Supporting Information

Local compressive strain regulation of atomically dispersed NiN$_4$ sites for enhancing CO$_2$ electroreduction to CO

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Materials

All the chemical materials were purchased in analytical grade and used without further purification.

Synthesis of Ni SA/H-CN.

The Ni SA/H-CN was synthesized follow by the synthesis of template (N-stearoyl-D-glutamic), helical carbon tube (H-NC) and Ni single atom catalyst.

For the template, a mixture of 1.78g D-glutamic acid, 7 mL deionized water, 6 mL acetone, and 0.96 g sodium hydroxide was prepared to maintain a pH of 12. Next, 3.00 g stearoyl chloride and 5 mL of 2 M sodium hydroxide solution was slowly added to the above mixture while maintaining the pH at 12 for 1.5 h. The resulting solution was then acidified with hydrochloric acid until a pH of 1 was reached, which yielded the carboxylic acid surfactant. The solids were washed with distilled water until the pH reached 7. After dried in vacuum N-stearoyl-D-glutamic was obtained as the template of helical carbon tube.

For synthesis the helical carbon tube (H-NC), 25mg of N-stearoyl-D-glutamic acid was dissolved in 13 mL of methanol. Under stirring, 160 uL of pyrrole was added to the solution, followed by 60 mL of water. The resulting suspension was stirred for 20 minutes before adding 550 mg of ammonium persulfate, dissolved in 1 mL of water. After stirring for 6 hours, the mixture was centrifuged to isolate black solids H-NC. The solids were washed with ethanol and water and then subjected to freeze drying.

Finally, the obtained H-NC was dispersed in 20 mL of water with sonication. Subsequently, 10 mg of Ni $(NO_3)_2$, which dissolved in 1 mL of water, was slowly added dropwise to the dispersion. The mixture was then sonicated for 3 hours, followed by overnight stirring and subsequent freeze-drying. The resulting solid was pyrolyzed for 2 h at 800°C under an inert atmosphere. To remove any potential metal particles or clusters, the production was washed with 0.5M hydrochloric acid. Finally, the product was annealed under an inert atmosphere at 800°C for 2 hours, gained Ni SA/H-NC.

Synthesis of Ni SA/NG.

Initially, 2,4-diamino-6-phenyl-1,3,5-triazine (DPT, 10 mmol) and $NiCl_2 \cdot 6H_2O$ (0.3 mmol) were mixed in 40 mL of deionized water and stirred for 6 h at room temperature. The resulting mixture was collected by centrifugation, washed with water, and dried in a vacuum at 50°C for 12 h. Subsequently, it was transferred to a porcelain boat, fully covering the carbon cloth at the bottom. The porcelain boat was heated under nitrogen to 550°C in a tubular furnace, with a heating rate of 2.3°C/min and held at 550°C for 2 h. The temperature was then progressively increased to 800°C, with a heating rate of 10°C/min and kept at 800°C for 1 h. After cooling down to room temperature, the grown samples on carbon cloth were extracted and washed with deionized water.

Characterizations

Powder X-ray diffraction patterns of samples were recorded on a Rigaku Miniflex-600 operating at 40 kV voltage and 15 mA current with Cu Kα radiation (λ=0.15406nm). TEM images were recorded by a Hitachi-7700 working at 100 kV. The high-resolution TEM, HAADF-STEM images the corresponding Electron energy-loss spectroscopy were recorded by a FEI Tecnai G2 F20 S-Twin high-resolution transmission electron microscope working at 200 kV and on a JEOL JEM-ARM200F TEM/STEM with a spherical aberration corrector working at 300 kV. X-ray photoelectron spectroscopy (XPS) was collected on scanning X-ray microprobe (PHI 5000 Verasa, ULAC-PHI, Inc.) using Al Kα radiation. For the core-level spectra, the binding energies were calibrated using the C 1s feature located at 285.0 eV as the reference. Metal content in the solid samples was detected by inductively coupled plasma atomic emission spectrometry (Optima 7300 DV). XAFS measurement and data analysis：XAFS spectra at the Cu K-edge was collected at the beamline 1W1B station of the Beijing Synchrotron Radiation Facility, China. The Fe K-edge, Cu K-edge and Ir L_3-edge XANES data were recorded in a fluorescence mode. Corresponding metal foil and metal oxide were used as references. The acquired EXAFS data were extracted and processed according to the standard procedures using the ATHENA module

implemented in the IFEFFIT software packages. The k_3-weighted EXAFS spectra were obtained by subtracting the post-edge background from the overall absorption and then normalizing with respect to the edge-jump step. Raman spectra were collected using a Raman spectrometer (WITEC Alpha500) by a 633 nm He–Ne laser.

Electrochemical Test

A CHI 660E electrochemical workstation was used for electrochemical measurements.

The CO_2 electroreduction was practiced with a flow cell, which was made up of a gas-diffusion layer (H14C9, Freudenberg,) and Ni foam (1 cm × 3 cm, 2 mm thickness) as cathode electrode and anode electrode, separated by an anion exchange membrane (Sustainion 37-50) and then these three components were positioned and clamped together using polytetrafluoroethylene (PTFE) spacers. The Ag/AgCl (saturated KCl) was as the reference electrode. The work electrode area was controlled at 1 cm^2. The catalysts loading was 1 mg/cm^{-2}. All potential measurements were converted to the RHE. The CO_2 flow was controlled at 50 mL min^{-1} by using a mass flow controller. The electrolyte (0.5 M KOH) was circulated through the electrochemical cell by using peristaltic pumps (BT 100M) with a silicone tubing. The electrolyte flow was kept at 10 mL min^{-1}. The gas products were analyzed by online gas chromatography (GC) systems (PANNA, A91) every 10 minutes equipped with a thermal conductivity detector (TCD) for H_2 quantification and a flame ionization detector (FID) for CO and other hydrocarbon gas quantification and high purity argon gas (99.9999%) was used as the carrier gas for the GC.

Faraday Efficiency calculation

The production rate of gas products ($\dot{n}_x$, mol s^{-1} cm^{-2}) were calculated by formular:

$$\dot{n}_x = \frac{\dot{V} * C_x}{A * V_M}$$

Where V stands for the CO_2 flow rate (L s^{-1}); C_x stands for the volumefraction of the product x detected by GC; A stands for the geometric area of the electrode (cm^{-2}); V_M is molar Volume (22.4 L mol^{-1}).

The Faraday Efficiency (%) of gas products were calculated by formular:

$$Faraday\ Efficiency_x = \frac{\dot{n}_x * z_x * F}{j_{Total}} * 100\%$$

Where $\dot{n}_x$ (mol s^{-1} cm^{-2}) stands for the generation rate of the product x, z_x stands for the electrons transferred for reduction to product x, F is Faradaic Constant (96485 C mol^{-1}), j_{Total} (A cm^{-2}) stands for total current density during CO_2 bulk electrolysis.

Computational Method

We have employed the first-principles to perform density functional theory (DFT) calculations within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) formulation. We have chosen the projected augmented wave (PAW) potentials to describe the ionic cores and take valence electrons into account using a plane wave basis set with a kinetic energy cutoff of 450eV. Partial occupancies of the Kohn−Sham orbitals were allowed using the Gaussian smearing method and a width of 0.05 eV. The electronic energy was considered self-consistent when the energy change was smaller than 10^{-4} eV. A geometry optimization was considered convergent when the energy change was smaller than 0.05 eV Å^{-1}. The vacuum spacing in a direction perpendicular to the plane of the structure is 18 Å for the surfaces. The Brillouin zone integration is performed using 2×2×1 Monkhorst-Pack k-point sampling for a structure. Finally, the adsorption energies (E_{ads}) were calculated as Eads= Ead/sub-Ead-Esub, where Ead/sub, E_{ad}, and E_{sub} are the total energies of the optimized adsorbate/substrate system, the adsorbate in the structure, and the clean substrate, respectively. The free energy was calculated using the equation:

G=Eads+ZPE-TS

where G, Eads, ZPE and TS are the free energy, total energy from DFT calculations, zero point energy and entropic contributions, respectively.
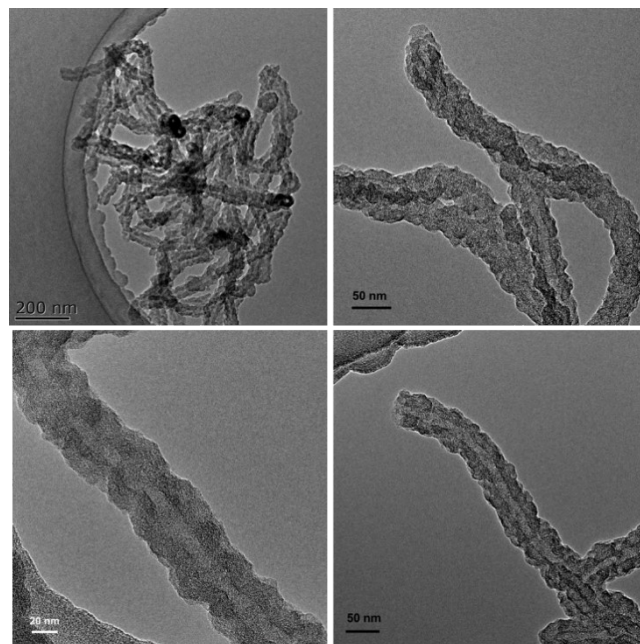
Supplementary Figures and Tables
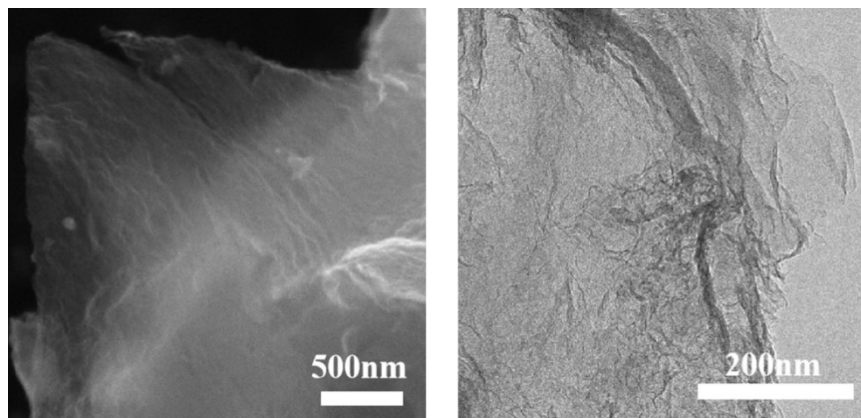

Figure S1. TEM images of Ni SA/H-NC.

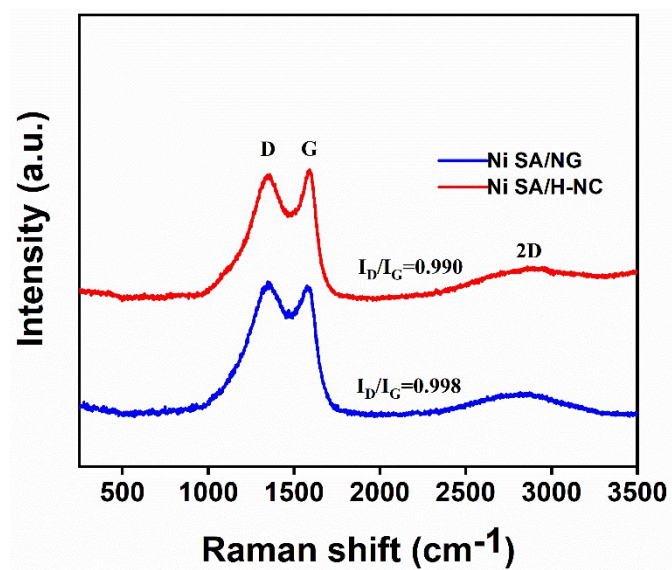**Figure S2.** SEM and TEM images of Ni SA/NG.

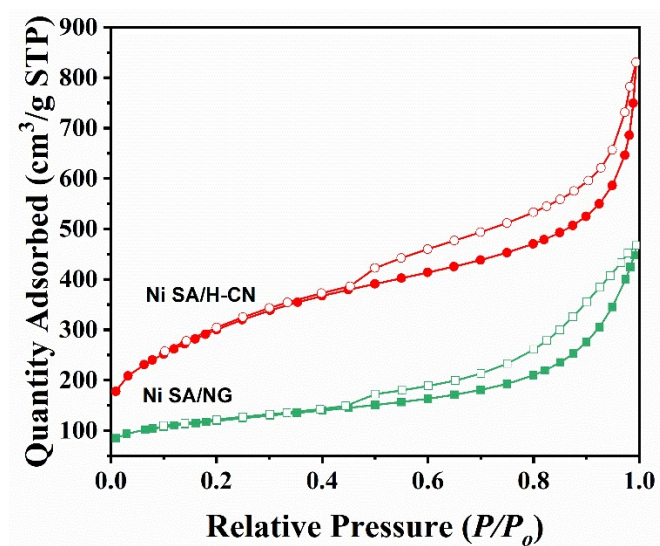**Figure S3.** Raman spectra of Ni SACs.

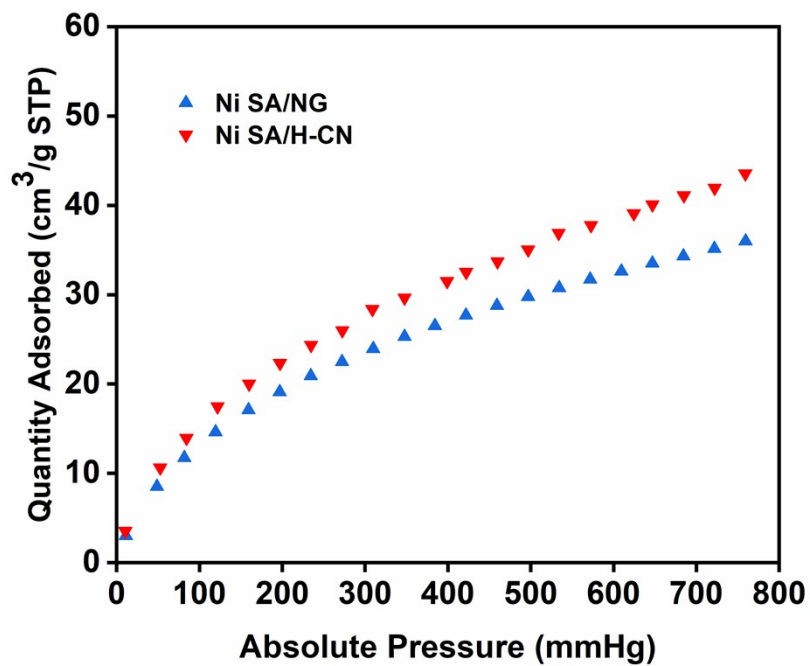**Figure S4.** N_2 adsorption/desorption isotherms of Ni SACs.

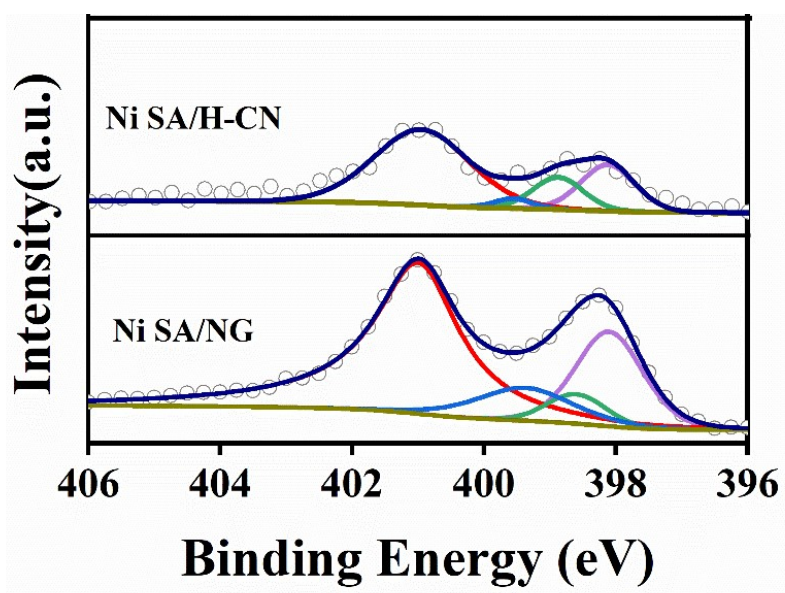**Figure S5.** CO_2 adsorption measuretment of Ni SACs.

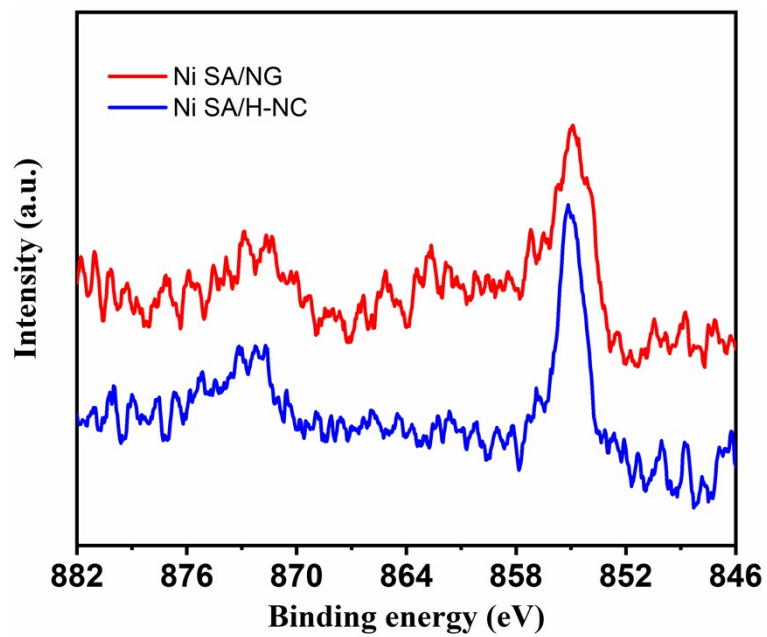**Figure S6.** N 1s XPS spectra of Ni SACs.

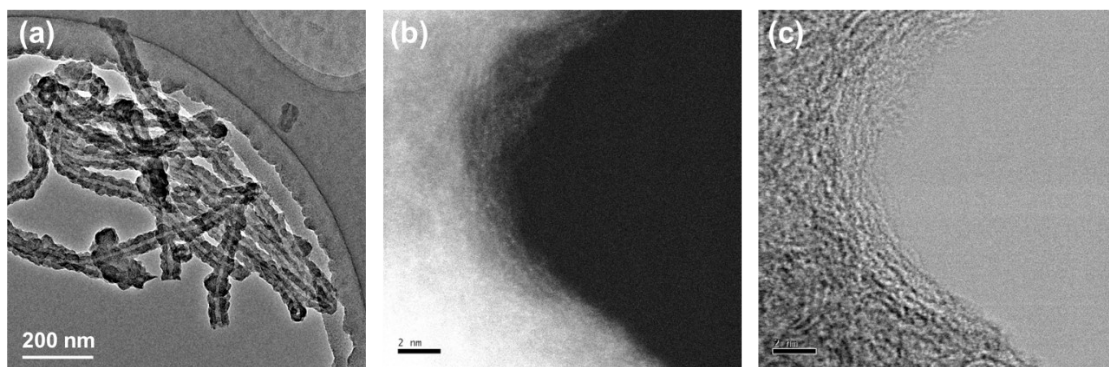**Figure S7.** Ni 2p XPS spectra of Ni SACs.

Figure S8. (a) TEM iamge and (c, d) aberration-corrected HAADF-STEM images of Ni SA/H-NC after long-term stability test.

Table S1. Metal content of Ni SACs measured by ICP.

Samples	Ni content（wt.%）
Ni SA/NG	1.03
Ni SA/H-NC	0.98

Table S2. EXAFS fitting parameters at the Ni K-edge for Ni SA/H-NC and Ni SA/NG.

Sample	Shell	N^a	R (Å) [b]	σ^2 (Å^2·10^{-3}) [c]	$\Delta E0$ (eV) [d]
Ni SA/H-NC	Ni-N	4.1±0.2	1.93±0.02	6.1±3.0	-1.7±0.2
Ni SA/NG	Ni-N	4.0±0.2	2.01±0.02	5.6±3.0	-1.8±0.2

[a] N: coordination numbers; [b] R: bond distance; [c] σ^2: Debye-Waller factors; [d] ΔE_0: the inner potential correction.