



Designer electron-reservoir single-atom electrocatalyst for efficient carbon dioxide reduction

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ABSTRACT

The electrochemical reduction of CO₂ is a promising approach for carbon fixation and conversion into value-added products. Single-atom catalysts featuring isolated metal site on carbon supports have garnered significant attention for their unique electronic properties and enhanced durability. However, achieving high power generation while maintaining substantial Faraday efficiency for desired product formation remains challenging with existing active sites. Herein, we present an advanced electron-reservoir single-atom electrocatalyst comprising ultrathin carbon-coated metal nanoparticles (NPs) integrated with a high-density Ni-N₄ active sites, which is achieved through a secondary loading method coupled with rapid thermal shock technology. Theoretical calculations and in situ characterizations reveal that the carbon-coated NPs function as polarized electron reservoirs, efficiently channeling stored electrons to surrounding single-atom active sites. This configuration minimizes the involvement of metal NPs in the side hydrogen evolution reaction while promoting electron and proton transfer to adsorbed CO₂ molecules thereby reducing the energy barrier for *COOH formation. As a result, the catalyst delivers outstanding CO₂ to CO conversion performance, achieving a high current density (*j*_{CO}) of 31.7 mA cm⁻² and good stability. This represents a fourfold improvement compared to catalysts with only Ni-N₄ single-atom sites, highlighting the potential of this approach for advancing CO₂ electroreduction technology.

1. Introduction

Electrochemical CO₂ reduction (ECR) has garnered significant attention as a method for sustainable CO₂ transformation, playing a key role in advancing a carbon-neutral economy [1,2]. To achieve practical applicability, an ideal electrocatalyst must possess a high density of exposed active sites, exclusively selectivity and long-term stability [3]. Following these design principles, substantial efforts have been directed toward transition metal-based electrocatalysts with a variety of geometric structure and electric states, from nanoparticles and nanoclusters to single-atom materials [4–7]. Single metal atoms anchored on nitrogen doped-carbon supports (M₁-NC) have emerged as a compelling alternative to conventional nanocatalysts, offering distinctive electronic properties, high atom utilization efficiency and, most importantly, the enhanced durability [8–14]. Normally, the catalytic efficiency of M₁-NC

materials is closely linked to the density of exposed active sites, with studies demonstrating that a greater number of active sites generally leads to improved catalytic performance [3,15]. However, most M₁-NC catalysts have limited active sites availability because, during the preparation process, if metal precursors are added beyond a certain threshold, the spare metal atoms tend to agglomerate. This agglomeration leads to the formation of larger metal particles that will reduce the overall surface density of active sites available for the catalytic process [7,16].

Therefore, enhancing the intrinsic activity of each active site in M₁-NC catalyst is important for advancing its overall performance. This approach not only involves overcoming thermodynamic barriers but also accelerates typically sluggish reaction kinetics, such as mass transport and electron transfer and is thus of paramount importance in achieving satisfy electrocatalytic performance [17,18]. While

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incorporating metal particles into M₁-NC materials has proven effective in facilitating electron transfer and improve the conductivity of the supports, their tendency to trigger undesirable side reactions and their limited long-term stability pose significant challenges [19,20]. These issues restrict the widespread adoption of this strategy, as the resulting catalytic systems may suffer from reduced durability and efficiency in practical applications, undermining the benefits of enhanced electron transfer architecture. Consequently, there is a pressing need to develop innovative solutions that balance enhanced electron transfer with the durability and selectivity required for sustainable and efficient catalytic applications.

To this end, we employed a secondary loading method coupled with rapid thermal shock technology to synthesize a hybrid electrocatalyst, Ni@NC₂₀/Ni, featuring few-layer graphite carbon fully coated Ni nanoparticles (NPs) synergistically catalyzed with surrounding high-density Ni-N₄ single atom sites [21–24]. The carbon coating on the Ni nanoparticles effectively prevents their participation in the hydrogen evolution reaction while serving as electron reservoirs to directional delivery of electrons to the active sites, as depicted in Scheme 1. Our theoretical calculation found that this configuration promotes the transfer of both electron and proton to the adsorbed CO₂ molecules, thereby reducing the energy barrier for *COOH formation. As a result, the hybrid electrocatalyst Ni@NC₂₀/Ni exhibits high activity, reaching a j_{CO} of 31.7 mA cm⁻², along with a high CO faradaic efficiency of 93 %, and stable operation at -0.7 V (vs. RHE) in H-type cells. This performance represents a fourfold improvement compared to samples containing only Ni-N₄ structures. These findings provide valuable insights into the role of carbon-coated Ni NPs in enhancing electrochemical CO₂ reduction at single atom sites, offering valuable guidance for advancing high-performance electrocatalysts.

2. Experimental section

2.1. Synthesis of Zn(C₂N₃H₂)₂ (MET-6)

The MET-6 was prepared at room temperature using a modified method according to the reported procedure [25]. In a typical synthesis, ZnCl₂ (5.0 g) was dissolved in a solvent mixture consisting of ethanol (50 mL), water (75 mL), ammonium hydroxide (25 %~28 %, 20 mL) and N, N-dimethylformamide (DMF, 50 mL). Then 1H-1,2,3-triazole (6.26 mL) was added dropwise to the mixture, which was stirred at room temperature for 24 h. Then the as-prepared white product was filtered

out, washed with ethanol and finally dried at 80 °C for 8 h to afford a white powder.

2.2. Synthesis of Ni@MET-6₂₀ and Ni@MET-6₁₀

118.41 mg and 236.82 mg of NiCl₂·6H₂O were dissolved in 200 mL methanol, respectively, and then MET-6 (2.0 g) was immersed in the obtained solution (MET-6 and NiCl₂·6H₂O were impregnated in methanol solution at molar ratio of 20:1 and 10:1, respectively). The mixture was stirred at the room temperature for 6 h. The obtained samples were cleaned with methanol and dried under vacuum at 100 °C for 8 h. Thus, Ni@MET-6₁₀ and Ni@MET-6₂₀ were prepared.

2.3. Synthesis of u-carbon, Ni@NC₂₀ and Ni@NC₁₀

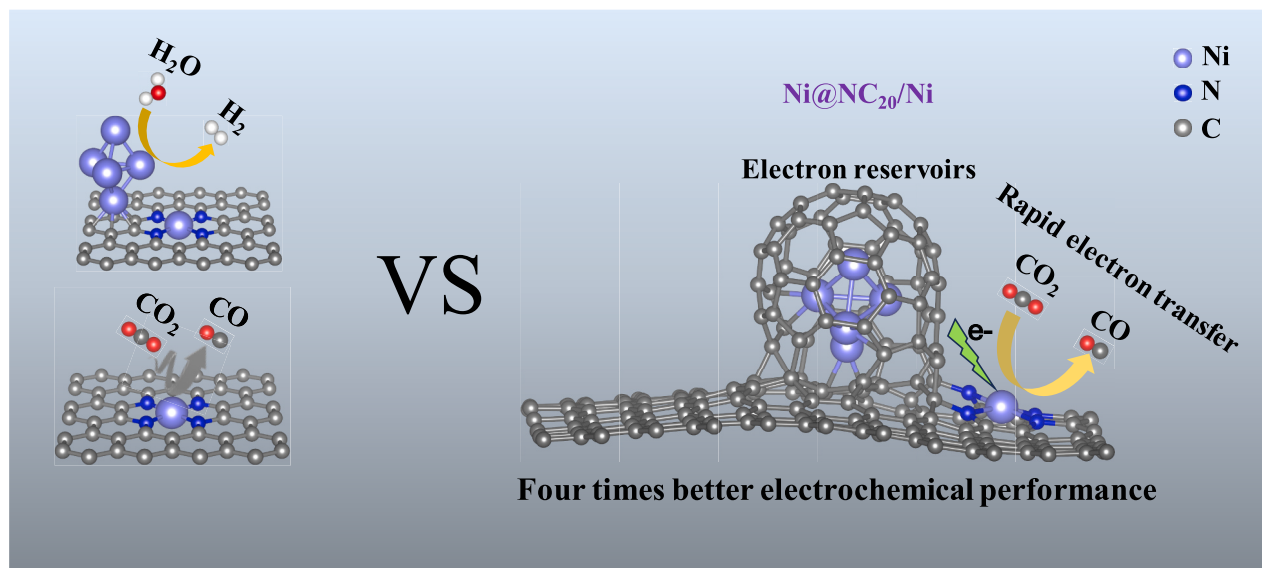
The as-prepared MET-6, Ni@MET-6₂₀ and Ni@MET-6₁₀ were separately transferred into a ceramic boat and placed in a temperature-programmed furnace, which was then heated to 1000 °C with a heating rate of 5 °C min⁻¹ and kept at 1000 °C for 2 h under a flowing argon atmosphere. Then the furnace naturally cooled to room temperature. The as obtained samples, which were derived from carbonization of MET-6, Ni@MET-6₂₀ and Ni@MET-6₁₀ were named as u-carbon, Ni@NC₂₀ and Ni@NC₁₀, respectively.

2.4. Synthesis of Ni@NC₂₀/Ni

Following that, 20 mg Ni@NC₂₀ and 10 mL ethanol were added into a 20 mL Pyrex vial and ultrasonically dispersed for 10 min. Subsequently, 0.3 mL ethanol solution of NiCl₂·6H₂O (20 mg/mL) was added into the dispersion solution of Ni@NC₂₀. After being heated at 85 °C for 5 h, the obtained black sample was collected by suction filtration, washed several times with ethanol and dried at 60 °C under vacuum. Then, the dried sample is rapidly heated to 700 °C and rapidly cooled using Joule heating equipment in an argon atmosphere for rapid thermal shock treatment (Fig. S1). Thus completing the second load of nickel, named Ni@NC₂₀/Ni.

2.5. Synthesis of Ni@NC/Ni(H₂)

Ni@MET-6₂₀ (20 mg) and NiCl₂·6H₂O (2.57 mg) were dispersed in 10 mL ethanol solution, ultrasonically dispersed for 30 min, and dried first by rotary evaporation and then in an oven at 80 °C. Finally, the



Scheme 1. Schematic illustration for the electrochemical CO₂ reduction of Ni@NC₂₀/Ni electro-reservoir single-atom electrocatalyst.

dried powder sample was placed in a horizontal furnace, heated to 400 °C (heating rate, 5 °C min⁻¹) for 5 h in a hydrogen/argon (5% /95%) flow.

3. Results and discussion

3.1. Materials synthesis and characterization

The synthetic procedure of Ni@NC₂₀/Ni catalyst is illustrated in Fig. 1a. Firstly, to prepare the carbon-supported single Ni catalyst, a Zn-based metal–organic framework, MET-6, with an optimal impregnation ratio of Zn to Ni at 20:1 (Figs. S2–S7) was impregnated in solution to obtain the Ni-containing precursor. This precursor was then pyrolyzed at 1000 °C under argon atmosphere, yielding Ni@NC₂₀, a carbon carrier with a high Ni single atoms loading under optimized conditions (Figs. S7–S8). Ni@NC₂₀ was subsequently used as the support for a secondary hydrothermal nickel loading process in nickel-containing solution. After washing and drying, the Ni@NC₂₀/Ni catalyst, which

features a synergistic combination of ultrathin carbon-coated Ni NPs and Ni single atoms, was obtained through rapid thermal shock treatment under argon atmosphere (Fig. S1). For comparison, the Ni@NC₂₀/Ni (H₂) catalyst, featuring Ni nanoparticles directly generated on the surface of a single atom Ni-loaded carbon support, was also prepared to emphasize the benefits of ultrathin carbon-coated Ni nanoparticles structure (Figs. S9–S10).

The X-ray diffraction (XRD) pattern of Ni@NC₂₀/Ni catalyst exhibits two broad peaks, characteristic of amorphous carbon, located at 20–30° and 40–50° (Fig. 1b). No obvious diffraction peaks corresponding to Ni crystals are observed, suggesting that Ni predominantly exists as single atoms or small nanoparticles. The effective prevention of large Ni nanocrystals formation is attributed to the rapid heating and cooling advantages provided by the thermal shock treatment. In contrast, using conventional furnace heat for Ni@NC₂₀/Ni synthesis results in the appearance of distinct metallic Ni peaks in the XRD analysis (Fig. S11). Scanning electron microscope (SEM) images revealed a highly porous morphology across all samples (Figs. S7a, S10a, S12a). High-angle

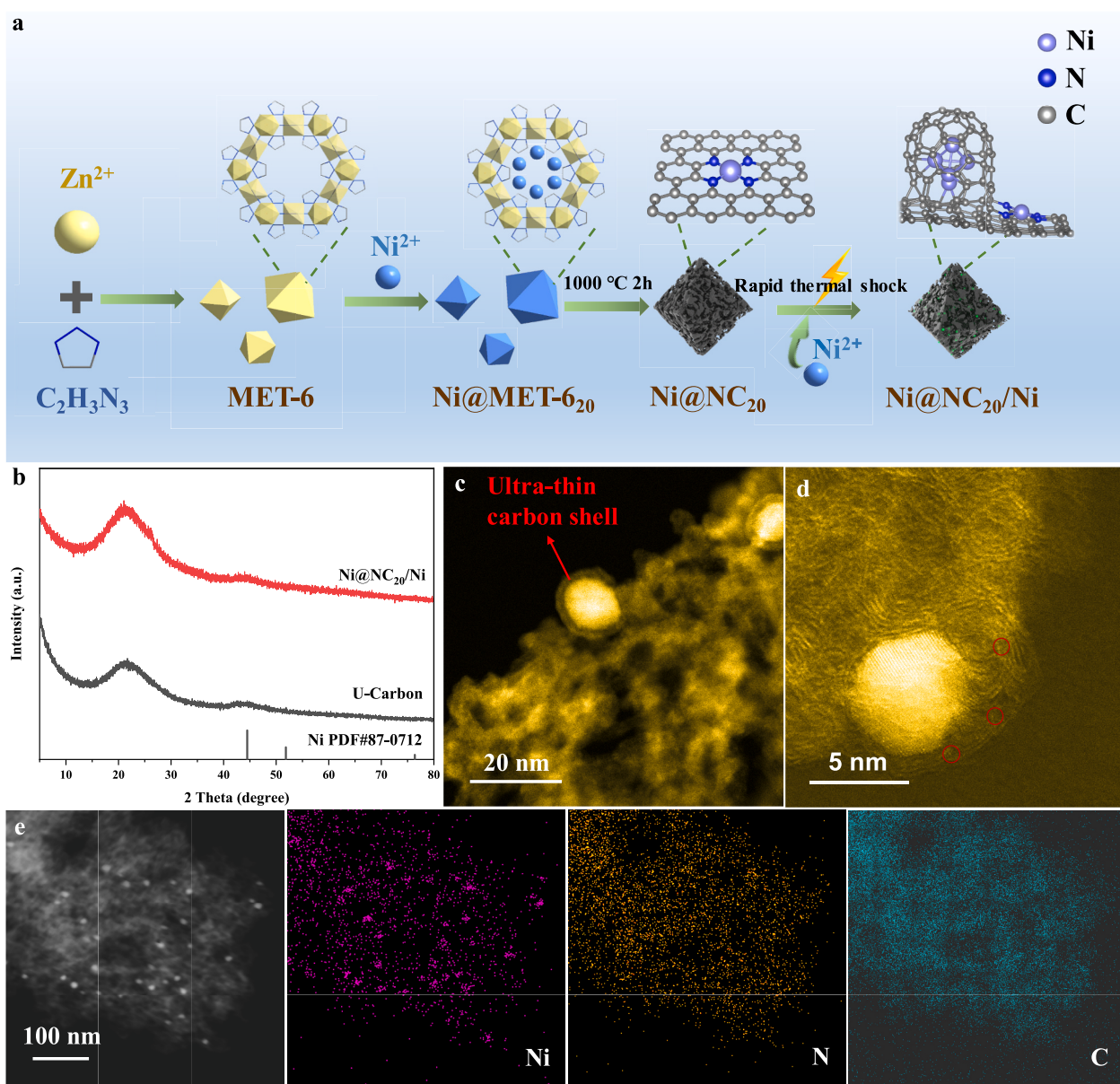


Fig. 1. Synthesis and characterization of the as-prepared catalysts. (a) Schematic illustration for the synthesis of Ni@NC₂₀ and Ni@NC₂₀/Ni catalysts. (b) XRD pattern of the Ni@NC₂₀/Ni catalyst. (c, d) HAADF-STEM images of the Ni@NC₂₀/Ni catalyst. (e) Dark-field transmission electron microscopy image and the corresponding EDS mapping of the Ni@NC₂₀/Ni catalyst.

annular dark-field scanning transmission electron microscopy (HAADF-STEM) showed uniformly dispersed Ni nanoparticles approximately 3–8 nm within Ni@NC₂₀/Ni catalyst (Fig. S12b). High-magnification aberration-corrected HAADF-TEM images (Fig. 1c, Fig. S12c) revealed that all Ni nanoparticles are encapsulated by an ultrathin carbon layer. Moreover, numerous bright spots, assigned to Ni single atoms, were observed surrounding the Ni nanoparticles on the carbon supports (Fig. 1d, Fig. S12d). Energy-dispersive X-ray spectroscopy (EDS) mapping (Fig. 1e) further validated the uniform distribution of Ni single atoms and Ni nanoparticles throughout the Ni@NC₂₀/Ni catalyst. Notably, due to the protective carbon layer, Ni NPs remain embedded within the carbon support even after undergoing acid treatment (Figs. S13–S14).

Raman spectroscopy was used to quantitatively assess the graphitization degree and surface defects (Fig. S15). The intensity ratio of D-peak to G-peak (I_D/I_G) in Ni@NC₂₀/Ni is 1.02, closely matching the pristine carbon carrier Ni@NC₂₀ (1.03). This similarity suggests that the introduction of carbon-coated Ni NPs via the rapid thermal shock process does not alter the defect levels or graphitization degree of the carbon carrier. The N₂ sorption curves (Fig. S16) of Ni@NC₂₀/Ni exhibit typical type-IV isotherms, with a specific surface area calculated to be 704 m²g⁻¹. In addition, the pore size distribution analysis indicates a substantial presence of both micropores and mesoporous structures.

Inductively coupled plasma emission spectroscopy measurement show Ni contents of 1.37 wt% in Ni@NC₂₀, 4.41 wt% in Ni@NC₂₀/Ni and 4.43 wt% in Ni@NC₂₀/Ni(H₂) (Fig. S17), indicating similar Ni levels in Ni@NC₂₀/Ni and Ni@NC₂₀/Ni(H₂) samples. The X-ray photoelectron spectroscopy (XPS) was used to analyze the surface element compositions and chemical valence states in each sample (Fig. S18). The high-resolution C 1s spectrum (Fig. S19) was divided into four peaks, corresponding to C – C (284.6 eV), C – N (285.6 eV), C – O (287.4 eV) and C = O (291.1 eV) bonds [26]. The high-resolution N1s spectrum could be deconvoluted into peaks [25,27] representing pyridinic-N ($\approx$ 398.3 eV), pyrrolic-N ($\approx$ 399.1 eV), graphitic-N ($\approx$ 400.8 eV), and oxidized-N ($\approx$ 402.5 eV) species (Fig. 2a, Fig. S20). The high-resolution Ni 2p XPS spectrum of Ni@NC₂₀/Ni revealed that two main peaks, corresponding to the coexistence of Ni⁰ and Ni²⁺ species (Fig. 2b), showing a similar peak profile to that observed in Ni@NC₂₀/Ni(H₂) sample (Fig. S21). The coordination environment of Ni species was analyzed using X-ray absorption spectroscopy (XAFS) spectroscopy. The Ni K-edge X-ray absorption near-edge structure (XANES) of Ni@NC₂₀/Ni indicated the average valence state of Ni species is situated between 0 and + 2 (Fig. 2c). The Fourier transform of the extended X-ray absorption fine structure (FT-EXAFS) spectrum displays two primary peaks at around 1.4 Å and 2.4 Å, which can be attributed to the scattering paths of Ni-N and Ni-Ni, respectively (Fig. 2d). This suggests the coexistence of single

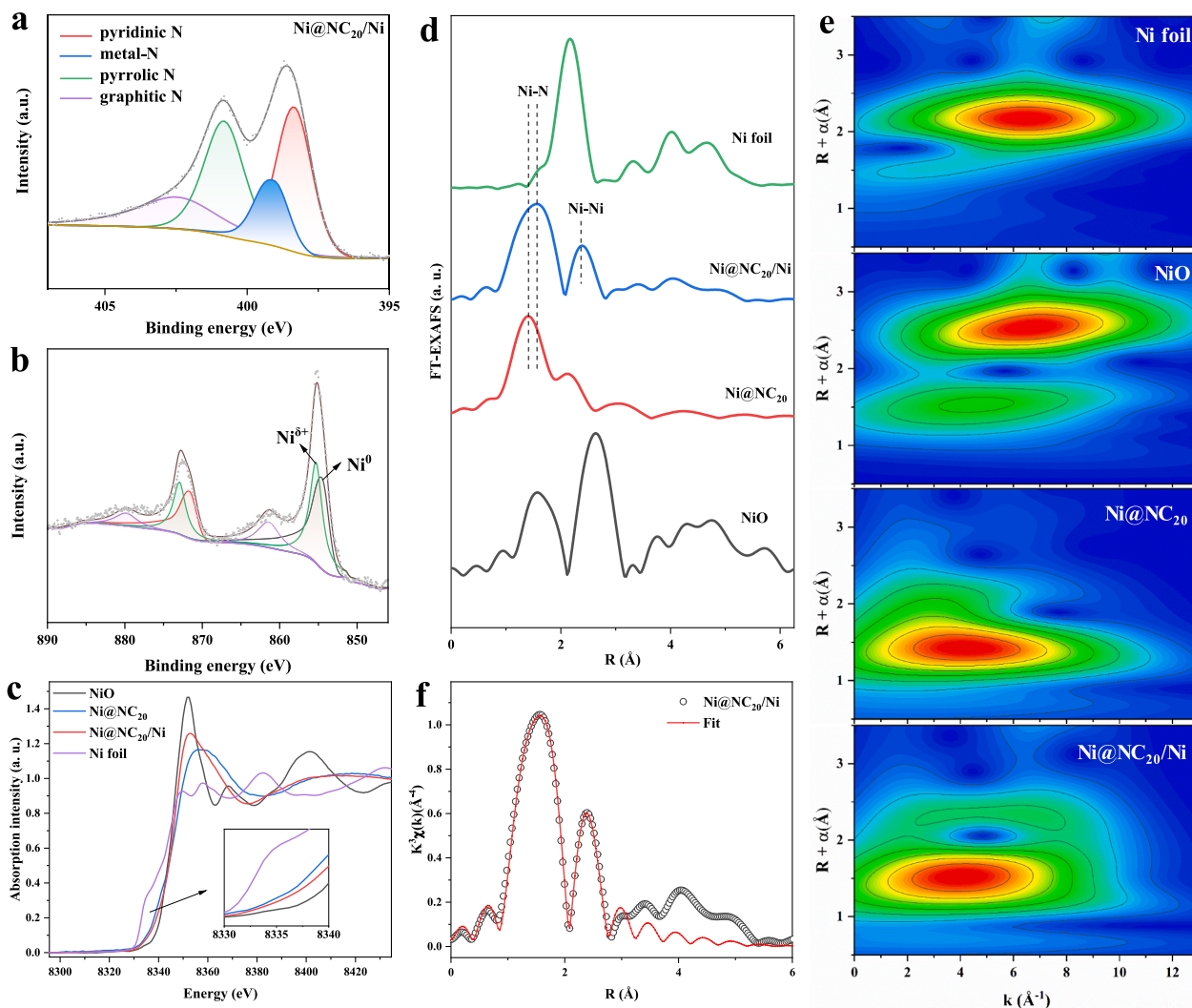


Fig. 2. X-ray photoelectron spectroscopy and X-ray absorption spectroscopy analyses. (a) N 1s and (b) Ni 2p spectra of Ni@NC₂₀/Ni catalyst. (c) XANES and (d) FT-EXAFS spectra at the Ni K-edge of Ni@NC₂₀ and Ni@NC₂₀/Ni catalysts with the reference samples. (e) WT-EXAFS contour plots of Ni foil, NiO, Ni@NC₂₀ and Ni@NC₂₀/Ni. (f) The fitting result of FT-EXAFS for Ni@NC₂₀/Ni catalyst.

Ni-N_x sites and Ni NPs in Ni@NC₂₀/Ni catalyst, which is in line with the HAADF-STEM observations. It is worth noting, the Ni-N bond length in Ni@NC₂₀/Ni is slightly longer than in Ni@NC₂₀ (Table S1), indicating a strong interaction between Ni NPs and Ni-N_x groups. In addition, contour plots from EXAFS wavelet transform (WT) analysis (Fig. 2e) revealed a single intensity maximum at approximately 4.1 Å⁻¹ in Ni@NC₂₀, corresponding to the Ni-N bond. Contour plots for Ni@NC₂₀/Ni showed an intensity maximum at around 4.1 Å⁻¹, attributed to the

Ni-N bond, along with a second intensity maximum at approximately 6.6 Å⁻¹, corresponding to the Ni-Ni bond. To further quantify the coordination structure around the Ni site, EXAFS curve fitting analysis was performed (Fig. 2f, Figs. S22-S24). The fitting results indicate coordination numbers of approximately 3.77 for the Ni-N bond and 6.13 for the Ni-Ni bond in Ni@NC₂₀/Ni catalyst. Meanwhile, the coordination number of the Ni-N coordination structure in Ni@NC₂₀ was about 3.87 (Table S1), supporting the presence of a well-defined single atom Ni-N₄

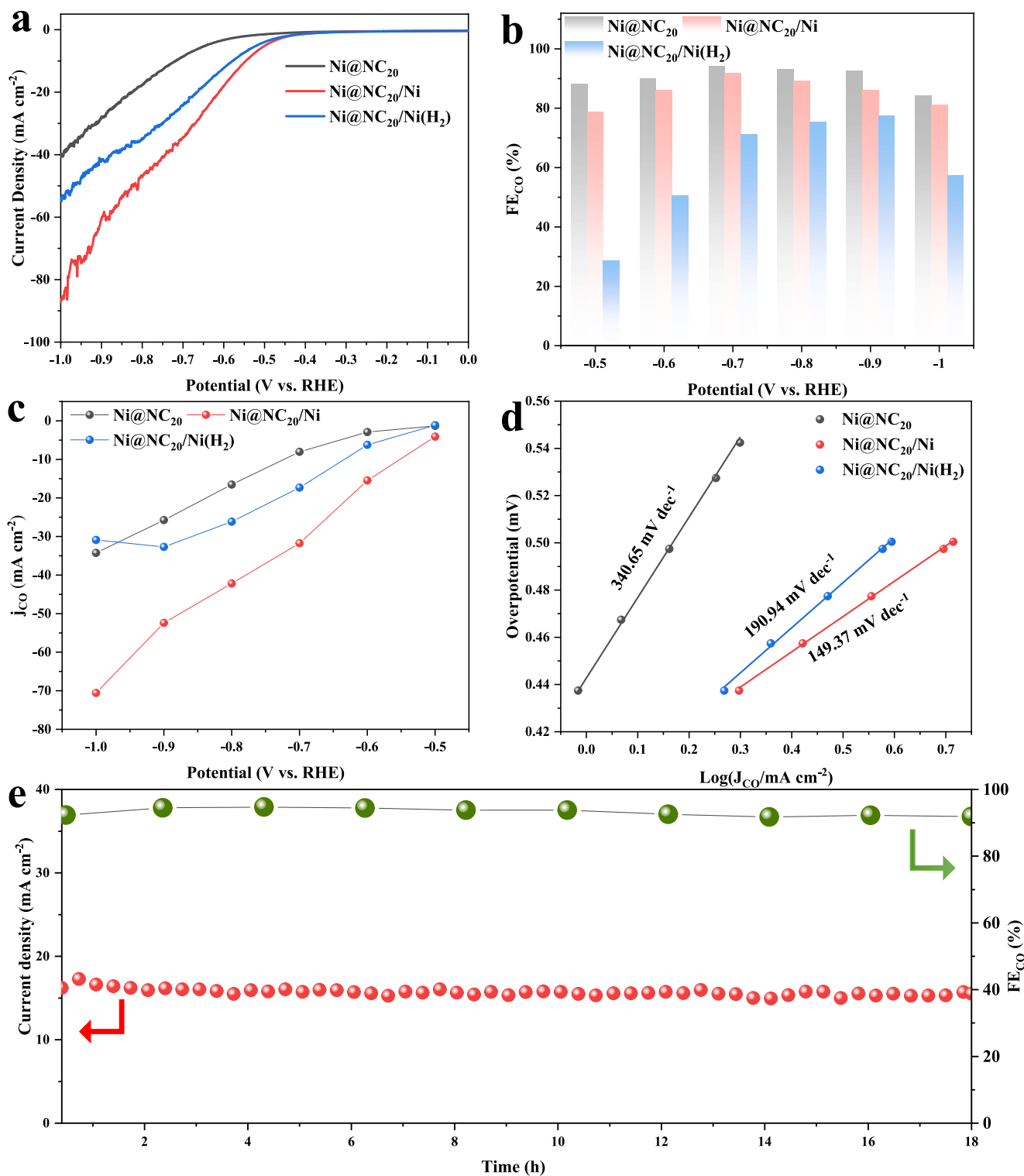


Fig. 3. CO₂ electroreduction performance. (a) LSV curves, (b) Faradaic efficiencies, (c) CO partial current densities and (d) Tafel plots of Ni@NC₂₀, Ni@NC₂₀/Ni and Ni@NC₂₀/Ni(H₂) catalysts in CO₂-saturated 0.5 M KHCO₃. (e) Durability test of Ni@NC₂₀/Ni catalyst at a constant potential of -0.7 V in CO₂-saturated 0.5 M KHCO₃.

site.

3.2. Electrochemical CO₂ reduction performance

The electrocatalytic CO₂ reduction performance of the Ni@NC₂₀, Ni@NC₂₀/Ni and Ni@NC₂₀/Ni(H₂) catalysts were firstly assessed by linear sweep voltammetry (LSV) in an H-type cell in CO₂ saturated 0.5 M KHCO₃ solution. Ni@NC₂₀/Ni exhibited a higher current density compared to Ni@NC₂₀ and Ni@NC₂₀/Ni(H₂) (Fig. 3a), highlighting its fast reaction dynamics for ECR. Potentiostatic electrolysis was conducted to analyze the reduction products using online gas chromatography and ¹H nuclear magnetic resonance (NMR) spectroscopy, revealing that CO and H₂ were the only gaseous products, with no liquid products detected (Fig. S25). Ni@NC₂₀/Ni exhibited the highest selectivity for CO generation, achieving a CO Faradaic efficiency (FE) of 93 % at a moderate potential of −0.7 V vs. RHE and maintaining over 86 % across the potential range from −0.6 V to −0.9 V (Fig. 3b). In contrast, Ni@NC₂₀/Ni(H₂) showed the lowest FE for CO, indicating that the exposure of Ni NPs on the carbon support diminishes CO selectivity. This observation aligns with the established catalytic role of Ni nanoparticles in promoting the side hydrogen evolution reaction (HER), resulting in increased H₂ production during electrolysis [19,20]. The ECR activity of the three catalysts was further evaluated by calculating the CO partial current density (*j*_{CO}). At −0.7 V vs. RHE, Ni@NC₂₀/Ni achieved a remarkable CO partial current density of 31.7 mA cm^{−2} (Fig. 3c), which is 1.8 times higher than that of Ni@NC₂₀/Ni(H₂) (17.3 mA cm^{−2}) and 4.0 times greater than that of Ni@NC₂₀ (8.0 mA cm^{−2}). Moreover, the Tafel slope of Ni@NC₂₀/Ni electrocatalyst was calculated to be 149.37 mV dec^{−1}, which is much lower than that of Ni@NC₂₀/Ni(H₂) (190.94 mV dec^{−1}) and Ni@NC₂₀ (340.65 mV dec^{−1}) (Fig. 3d), indicating that Ni@NC₂₀/Ni has a faster kinetics towards CO production. The long-term stability test, as evidenced by the consistent current density and FE_{CO} of Ni@NC₂₀/Ni over an 18 h period (Fig. 3e), highlighting its good for durability for ECR applications.

To explore the origin of the improved ECR activity on Ni@NC₂₀/Ni (Fig. 4a-c), the electrochemically active surface area (ECSA) was estimated using a double-layer capacitor (*C*_{dl}) method. As shown in Fig. 4d, the *C*_{dl} value values of the three catalysts do not directly correlate with their observed activities, with Ni@NC₂₀/Ni having a *C*_{dl} value of 7.86 mF cm^{−2}, positioned between Ni@NC₂₀ (11.1 mF cm^{−2}) and Ni@NC₂₀/Ni(H₂) (5.56 mF cm^{−2}). This suggests that the improved ECR activity of Ni@NC₂₀/Ni is primarily attributed to its intrinsic catalytic activity rather than an increase in surface area. The intrinsic activity of the catalyst was also reflected by the CO partial current density per unit active area. As shown in Fig. 4e, CO produced by Ni@NC₂₀/Ni has the highest intrinsic activity per site, highlighting that carbon-coated Ni nanoparticles can effectively improve the intrinsic activity of the single atom Ni-N₄ site. Electrochemical impedance spectroscopy (EIS) test reveals that Ni@NC₂₀/Ni has the lowest charge transfer resistance compared to Ni@NC₂₀ and Ni@NC₂₀/Ni(H₂) (Fig. 4f), indicating a significantly accelerated charge transfer process and enhanced electronic conductivity facilitated by the carbon-coated Ni NPs, which ultimately boosting its ECR activity. The performance of some advanced materials with highly dispersed MN_x units was also compared, and the Ni@NC₂₀/Ni shows a significantly high activity and selectivity among these representative catalysts (Table S2).

3.3. Mechanism analysis

In situ attenuated total reflectance surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) was employed to investigate the ECR process, allowing for an in-depth analysis of the reaction mechanisms at the molecular level. As shown in Fig. 5a and b, the peaks at 1218 cm^{−1} and 1486 cm^{−1} are assigned to HCO₃[−] and CO₃^{2−}, respectively [28], while the peaks at 1646 cm^{−1} and 2347 cm^{−1} corresponded to the δ (H – O – H) bending vibration of water molecules and the CO₂ dissolved in the solution [29–33]. Notably, peaks observed at 1377 cm^{−1} and 1574 cm^{−1} were assigned to the symmetric and asymmetric C – O

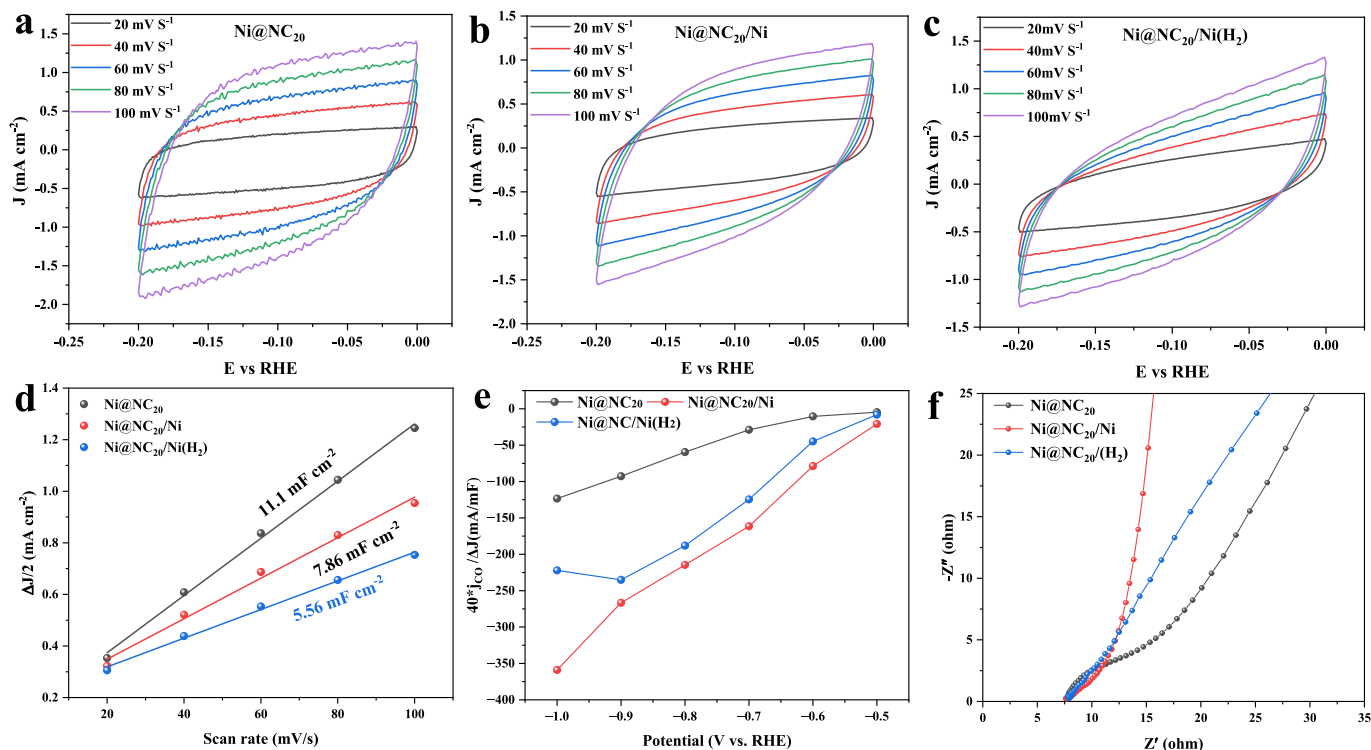


Fig. 4. CO₂ electroreduction performance. (a-c) Cyclic voltammetry profiles at different scan rates (20–100 mV), (d) Half of the capacitive current density difference as a function of scan rates, (e) Intrinsic activity of the sample (CO partial current density of the sample divided by the active area ($40*j_{\text{CO}}/C_{\text{dl}}$)) and (f) Nyquist plots (measured at open-circuit voltage) of Ni@NC₂₀, Ni@NC₂₀/Ni and Ni@NC₂₀/Ni(H₂) catalysts in CO₂-saturated 0.5 M KHCO₃.

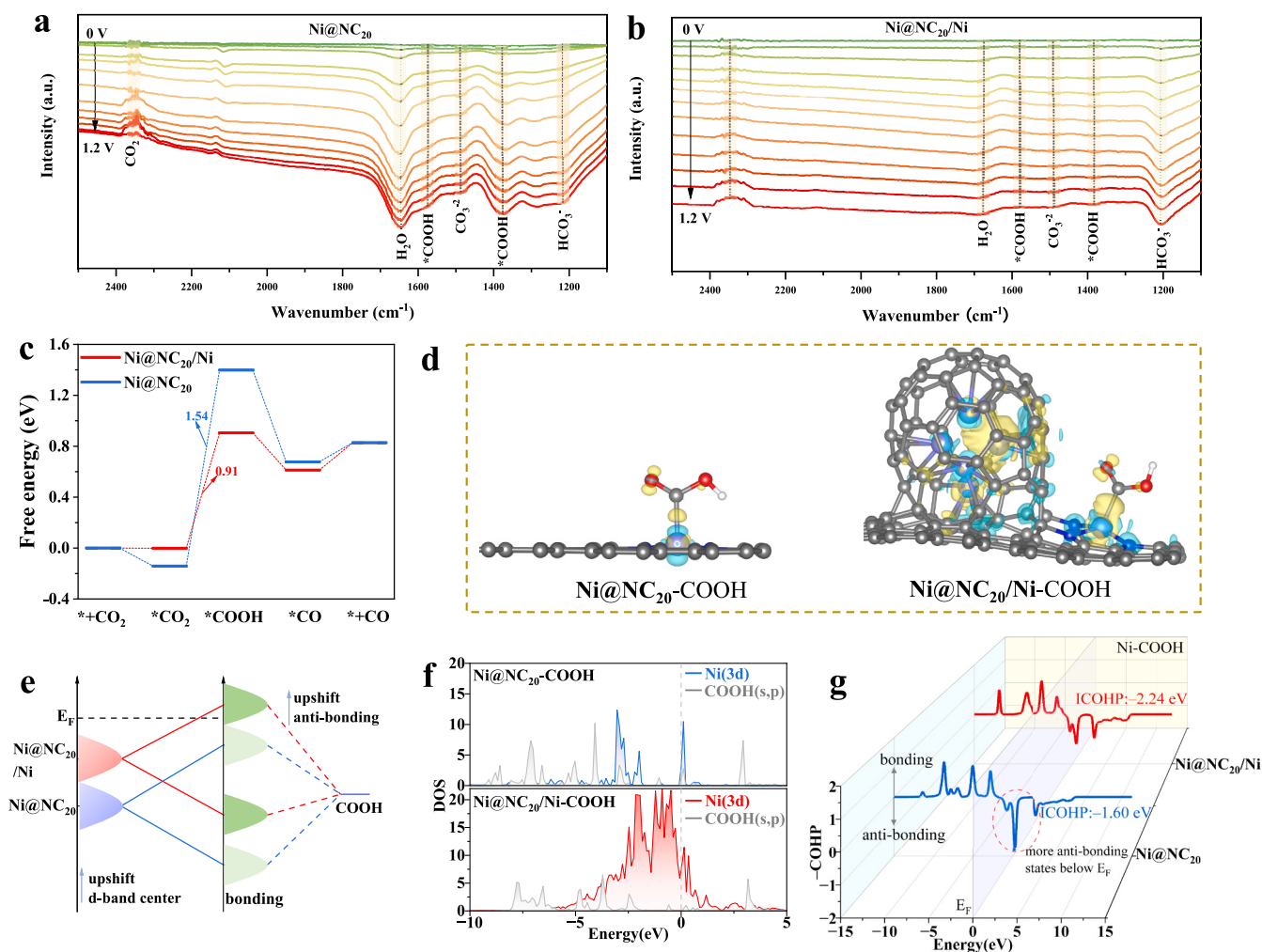


Fig. 5. In situ ATR-SEIRAS spectra of (a) Ni@NC₂₀ and (b) Ni@NC₂₀/Ni catalysts. (c) Free-energy diagrams of ECR over Ni@NC₂₀/Ni and Ni@NC₂₀. (d) Charge density difference distribution of the *COOH intermediate adsorbed on Ni@NC₂₀ and Ni@NC₂₀/Ni. (e) Schematic diagram illustrating the change in Ni-COOH interaction by shifting the d-band center of Ni. (f) Electronic density of states (DOS) of Ni@NC₂₀-COOH and Ni@NC₂₀/Ni-COOH. Ni@NC₂₀-COOH and Ni@NC₂₀/Ni-COOH indicates that the *COOH intermediate adsorption on the Ni site of Ni@NC₂₀ and Ni@NC₂₀/Ni systems. (g) Crystal orbital Hamilton population (COHP) of Ni-C bond in Ni@NC₂₀-COOH (blue) and Ni@NC₂₀/Ni-COOH (red). The positive and negative values of -COHP represent bonding and antibonding contributions, respectively. ICOHP represents the integration of COHP with respect to energy below the Fermi level. The more negative the value of ICOHP, the stronger the interaction between the COOH intermediate and Ni site.

stretching of *COOH intermediates [29,33,34], which are widely considered as pivotal intermediates in the electroreduction of CO₂ to CO [28,33]. The intensity of the *COOH peak increased with higher voltage for the Ni@NC₂₀ catalyst, highlighting that *COOH generation is a rate-limiting step in the ECR process. The significantly lower peak intensity of the *COOH intermediate in Ni@NC₂₀/Ni suggests its faster ECR capability, enabling adsorbed intermediates to convert to CO more swiftly and leave the catalyst surface, resulting in a weaker intermediate peak compared to Ni@NC₂₀. To better understand the role played by carbon-coated Ni NPs in the enhancement of ECR performance, the atomic-level reaction mechanisms were explored based on density functional theory (DFT) calculations. Previous studies indicated that CO₂ reduction to CO follows two proton-coupled electron transfer steps [35,36], forming COOH* and CO* intermediates (Fig. S26). The free energy diagrams (Fig. 5c) show that the formation of *COOH is the rate-determining step for Ni@NC₂₀, with a high free energy barrier of 1.54 eV [1,37]. By incorporating carbon-coated Ni NPs, this barrier is reduced to 0.91 eV in Ni@NC₂₀/Ni, exhibiting improved catalytic activity for CO production. Moreover, the d-band center of Ni@NC₂₀/Ni was found to be closer to the Fermi level than that of Ni@NC₂₀. This explains why the free energy level of *CO intermediate on Ni@NC₂₀/Ni is slightly deeper

than that on Ni@NC₂₀ (Fig. S27).

From a mechanistic perspective, catalysis is closely related to charge transfer, which can be examined from charge density difference plots (Fig. 5d and Fig. S28), showing the electron accumulation (in yellow) and depletion (in blue) regions of Ni@NC₂₀ and Ni@NC₂₀/Ni. One can see that during the generation of *COOH on Ni@NC₂₀/Ni, electrons accumulate around the catalytically active Ni site due to the transfer of electrons from the carbon-coated Ni NPs to the single Ni site. To further explore the impact of introducing carbon-coated Ni NPs into the Ni-N₄ structure on CO₂ electrocatalytic performance, calculations were carried out for the d-band center, electronic density of states (DOS), and crystal orbital Hamilton population (COHP) of the Ni single atom site in Ni@NC₂₀ and Ni@NC₂₀/Ni. As shown in Fig. 5e-g, which upon loading the carbon-coated Ni NPs, the d-band center of the Ni single atom shifts toward the Fermi level, raising the energy level of the Ni-C antibonding orbitals. This results in a decrease in the electron occupancy of the Ni-C antibonding orbital and enhancing the binding affinity of *COOH intermediate at the Ni single atom site. In the Ni@NC₂₀/Ni-COOH system (Fig. 5f), the hybridization between the Ni-3d and the s p orbitals of *COOH is more pronounced near the Fermi level and more Ni-3d states are occupied than those in Ni@NC₂₀-COOH. This indicates that the

single Ni site become more favorable for the adsorption of the $^*\text{COOH}$ intermediate after introducing the carbon-coated Ni NPs. Moreover, the Ni-C bond in $\text{Ni@NC}_{20}/\text{Ni-COOH}$ has less antibonding populations (ICOHP: -2.24 eV) at occupied states compared to $\text{Ni@NC}_{20}\text{-COOH}$ system (-1.60 eV) (Fig. 5g), consistent with the analysis of the d-band center characteristic.

Based on our DFT analysis, the carbon-coated Ni NPs act as electron reservoirs on the carbon substrate [38], continuously supplying electrons to nearby Ni atomic sites and promoting electron transfer. This enhances electron-donating capacity facilitates the hydrogenation of $^*\text{CO}_2$ to $^*\text{COOH}$ formation [39], thus promoting the CO_2 reduction process. In addition, the presence of carbon-coated Ni NPs strengthens the Ni-COOH interaction, lowering the thermodynamic barrier for $^*\text{COOH}$ formation. Consequently, the free energy (ΔG_{COOH^*}) required to form COOH^* intermediate on $\text{Ni@NC}_{20}/\text{Ni}$ is reduced to 0.91 eV from 1.54 eV needed for Ni@NC_{20} . In other words, the carbon-coated Ni NPs facilitate electron transfer at the surrounding active site, thus, enabling $\text{Ni@NC}_{20}/\text{Ni}$ to reduce CO_2 more effectively. To further verify the inhibition of HER by carbon-coated Ni NPs, we calculated the Gibbs free energy diagrams of HER on Ni exposed NPs (Ni_5 model, Fig. S29a) and carbon-coated Ni NPs ($\text{C}_{60}\text{-Ni}_5$ model, Fig. S29b). As shown in Fig. S30, the formation energy of H_2 on Ni_5 is significantly lower than that on $\text{C}_{60}\text{-Ni}_5$, indicating that the Ni_5 is conducive to the H_2 precipitation, whereas $\text{C}_{60}\text{-Ni}_5$ is not. This is mainly because the carbon coating immobilizes the Ni NPs, preventing them from participating in HER, and the carbon exposed at the surface lacks strong HER activity. These DFT results support the observed higher ECR efficiency of $\text{Ni@NC}_{20}/\text{Ni}$ (with a carbon layer) compared to $\text{Ni@NC}_{20}/\text{Ni}(\text{H}_2)$ (without a carbon layer) as shown in Fig. 3a-c, elucidating the mechanism of carbon-coated Ni NPs in enhancing the catalytic effectiveness of ECR.

4. Conclusion

In summary, we successfully developed an energy-efficient CO_2 electroreduction catalyst, $\text{Ni@NC}_{20}/\text{Ni}$, using a secondary loading method enhanced by rapid thermal shock technology. This hybrid catalyst combines ultrathin carbon-coated Ni NPs with abundant Ni- N_4 sites, leveraging the synergistic catalytic effects of these components to facilitate CO_2 reduction to CO. $\text{Ni@NC}_{20}/\text{Ni}$ delivers a high FE for CO (93 %) at -0.7 V vs. RHE in H-type cells, alongside substantial activity (31.7 mA cm^{-2} CO partial current density) and good stability. This performance represents a fourfold increase over catalysts with only Ni- N_4 sites. Mechanistic investigations, including controlled experiments, in situ characterizations, and theoretical calculations, reveal that the ultrathin carbon-coated Ni NPs not only inhibit HER by preventing Ni NPs participation but also serve as polarized electron reservoirs. This accelerates electron and proton transfer to adsorbed CO_2 molecules while lowering the energy barrier for $^*\text{COOH}$ formation. These results underscore the potential of ultrathin carbon-coated metal NPs in enhancing CO_2 electroreduction and provide insights for the design of high-performance single atom electrocatalysts.

CRedit authorship contribution statement

Wanli Yi: Writing – review & editing, Writing – original draft, Project administration, Methodology, Formal analysis, Data curation, Conceptualization. **Changsheng Hou:** Software. **Renyi Li:** Software. **Yinji Wan:** Data curation. **Xuan Zhang:** Resources, Investigation. **Bing Ma:** Resources. **Wenchao Hu:** Data curation. **Shenghui Han:** Conceptualization. **Mulin Qin:** Investigation. **Limeng Sun:** Investigation. **Qian Wang:** Software. **Yonggang Wang:** Project administration, Investigation, Conceptualization. **Xiao Hai:** Project administration, Investigation, Conceptualization. **Ruqiang Zou:** Resources, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2025.160387>.

Data availability

Data will be made available on request.

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