

Fluorine tuning of nickel phthalocyanine electrocatalysts for stable and rapid CO₂ reduction to CO

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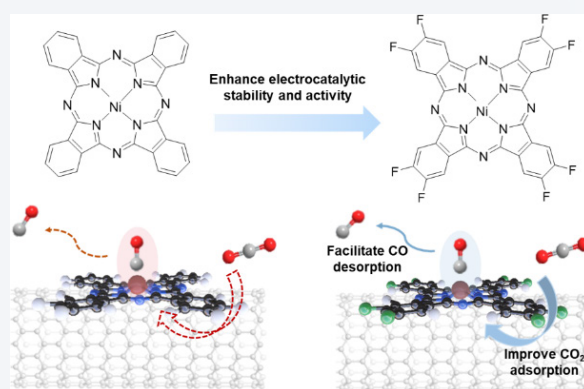
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ABSTRACT: Due to their high selectivity, nickel phthalocyanine (NiPc) based molecular electrocatalysts supported on carbon nanotubes have been regarded as promising candidates for electrochemical CO₂-to-CO conversion. However, it lacks effective strategies to simultaneously enhance the intrinsic activity and stability of NiPc electrocatalysts. Here, we show that fluorine tuning of NiPc can address this limitation. As a bridging study, incorporating polytetrafluoroethylene (PTFE) is shown to facilitate CO desorption near active sites, thereby enhancing electrochemical stability but reducing activity due to partial site masking. Building on this insight, β -site fluorination of NiPc affords a robust electrocatalyst (NiPc-F) with enhanced intrinsic CO₂-to-CO activity and durability. Microenvironment and *operando* studies reveal that fluorination improves CO₂ adsorption and enhances CO desorption, resulting in intact Ni-N₄ coordination during electrocatalysis. The optimized NiPc-F catalyst delivers stable operation at $-300 \text{ mA} \cdot \text{cm}^{-2}$ for 45 h in neutral electrolytes, with CO Faradaic efficiencies over 98%.



KEYWORDS: CO₂ reduction reaction, carbon monoxide, nickel phthalocyanine, fluorine, molecular engineering

1 Introduction

The electrochemical CO₂ reduction reaction (CO₂RR) provides a promising way to convert captured CO₂ into valuable chemicals and fuels using renewable electricity [1–4]. CO₂RR can generate a variety of products, including CO, formate, alcohols, and hydrocarbons [5–10]. Among them, CO is an easily accessible two-electron product and a key intermediate toward more deeply reduced carbon products, making CO₂-to-CO conversion appealing from practical perspectives [11–14]. Nevertheless, achieving industrially relevant current densities in CO production is still hindered by low energy efficiency and limited selectivity. These limitations stem from the competitive hydrogen evolution reaction (HER) at cathodic potentials, the slow kinetics of the coupled

proton–electron transfer, and mass-transport constraints, which collectively impair catalytic performance during high-rate operation [15–18]. Therefore, developing efficient CO₂-to-CO electrocatalysts and customizing the interfacial microenvironment are crucial for overcoming these barriers.

Metal macrocyclic catalysts, with well-defined and easily adjustable ligand frameworks, offer an appealing platform for both improving performance and investigating mechanisms [19–22]. In particular, nickel phthalocyanine (NiPc) catalysts with a stable Ni-N₄ structure have been extensively studied for selective CO production [23–27]. For example, the molecularly dispersed electrocatalysts (MDEs) with NiPc-based molecules on carbon nanotubes (CNTs) demonstrated nearly 100% selectivity for converting CO₂ to CO [23]. Han and co-workers linked hydrogen bonding to the reversible structural deformation of NiPc and utilized this interaction to improve CO₂ electrolysis in aqueous media [24]. Shan and co-workers developed an azobenzene-derived coordination polymer assembly based on NiPc that enables the capture and conversion of dilute CO₂ at high current densities [25].

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Despite these advances, it remains challenging to achieve improvements in both performance and durability simultaneously.

Hydrophobic microenvironment engineering has recently been adopted as an effective method for enhancing electrocatalytic performance [28–32]. It can modulate the solvation structure and local proton activity near catalytic sites, which alters interfacial adsorption and reaction pathways. By suppressing water-driven parasitic processes and stabilizing the coordination environment of active sites, it can improve CO₂RR activity while enhancing selectivity and long-term durability.

Here, we present a fluorine (F) microenvironment tuning strategy to improve the electrocatalytic performance of NiPc-based catalysts for CO₂RR. Introducing polytetrafluoroethylene (PTFE) into NiPc MDE is found to improve electrocatalytic stability, and such improvement is attributed to enhanced CO desorption. Building on this finding, an optimized MDE is developed by β -site fluorination of NiPc. This MDE shows higher activity and better stability than NiPc MDE for CO production in neutral electrolytes. Microenvironment and *operando* studies provide mechanistic insights into fluorine substitution. High-current-density performance is further studied in gas-diffusion electrodes (GDEs).

2 Results and discussion

NiPc MDE was constructed by anchoring NiPc molecules on CNTs [23]. The Ni content in all NiPc-based electrocatalysts was tuned to be around 0.65 wt.% (Table S1 in the Electronic Supplementary Material (ESM)). To study the effects of hydrophobic microenvironment engineering, a hydrophobic PTFE component (8 wt.%) was introduced when depositing NiPc MDE on the carbon paper substrate, affording NiPc MDE+PTFE (Fig. 1(a)). The scanning electron microscopy (SEM) measurement reveals that both NiPc MDE and NiPc MDE+PTFE show an interconnected, porous CNT framework (Fig. 1(b)), and no discernible molecular

aggregates are observed. These results show that adding a small amount of PTFE does not significantly alter the catalyst layer morphology. The contact-angle measurements show that water repellency increases after PTFE addition, with the contact angle rising from 141.7° for NiPc MDE to 146.3° for NiPc MDE+PTFE (Fig. S1 in the ESM). Interfacial adsorption properties relevant to CO₂RR were then examined by the temperature-programmed desorption (TPD) analysis. CO₂-TPD profiles show nearly identical CO₂ desorption temperatures for NiPc MDE and NiPc MDE+PTFE (~ 109.2 °C, Fig. S2 in the ESM). In contrast, no CO₂ desorption feature is observed for the CNTs+PTFE control, indicating that CO₂ adsorption mainly stems from NiPc rather than CNTs or PTFE components. CO-TPD reveals that CO desorbs at a lower temperature for NiPc MDE+PTFE (88.5 °C) when compared to NiPc MDE (98.6 °C) (Fig. 1(c)), implying that PTFE introduction facilitates a weaker CO binding environment. CNTs+PTFE exhibits no discernible CO desorption peak, suggesting NiPc as the primary CO-binding motif.

Electrocatalytic performance was first evaluated in an H-cell setup with CO₂-saturated 0.5 M KHCO₃. Linear sweep voltammetry (LSV) indicates that more negative potentials are required for NiPc MDE+PTFE to reach −0.1 and −10 mA·cm^{−2} (−0.48 and −0.68 V, respectively) when compared with those of NiPc MDE (−0.45 and −0.64 V) (Fig. 1(d)), all reported potentials are converted to versus the reversible hydrogen electrode (RHE) with *iR* corrections). However, NiPc MDE+PTFE achieves slightly higher CO Faradaic efficiencies (FE_{CO}) with lower H₂ formation across the explored potential range (Fig. 1(e) and Fig. S3 in the ESM). As shown in Fig. 1(f), chronoamperometry reveals a continuous decay in current density for NiPc MDE over a 2400 s period at −0.69 and −0.73 V. In contrast, NiPc MDE+PTFE maintains a stable response under identical conditions. Previous studies indicated that the Ni–N₄ bond in NiPc can undergo structural distortion under cathodic bias for CO₂RR, rendering the active sites susceptible to deactivation and

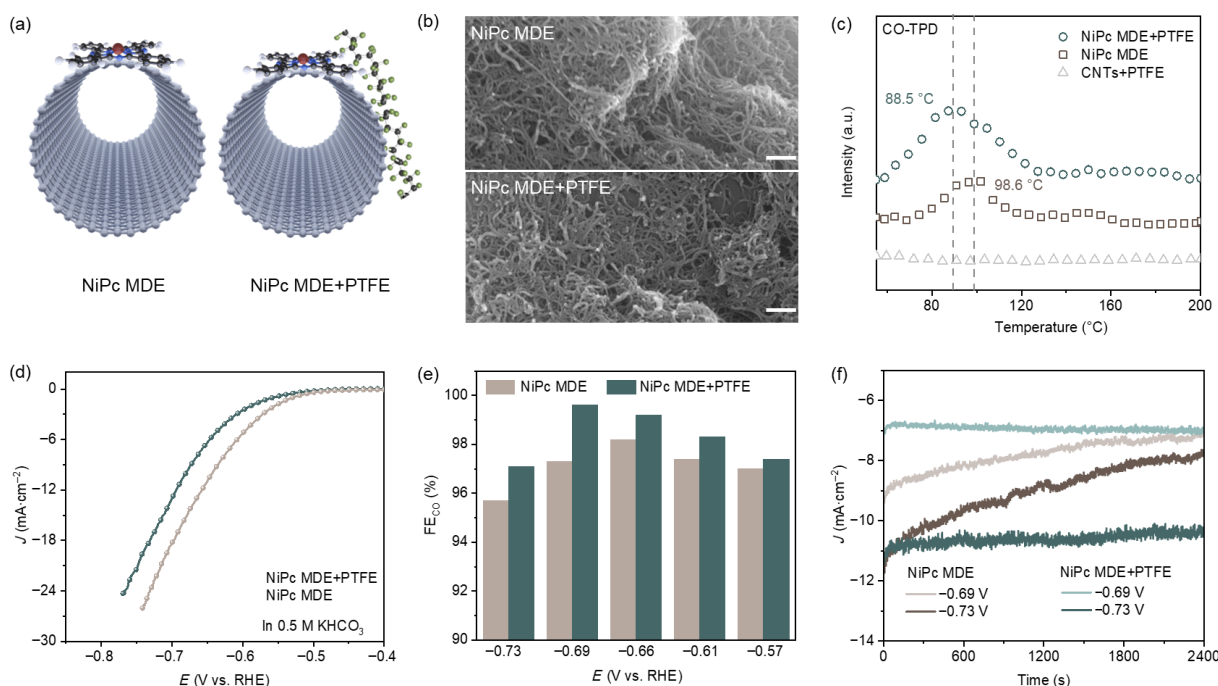


Figure 1 (a) Schematic illustration of NiPc MDE and NiPc MDE+PTFE. (b) SEM images of NiPc MDE and NiPc MDE+PTFE (scale bar, 200 nm). (c) CO-TPD profiles of NiPc MDE, NiPc MDE+PTFE, and CNTs+PTFE. (d) LSV curves, (e) FE_{CO}, and (f) chronoamperometry of NiPc MDE and NiPc MDE+PTFE in H-cell with CO₂-saturated 0.5 M KHCO₃.

leading to significant instability at high reductive current densities [23]. Efficient desorption of the CO product can rapidly regenerate active sites and improve the operational stability of the molecular catalyst. In this context, PTFE-enabled hydrophobic microenvironment engineering can regulate interfacial CO adsorption, affording improved operational stability in aqueous CO₂-to-CO electrolysis. However, this microenvironment optimization results in an activity penalty for NiPc MDE+PTFE, possibly due to partial burial of accessible active sites by PTFE (Fig. S4 in the ESM).

Inspired by the PTFE-enabled hydrophobic engineering, fluorine substituents were introduced at the eight β positions of NiPc, affording NiPc-F molecule (Fig. 2(a), see the ESM for details of synthesis). Ultraviolet–visible spectroscopy shows that NiPc-F exhibits a blue-shifted absorption relative to both NiPc and the previously reported methoxy (OMe) substituted analog NiPc-OMe (Fig. S5 in the ESM) [23]. Similarly, NiPc-F MDE was constructed by anchoring NiPc-F molecules on CNTs. The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image reveals abundant isolated bright features uniformly distributed across the CNT framework (Fig. 2(b)). Since Ni is the only high-Z (where Z denotes the atomic number) element in NiPc-F MDE, these differences clearly show the molecular dispersion of NiPc-F on the CNT surface. Figure 2(b) inset schematically shows the corresponding anchoring configuration. Consistently, the energy-dispersive X-ray spectroscopy (EDS) mapping (Fig. S6 in the ESM) resolves the one-dimensional curved CNT backbone and shows C as the dominant constituent. At the same time, weak yet discernible F and Ni signals are co-localized within the CNT contours, further corroborating the successful immobilization of NiPc-F on CNTs.

The local electronic and coordination environment of Ni is further examined through Ni K-edge X-ray absorption

spectroscopy. The X-ray absorption near-edge structure (XANES) profiles (Fig. 2(c)) show a distinct near-edge signature for molecular electrocatalysts when compared to the Ni foil, consistent with a coordination-defined Ni–N₄ environment rather than Ni–Ni metallic bonding. Notably, NiPc-F MDE shows a slight positive shift in the absorption edge feature compared to NiPc MDE (highlighted in the magnified inset), which is caused by the strong electron-withdrawing effect of β -site F substituents that reduces electron density at the Ni center, making it more Ni^{δ+}. The extended X-ray absorption fine structure (EXAFS) analysis (Fig. S7 in the ESM) shows prominent short-range Ni–N scattering for the molecular electrocatalysts, with no Ni–Ni signals typical of metallic Ni, confirming that fluorination does not cause Ni aggregation and that the active sites stay molecularly dispersed.

As shown in Fig. 2(d), linear sweep voltammetry recorded in CO₂-saturated 0.5 M KHCO₃ indicates that NiPc-F MDE exhibits a substantially enhanced CO₂RR activity when compared to NiPc MDE and NiPc-OMe MDE. NiPc-F MDE requires only –0.43 and –0.60 V to reach –0.1 and –10 mA·cm^{–2}, respectively, outperforming NiPc-OMe MDE, which requires –0.45 and –0.63 V to achieve the same current densities. This finding confirms that electron-withdrawing substituents on NiPc can facilitate formation of the reduced active sites at lower overpotentials and thus afford higher catalytic activity than unsubstituted or electron-donating-group-substituted NiPc [23]. Product analysis reveals near 100% selectivity to CO across the investigated potential window with negligible H₂ formation for NiPc-F MDE (Fig. 2(e)). Consistently, the CO partial current density (J_{CO}) increases with rising overpotential, reaching –23.4 mA·cm^{–2} at –0.68 V, and stays higher than NiPc MDE and NiPc-OMe MDE across the measured potential range (Fig. S8 in the ESM). The operational durability was further evaluated by chronoamperometry (Fig. 2(f)), in which NiPc-F MDE

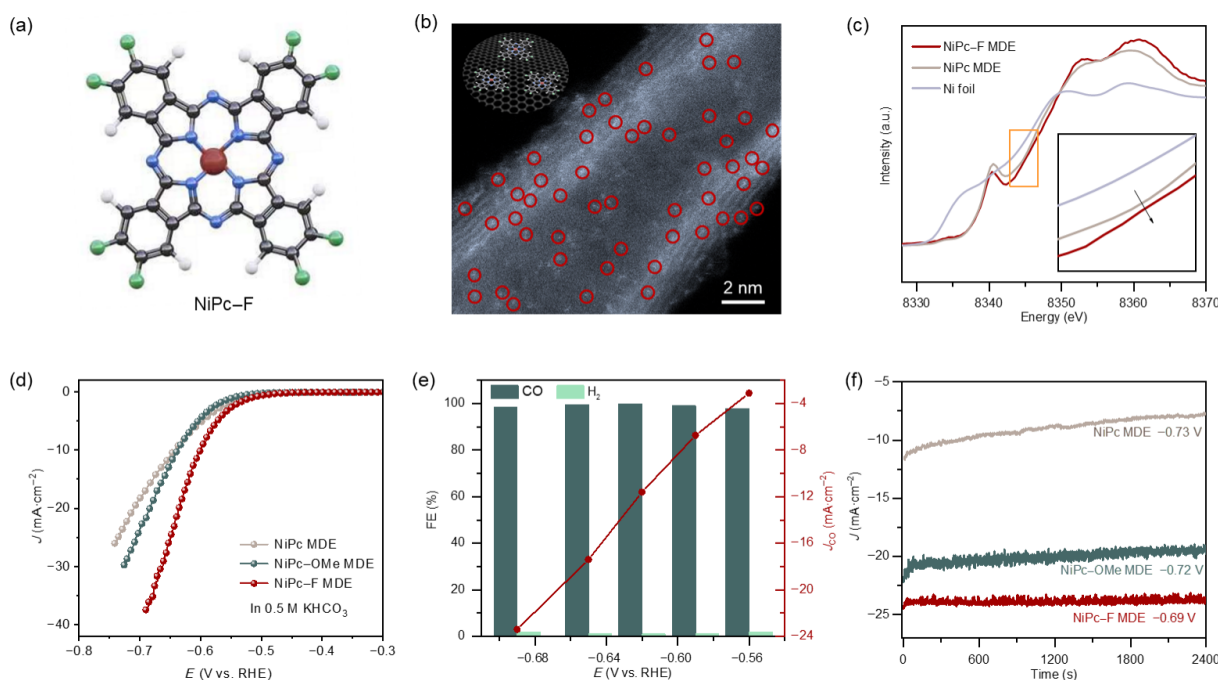


Figure 2 (a) Schematic molecular structure of NiPc-F. (b) Aberration-corrected HAADF-STEM image of NiPc-F MDE (inset shows the schematic of NiPc-F molecules anchored on CNTs). (c) Ni K-edge XANES of NiPc-F MDE, NiPc MDE, and Ni foil. (d) LSV curves of NiPc-F MDE, NiPc MDE, and NiPc-OMe MDE in CO₂-saturated 0.5 M KHCO₃. (e) FE for CO and H₂ (bars, left axis) and the corresponding CO partial current density (red line, right axis). (f) Chronoamperometry of NiPc MDE, NiPc-OMe MDE, and NiPc-F MDE in H-cell with CO₂-saturated 0.5 M KHCO₃.

demonstrates good stability comparable to the previously reported NiPc-OMe MDE, while providing higher current densities at a less cathodic potential (-0.69 V). Furthermore, stable electrolysis at a constant -10 mA·cm $^{-2}$ is sustained for 60 h with FE $_{\text{CO}}$ over 99% (Fig. S9 in the ESM). Collectively, these results show that fluorine substitution balances the activity–stability trade-off in NiPc MDEs through two distinct roles: Microenvironment regulation mainly accelerates CO desorption and improves stability, whereas electronic modulation primarily strengthens CO $_2$ adsorption and enhances the intrinsic catalytic activity for CO $_2$ -to-CO conversion.

In Fig. 3(a), normalized *operando* Ni K-edge XANES spectra collected in CO $_2$ -saturated 0.5 M KHCO $_3$ show a progressive shift

of the white-line/edge feature toward lower photon energy upon applying cathodic bias from open circuit voltage (OCV) to -0.45 V and further to -0.59 V. This negative energy shift indicates an increased electron density and a lower effective oxidation state at the Ni center during electrocatalysis, suggesting that the catalytically active state is an electrochemically reduced Ni species. Notably, upon returning the potential to OCV, the XANES feature reverts to its initial position, indicating a reversible redox/electronic response rather than irreversible structural degradation or metal aggregation during CO $_2$ RR. Consistently, the corresponding Fourier-transformed EXAFS profiles (Fig. 3(b)) are dominated by a single first-shell Ni–N contribution peaked at ~ 1.43 Å, and this peak

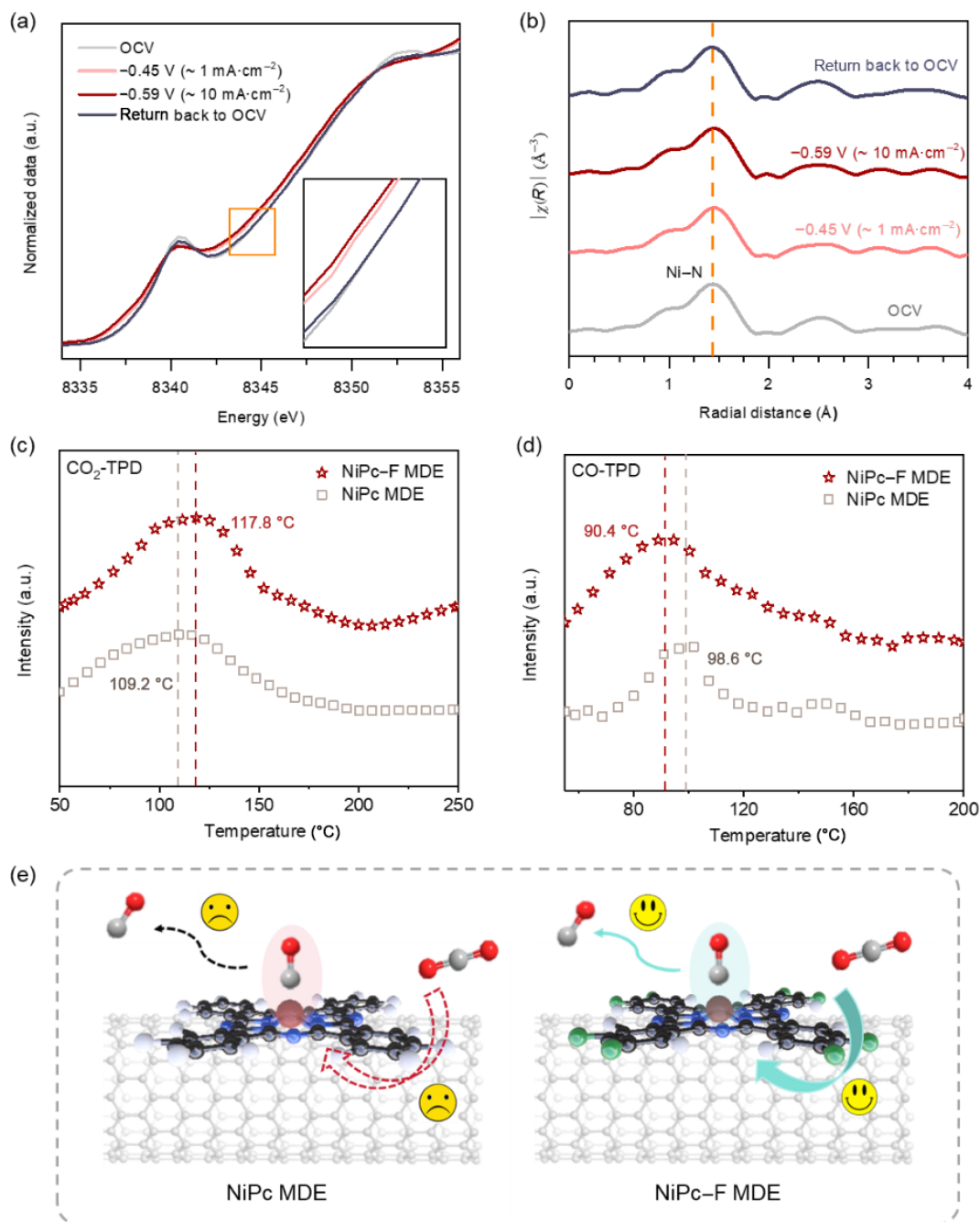


Figure 3 (a) Normalized *operando* Ni K-edge XANES spectra and (b) EXAFS of NiPc-F MDE at OCV and potentials with current densities of around -1 mA·cm $^{-2}$ (less negative potentials) and around -10 mA·cm $^{-2}$ (more negative potentials) in CO $_2$ -saturated 0.5 M KHCO $_3$, (c) CO $_2$ -TPD and (d) CO-TPD profiles of NiPc-F MDE and NiPc MDE. (e) Schematic illustration of reaction microenvironment optimization for aqueous CO $_2$ -to-CO electrolysis.

position remains essentially unchanged across OCV and the applied potentials. The consistent Ni–N main peak shows that the Ni–N₄ coordination structure in NiPc–F remains stable during cathodic polarization, highlighting the durability of the molecularly dispersed active sites throughout CO₂ electrolysis.

CO₂-TPD and CO-TPD measurements were conducted to investigate the mechanism by which fluorine substitution regulates the microenvironment. As shown in Fig. 3(c), NiPc–F MDE exhibits a CO₂ desorption peak at 117.8 °C, which is upshifted relative to NiPc MDE (109.2 °C), indicating strengthened CO₂ adsorption/retention upon β -site fluorination. In contrast, the CO-TPD profiles (Fig. 3(d)) show a pronounced downshift in the CO desorption temperature for NiPc–F MDE (90.4 °C) relative to NiPc MDE (98.6 °C), consistent with weaker CO binding that facilitates product desorption and mitigates site blocking. Contact-angle measurements further confirm the enhanced hydrophobicity of NiPc–F MDE relative to NiPc MDE (Figs. S1 and S10 in the ESM). Figure 3(e) illustrates a schematic comparing the interfacial reaction microenvironments of NiPc MDE and fluorinated NiPc–F MDE during CO₂-to-CO electrolysis. Within this regulated interface, CO₂ adsorption/activation is promoted in NiPc–F MDE, while CO binding is weakened to accelerate product desorption. Thus, NiPc–F MDE shows not only enhanced activity but also improved stability for CO₂RR when compared to NiPc MDE.

NiPc–F MDE was integrated into a GDE to evaluate CO₂-to-CO electrolysis at industrially relevant current densities. Cross-sectional SEM imaging confirms that the catalyst layer is uniformly deposited on a commercial gas-diffusion substrate (Fig. S11 in the ESM). CO₂RR testing was performed in a flow cell containing 1.0 M KHCO₃ (Fig. 4(a)). Under stepped galvanostatic operation from –5 to –600 mA·cm^{–2}, with each current density held for 1 h, the electrode exhibits stable potentials across the entire current density

range (Fig. 4(b)). High CO selectivity is maintained, with FE_{CO} remaining above 98% from –5 to –400 mA·cm^{–2} and still exceeding 96% at –600 mA·cm^{–2} (Fig. 4(c)). At –600 mA·cm^{–2}, the corresponding CO partial current density reaches –576 mA·cm^{–2}, benchmarking among the best-performing Ni-based electrocatalysts for CO production in neutral media reported to date (Fig. 4(d)). Long-term electrolysis at –300 mA·cm^{–2} further demonstrates durable operation, maintaining stable performance for 45 h with minimal potential fluctuation and FE_{CO} consistently $\geq$ 98% (Fig. 4(e)). Post-electrolysis characterization was performed on NiPc–F MDE GDE after 45 h of electrolysis to probe the origin of the gradual performance decay. The SEM image shows no obvious morphological collapse or particle aggregation relative to the fresh electrode (Fig. S12(a) in the ESM). HAADF-STEM further confirms that the catalyst largely retains its molecularly dispersed character, with isolated Ni bright features distributed on the carbon framework (Fig. S12(b) in the ESM). In contrast, pronounced flooding was observed after long-term operation. These results indicate that the gradual activity decline primarily arises from GDE flooding rather than intrinsic deactivation of NiPc–F MDE.

3 Conclusions

This work demonstrates a fluorine-regulated strategy that concurrently improves both the intrinsic activity and operational stability of NiPc-based electrocatalysts for CO₂-to-CO conversion. Inspired by the enhanced stability with PTFE introduction in NiPc MDE, NiPc–F MDE with F substitution at β positions is developed as an optimized electrocatalyst. Such F substitution can promote CO₂ retention and accelerate CO release, leading to simultaneous enhancement of activity and stability for NiPc–F MDE when compared to NiPc MDE in neutral electrolytes. In a flow-cell gas-diffusion configuration, the optimized NiPc–F MDE electrode

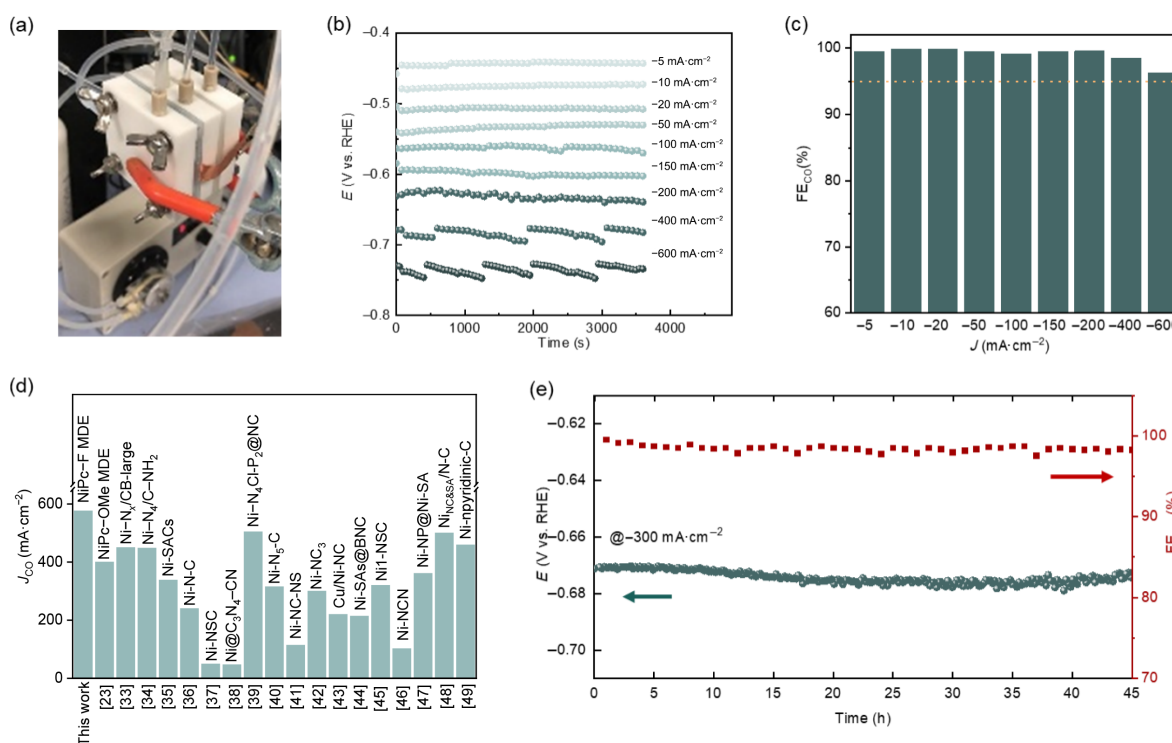


Figure 4 (a) Photograph of the flow-cell setup for CO₂RR. (b) Chronopotentiometric profiles and (c) FE_{CO} recorded in the flow-cell at sequential current densities from –5 to –600 mA·cm^{–2}. (d) Comparison of the J_{CO} achieved by the catalyst in this work with recent Ni-based CO₂RR-to-CO catalysts reported in Refs. [23, 33–49]. (e) Chronoelectrolysis at –300 mA·cm^{–2} in a flow cell, showing the stable operation potentials and the corresponding FE_{CO} over time.

shows high FEs for CO of > 96% even at $-600 \text{ mA}\cdot\text{cm}^{-2}$. This work not only provides an improved NiPc-based electrocatalyst for CO_2 electroreduction to CO, but also offers an effective design paradigm for molecular electrocatalysts by optimizing the microenvironment.

Electronic Supplementary Material: Supplementary material (including contact-angle measurements, CO_2 -TPD profiles, UV-visible absorption spectra, HAADF-STEM images, EXAFS spectra and fitting results, SEM images, and additional CO_2 RR electrochemical data) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908793>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

H. L. conceived and designed the experiments. Y. Y. L. conceived and supervised the project. H. L. and H. Z. Z. carried out the preparation, characterization, and electrochemical measurements of the catalysts. H. L., H. Z. Z., Y. B. Y., Y. W., Z. J., and Y. Y. L. analysed the data. H. L. and Y. Y. L. wrote the manuscript. All the authors have approved the final manuscript.

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None.

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