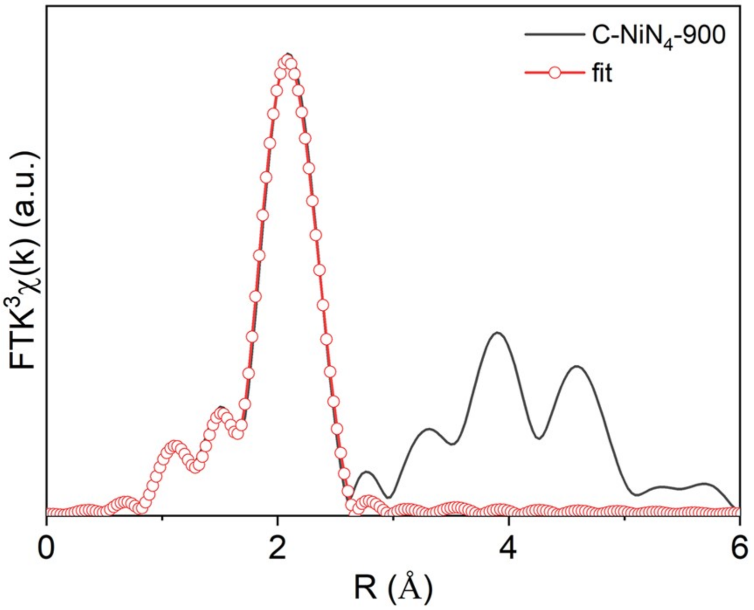

Figure S9. XAFS fitting curve of C-NiN$_4$-900.

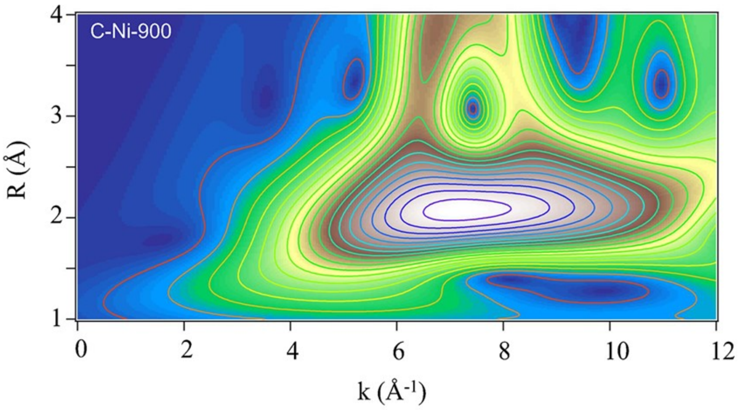

Figure S10. WT-EXAFS of C-NiN_4-900.

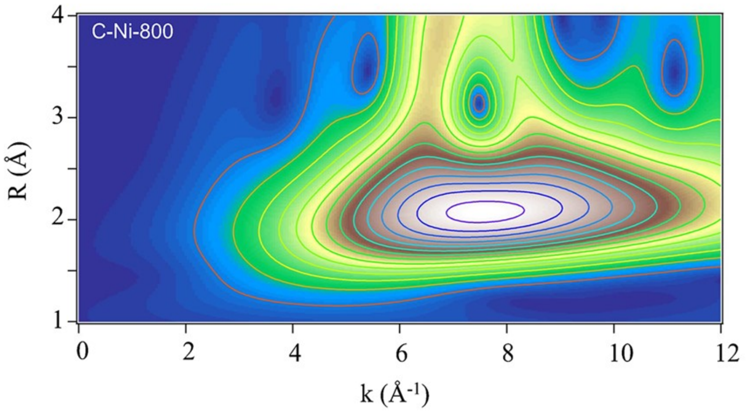

Figure S11. WT-EXAFS of C-NiN_4-800.

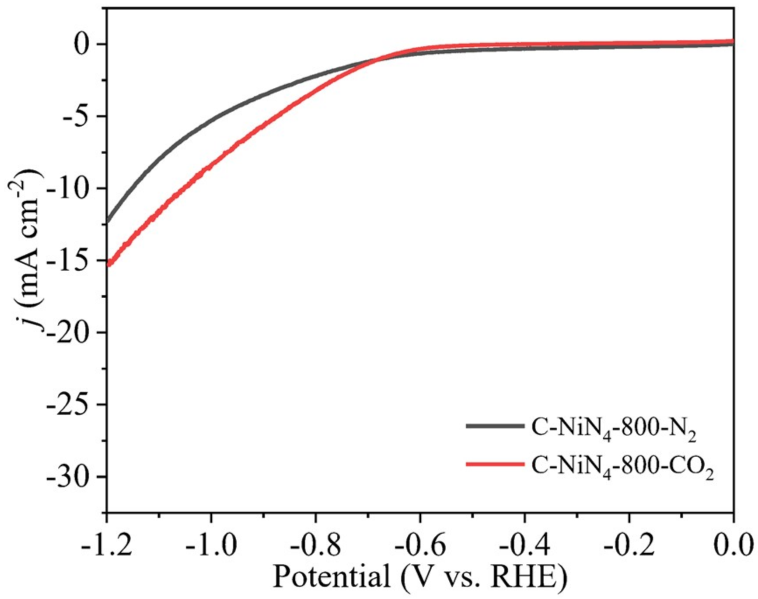

Figure S12. The linear sweep voltammetric (LSV) curves of C-NiN$_4$-800 respectively in CO$_2$-saturated and N$_2$-saturated 0.5 M KHCO$_3$ electrolyte on carbon paper at scan rate of 10 mV s^{-1}.

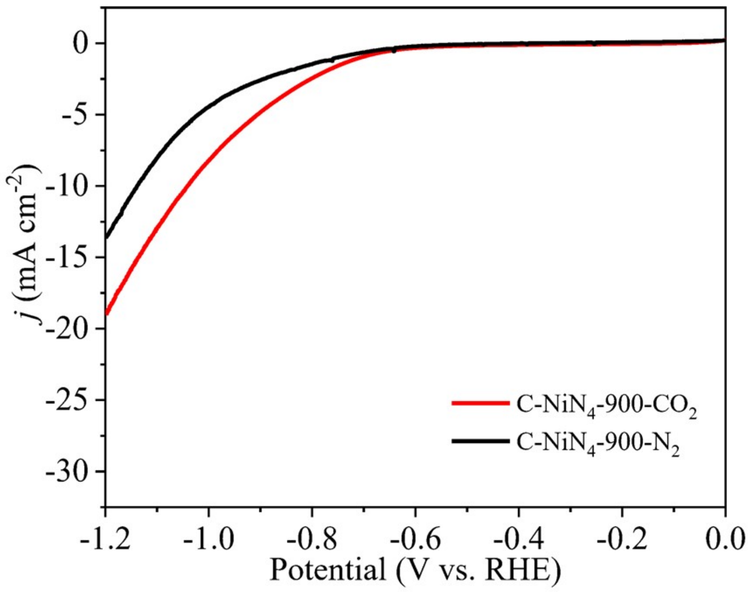

Figure S13. The linear sweep voltammetric (LSV) curves of C-NiN_4-900 respectively in CO_2-saturated and N_2-saturated 0.5 M $KHCO_3$ electrolyte on carbon paper at scan rate of 10 mV s^{-1}.

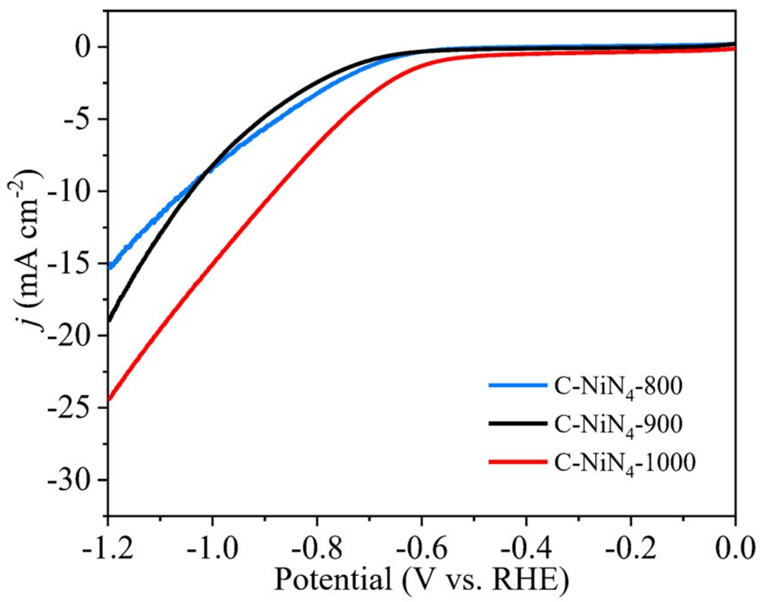

Figure S14. The linear sweep voltammetric (LSV) curves of C-NiN_4-800, C-NiN_4-900, and C-NiN_4-1000 respectively in CO_2-saturated 0.5 M $KHCO_3$ electrolyte on carbon paper at scan rate of 10 mV s^{-1}.

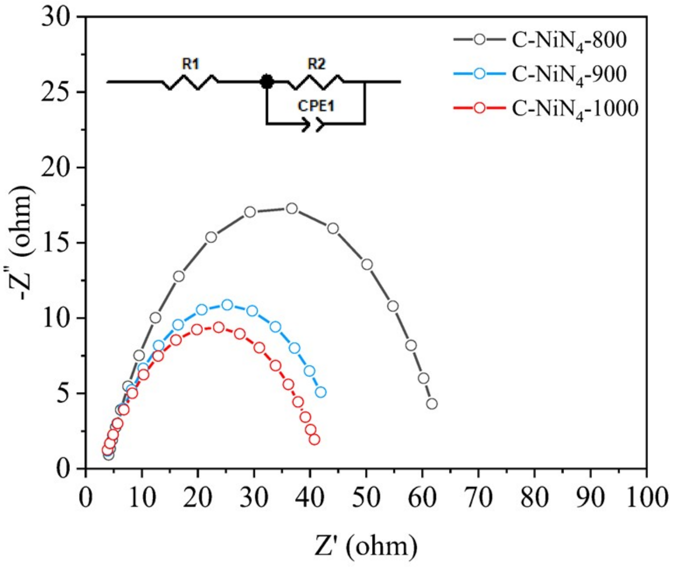

Figure S15. The fitted EIS curves of Nyquist plots of the series samples and the equivalent circuit.

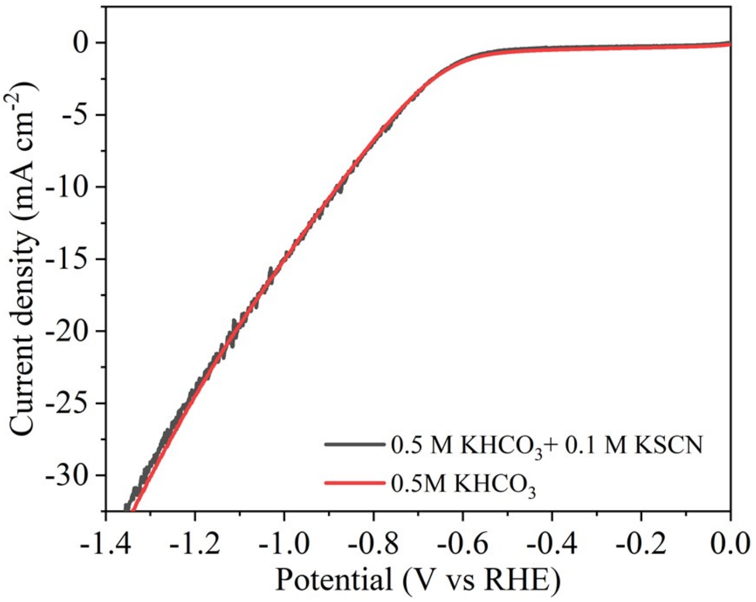

Figure S16. LSV curves of C-NiN$_4$-1000 under 0.5 M KHCO$_3$ and 0.5 M KHCO$_3$ containing 0.1 M KSCN to reveal the poison resistance of active sites.

Table S1. FT-EXAFS fitting results of the as-prepared samples

Sample	Path	N	R(Å)	σ^2 (10^{-3} Å^2)
Ni foil	Ni-Ni	12	2.48	-.57
C-Ni-1000	Ni-N	3.54	1.85	0.39
	Ni-Ni	1.32	2.45	0.26
C-Ni-900	Ni-Ni	6.21	2.48	0.76
C-Ni-800	Ni-Ni	9.76	2.47	0.64

Here, N represents the coordination number, R represents the bond distance, σ^2 represents the Debye-Waller factor value. $S0^2$ was fixed to 0.714 as determined from Ni foil fitting.

References:

[1] G. Kresse, J. Furthmuller, Phys Rev B Condens Matter 1996, 54, 11169.

[2] J. P. Perdew, K. Burke, M. Ernzerhof, Phys Rev Lett 1996, 77, 3865.

[3] P. E. Blochl, Phys Rev B Condens Matter 1994, 50, 17953.