

Supporting Information

Electroreduction of CO₂ to syngas with controllable H₂/CO ratios in a wide potential range over Ni-N co-doped ultrathin carbon nanosheets

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Chemicals and reagents

All chemicals were of analytical grade and used without further treatments. Medium temperature coal tar pitch was provided by Maanshan Iron and Steel Co., Ltd. Nickel (II) chloride hexahydrate, potassium chloride, potassium hydrogen carbonate, urea, sodium chloride, ethanol absolute, hydrochloric acid, and nitric acid were obtained from Sinopharm Chemical Reagent Co., Ltd. Nafion solution (5.0 wt%) was purchased from Sigma-Aldrich and N-117 membranes were provided by Shanghai Chuxi Industrial Co., Ltd. Deionized water (≥ 15 megohm \cdot cm) was obtained from Hefei Jingchun Water Sales Co., Ltd.

Catalyst preparation

Synthesis of Ni/N-C-900 catalysts

In a typical synthesis, 1 g of medium-temperature coal tar pitch and 30 g of mixed salt ($M_{\text{NaCl}}/M_{\text{KCl}}=1$) were mixed with a mortar, and then put into a porcelain boat and heated at 1000 °C for 2 h under Ar atmosphere in a tube furnace with a heating rate of 5°C/min. After cooling to room temperature, the sample was added to concentrated nitric acid, condensed, and refluxed at 70°C for 4 h, and then washed with deionized water until neutral and dried. The dried samples were dispersed in a 3 mg/mL NiCl₂ solution, stirred uniformly for 12 h, and mixed with 10 g of urea with a mortar after filtration and drying. It was placed in a porcelain boat and re-carbonization at 900 °C for 2 h under Ar atmosphere in a tube furnace with a heating rate of 5°C/min. After cooling down to room temperature, the samples were dispersed in 3 M HCl solution and stirred for 12 h. Ni/N-C-900 powder was obtained after filtration with deionized water and drying in a vacuum oven at 60°C overnight.

Synthesis of Ni/N-C-700, 800, and 1000 catalysts

The samples were prepared using a similar identical procedure, and only were heat-treated at 700°C, 800°C, and 1000°C in the re-carbonization process.

Synthesis of N-C and Ni-C catalysts

Nitrogen-doped carbon (N-C) and metallic Ni nanoparticles decorated carbon (Ni-C) were prepared through the similar synthesis route with Ni/N-C-900, which N-C is not

doped with nickel, and Ni-C is not doped with nitrogen.

Characterization

The crystalline and graphitization degrees of various samples were investigated by X-ray diffraction (XRD, Ultima IV) and Raman spectroscopy (JYLab-Raman HR800), respectively. The morphologies of the as-prepared products were obtained from a scanning electron microscope (SEM, TESCAN MIRA LMS, Czech). Transmission electron microscopy, and the corresponding energy-dispersive X-ray (EDX) mapping were recorded using a transmission electron microscope (TEM, JEOL-2100). X-ray photoelectron spectroscopy (XPS) was measured using a high-performance electron spectrometer equipped with the excitation source of monochromatic Al-K α radiation ($h\nu = 1486.6$ eV) (Thermo Scientific K-Alpha). **Specifically, we have controlled the consistency of the FWHM (1.2-1.3) in each separated peak and set the value of %Lorentzian-Gaussian to 80 in deconvolution process (XPS fitting Software: XPSPEAK41).** Ni contents were recorded on an inductively coupled plasma atomic emission spectrometer (ICP-PMS) (Agilent 7700).

Cathode preparation

Electrochemical measurements were carried out by using an electrochemical workstation (CHI 760E) coupled with a three-electrode H-cell with a working electrode, a saturated Ag/AgCl reference electrode, and a platinum foil as a counter electrode. To prepare the working electrode, 5.0 mg of catalyst was ultrasonically dispersed in a 500 μ L Deionized water, 470 μ L absolute ethanol and Nafion solution (5 wt.%, 30 μ L) solution to form homogeneous ink. Then, 10 μ L of catalyst ink was drop-cast onto a 0.19625 cm² glassy carbon electrode and dried naturally to obtain a working electrode. In the case of H cells, each compartment was filled with 80 mL of 0.1 M KHCO₃, and the two compartments were separated by a piece of Nafion-117 membrane. To prepare a CO₂-saturated KHCO₃ solution, flow 20 mL min⁻¹ of CO₂ (99.999%) for 30 min using a mass flow controller (D08-4B/ZM). A continuous flow

of CO₂ was introduced into the cell at a similar flow rate throughout the test. Cyclic voltammetry (CV) was repeated before other tests until a stable CV curve was observed.

Electrochemical measurements

The experiments were performed in a gas-tight H-type cell separated by a Nafion N117 membrane. Each compartment contained 80 mL electrolyte (0.1 M KHCO₃ aqueous solution). The electrocatalytic performance of samples were test in Ar (99.999%)-saturated or CO₂ (99.999%)-saturated 0.1 M KHCO₃ with Pt foil (1 cm²) as the counter electrode and Ag/AgCl (saturated KCl) as the reference electrode.

All potentials in the experiments were measured against an Ag/AgCl reference electrode and rescaled to reversible hydrogen electrode (RHE):

$$E (vs . RHE) = E (vs . Ag/AgCl) + 0.197V + 0.0591 \times pH$$

During the experiments, CO₂ gas was delivered at an average flow rate of 20 sccm.

Electrocatalytic CO₂ reduction was conducted in CO₂-saturated KHCO₃ solution (0.1 M) at room temperature and atmospheric pressure. CO₂ was purged into the KHCO₃ solution for at least 30 min to remove residual air in the electrolyze. Linear sweep voltammograms in Ar- or CO₂ atmosphere were carried out in a three-electrode system using Ag/AgCl as reference electrode, Pt wire as counter electrode, and glassy carbon as working electrode on a CHI 760E potentiostat (CHI 760E, Shanghai CH Instruments Co., China). The electrolyte is 0.1 M KHCO₃ solution with Ar or CO₂ purged for at least 30 min. For the faradaic efficiency analysis, gas products were detected by gas chromatograph (GC-2014. SHIMADZU).

ECSA was calculated based on the definition:

$$ECSA = R_f \times S$$

Where R_f is roughness factor that estimated from the ratio of the C_{dl} values of catalyst and graphene ($\sim 21 \mu F \text{ cm}^{-2}$), $R_f = C_{dl}/21 \mu F \text{ cm}^{-2}$; S is surface area of the working electrode, equal to 0.19625 cm² in this work.

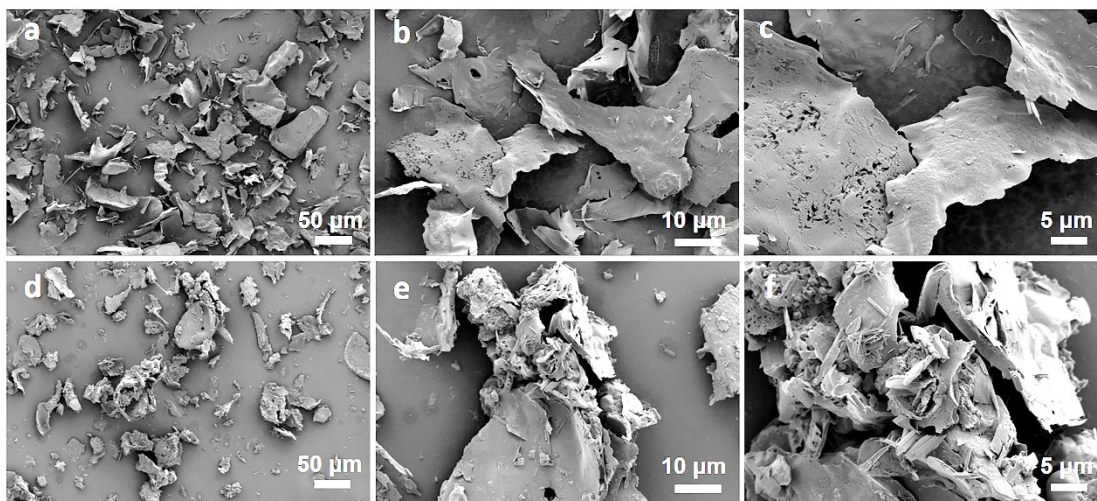


Fig. S1 Different-magnification SEM images of N-C a-c) and Ni-C d-f).

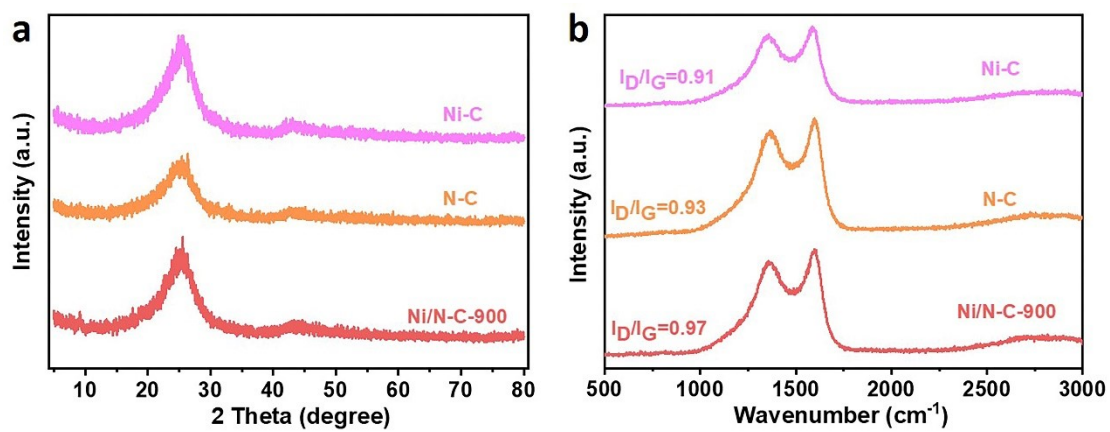


Fig. S2 (a) X-ray diffraction patterns of Ni/N-C-900, N-C, and Ni-C. (b) Raman spectra of Ni/N-C-900, N-C, and Ni-C.

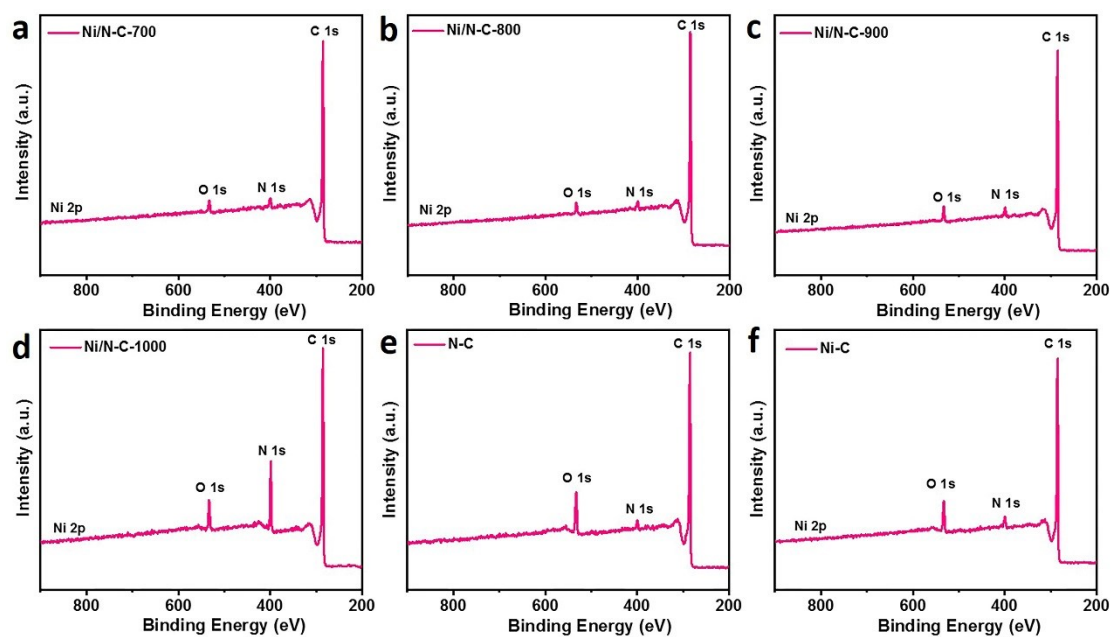


Fig. S3 XPS survey spectra of Ni/N-C-700 a), Ni/N-C-800 b), Ni/N-C-900 c), Ni/N-C-1000 d), N-C e) and Ni-C f).

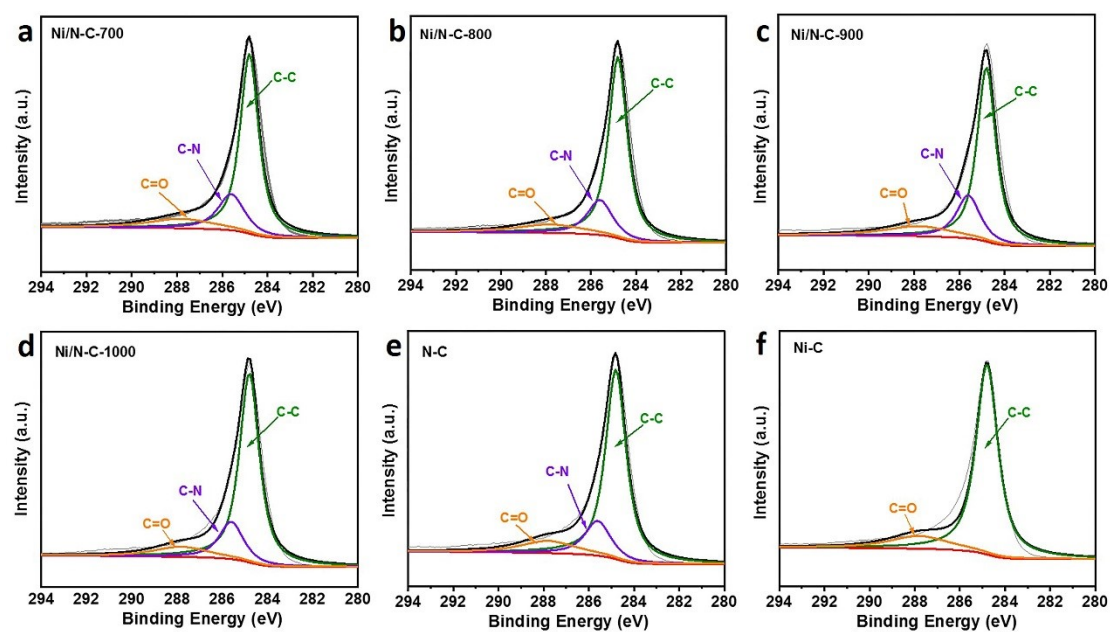


Fig. S4 C 1s XPS spectra of Ni/N-C-700 a), Ni/N-C-800 b), Ni/N-C-900 c), Ni/N-C-1000 d), N-C e) and Ni-C f).

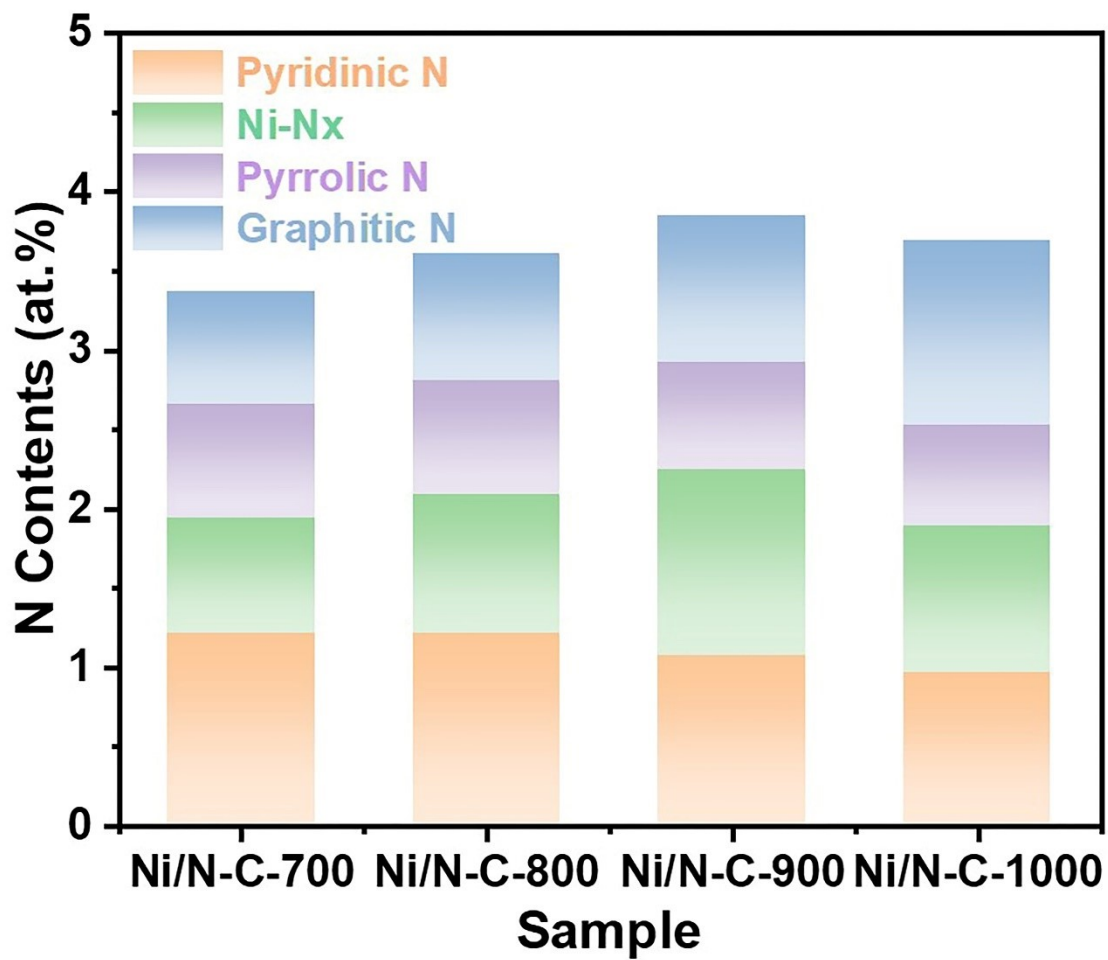


Fig. S5 The percentage of different N species in Ni/N-C-700, Ni/N-C-800, Ni/N-C-900, and Ni/N-C-1000.

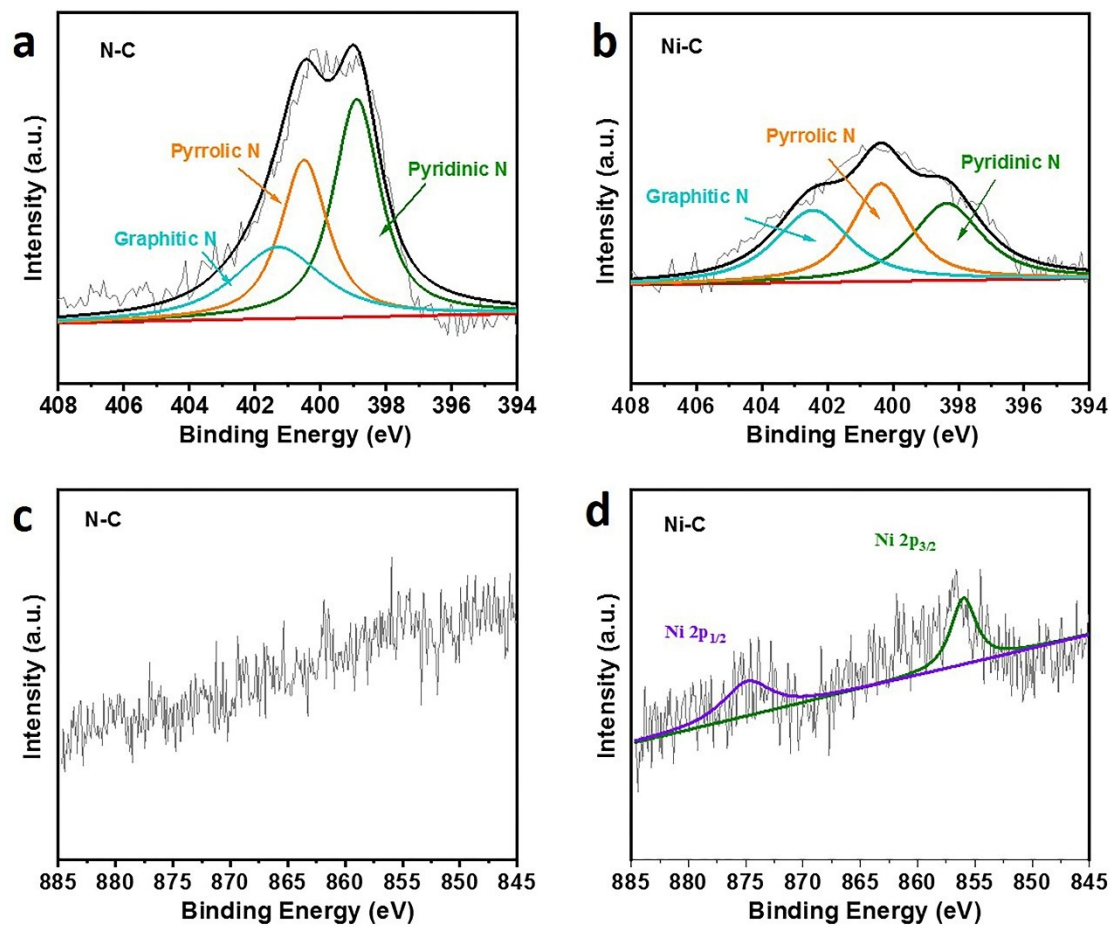


Fig. S6 High resolution XPS N 1s spectra of N-C a) and Ni-C b); high resolution XPS Ni 2p spectra of N-C c) and Ni-C d).

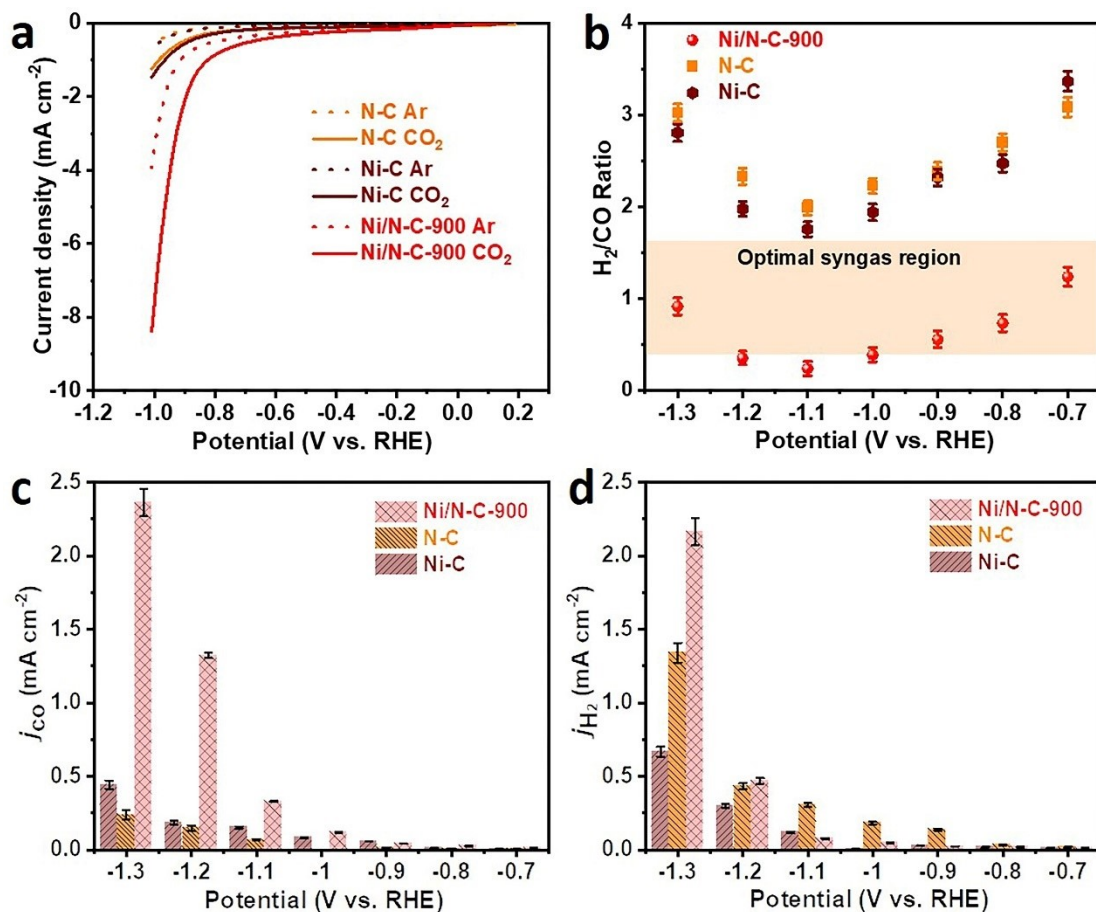


Fig. S7 (a) Linear sweep voltametric (LSV) curves of various samples at CO₂ and Ar-saturated 0.1 M KHCO₃ solution. (b) Dependence of H₂/CO ratio with applied potentials and ratios of Ni/N-C-900, N-C and Ni-C. (c) Partial current densities for CO at different applied potentials. (d) Partial current densities for H₂ at different applied potentials.

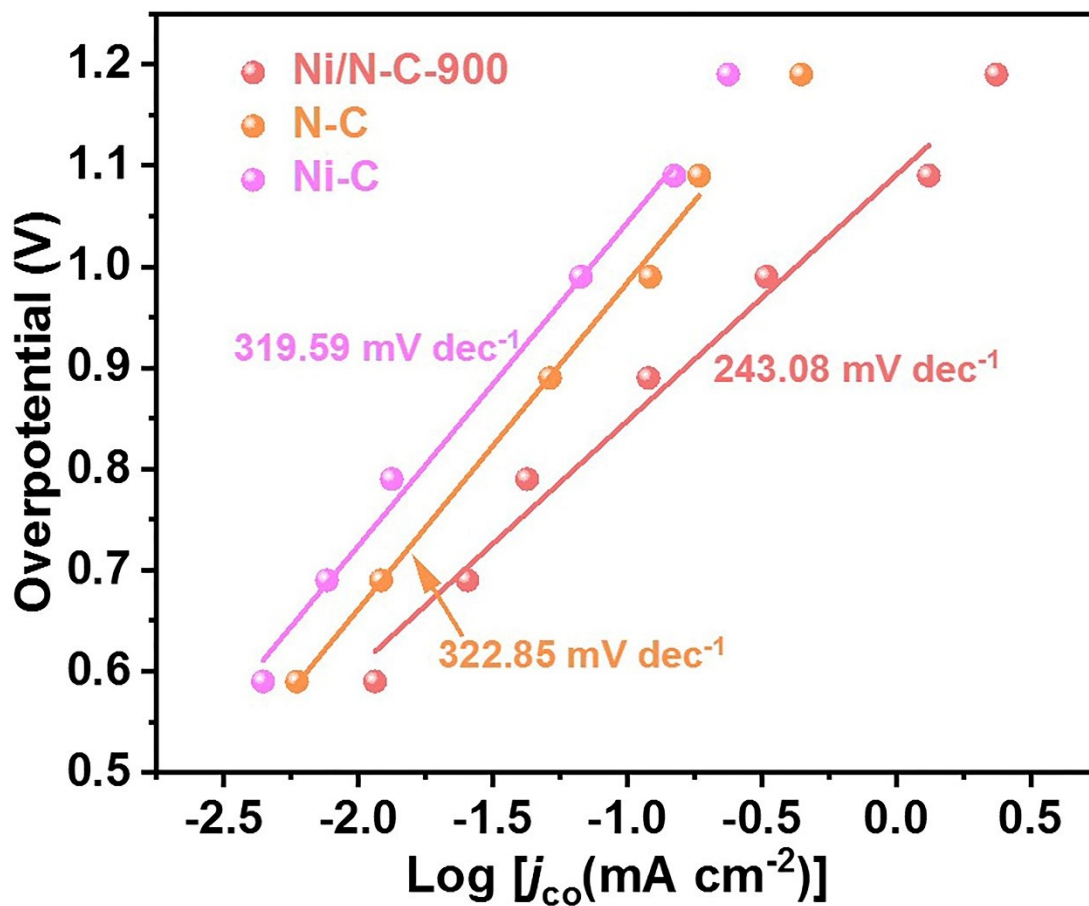


Fig. S8 Tafel plots based on j_{CO} for Ni/N-C-900, N-C and Ni-C in the CO₂-saturated KHCO₃ electrolyte.

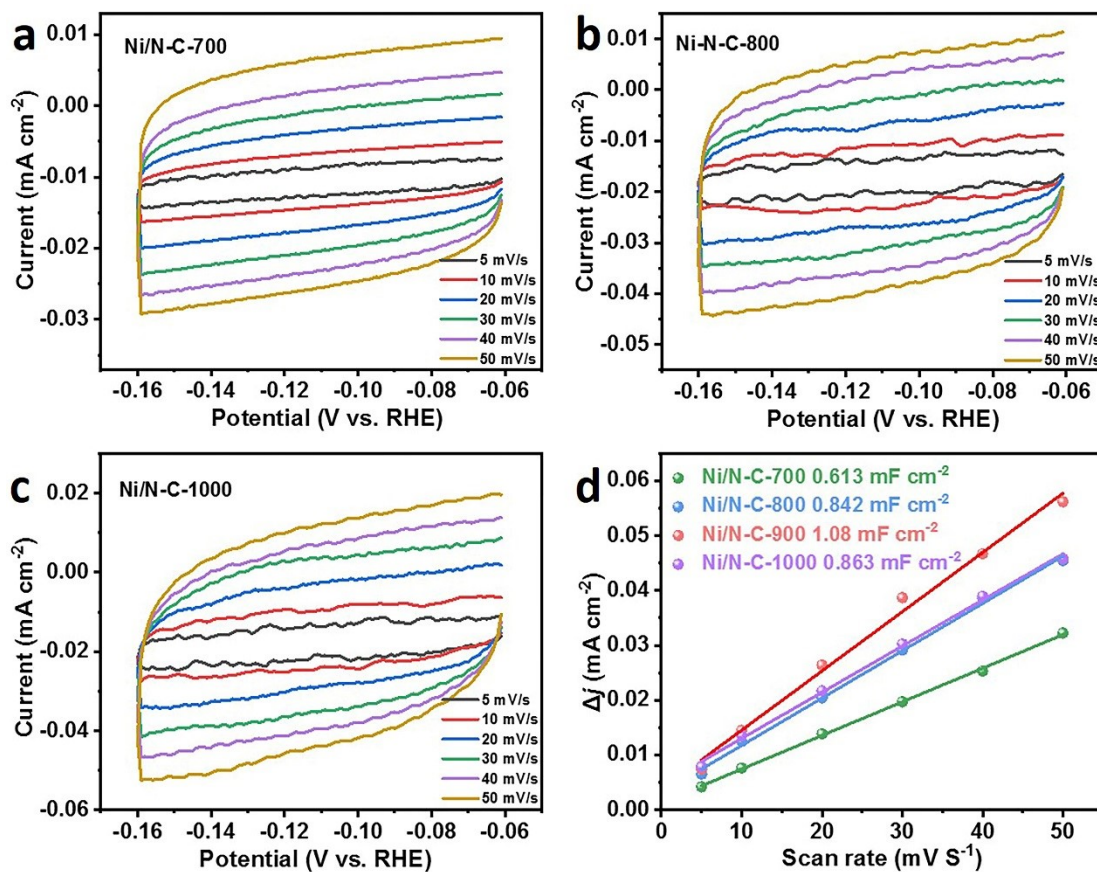


Fig. S9 Ni/N-C-700 a), Ni/N-C-800 b), Ni/N-C-1000 c) at different scan rates (5, 10, 20, 30, 40 and 50 mV s⁻¹). d) The plot of charging current density differences Δj against the scan rate for the calculation of ECSA of various Ni/N-C samples.

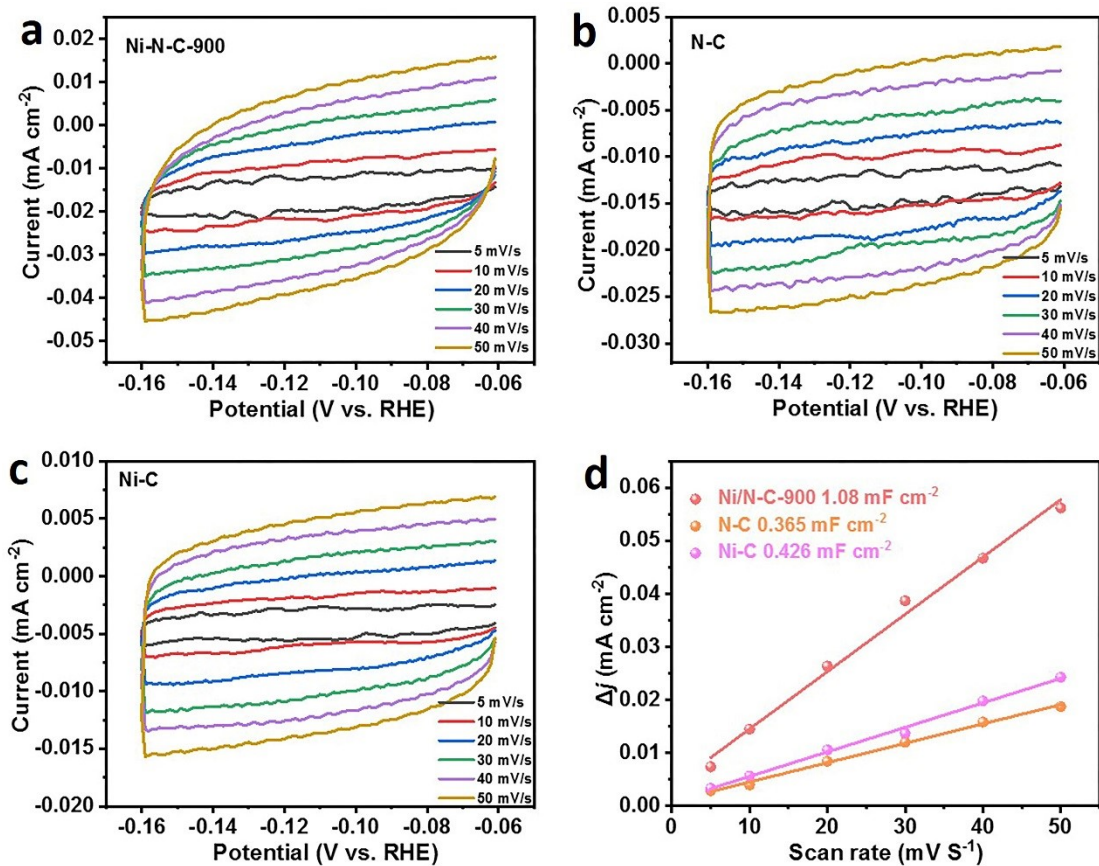


Fig. S10 Ni/N-C-900 a), N-C b), Ni-C c) at different scan rates (5, 10, 20, 30, 40 and 50 mV s^{-1}). d) The plot of charging current density differences Δj against the scan rate for the calculation of ECSA of various samples.

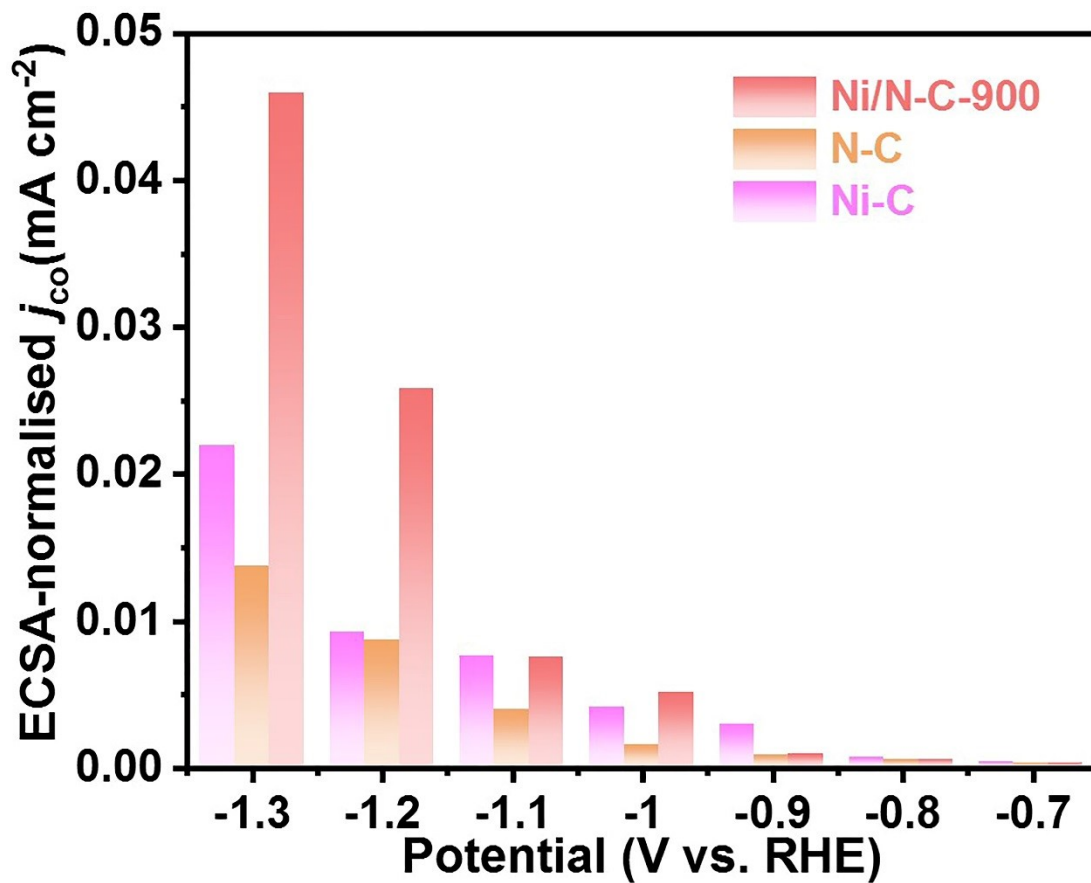


Fig. S11 ECSA-normalised j_{Co} of Ni/N-C-900, N-C and Ni-C.

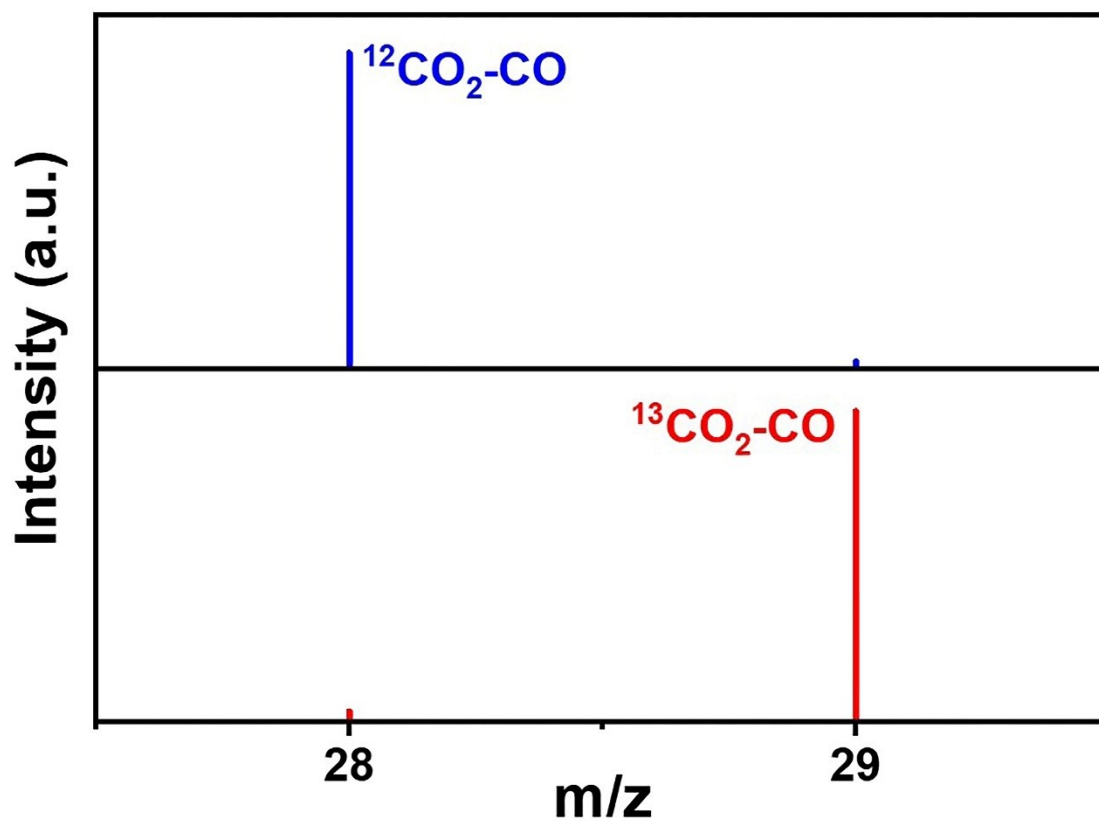


Fig. S12 Isotopic composition of CO.

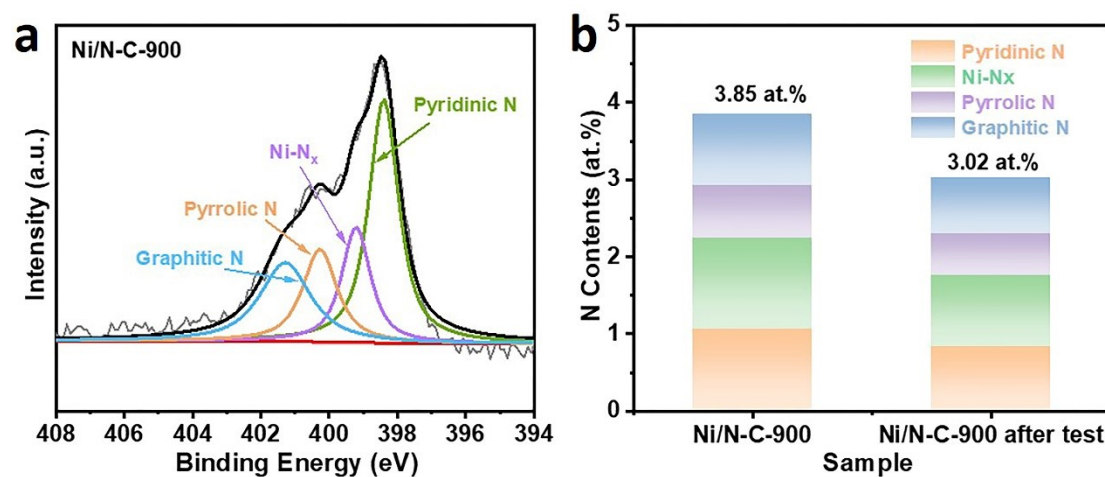


Fig. S13 (a) The high-resolution XPS spectra of N 1s of Ni/N-C-900 after 10 h test. (b) The content and types of N in Ni/N-C-900 and Ni/N-C-900 after 10 h test.

Table S1. Summary of Ni content in different catalysts determined by XPS.

Catalyst	Ni (at.%)
Ni/N-C-700	0.09
Ni/N-C-800	0.10
Ni/N-C-900	0.16
Ni/N-C-1000	0.13
Ni-C	0.07

Table S2. ICP-OES measurements for Ni weight percent.

Catalyst	Ni (wt.%)
Ni/N-C-700	0.00230
Ni/N-C-800	0.00283
Ni/N-C-900	0.00936
Ni/N-C-1000	0.00381
Ni-C	0.00188