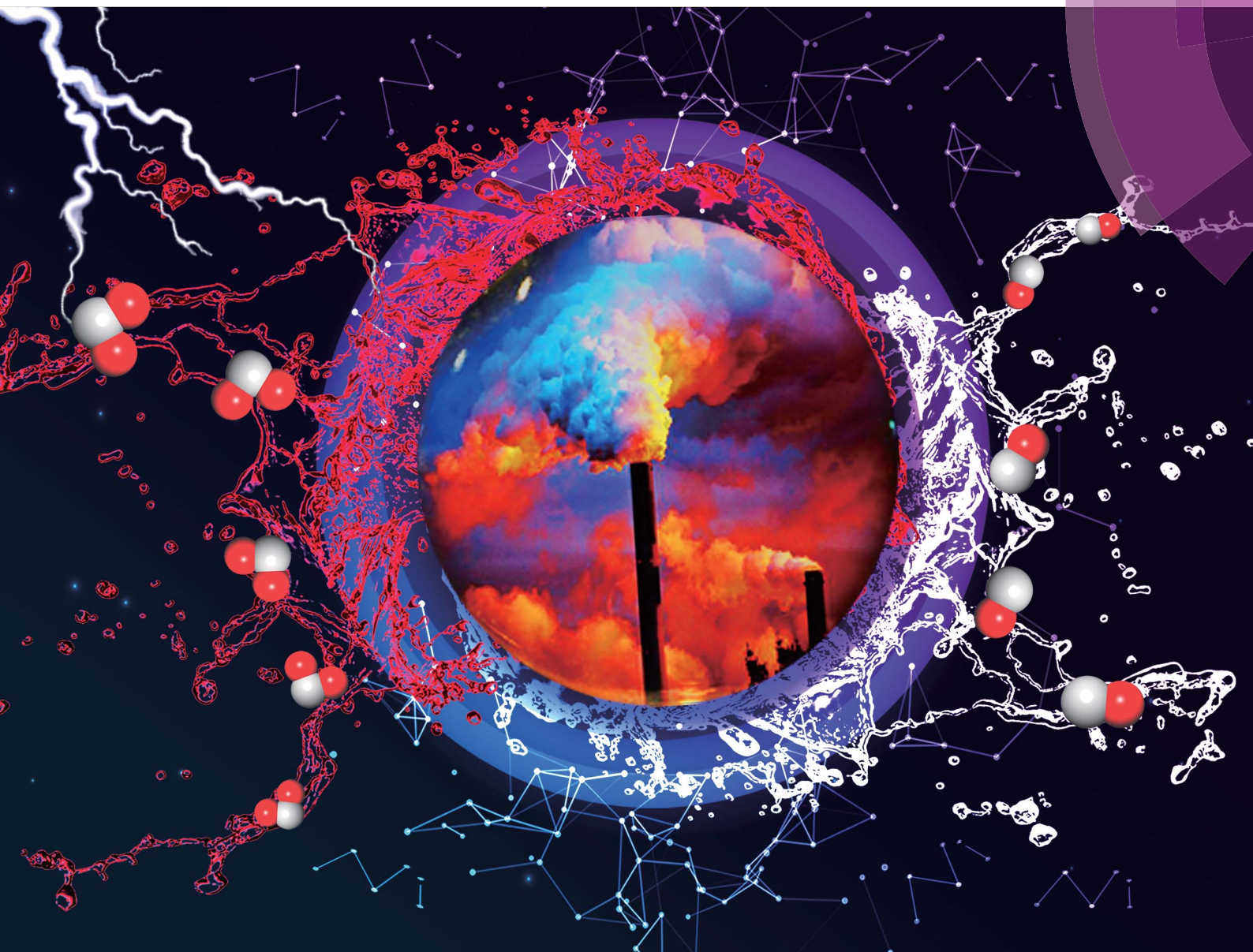


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Carbon-supported Ni nanoparticles for efficient CO₂ electroreduction†

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The development of highly selective, low cost, and energy-efficient electrocatalysts is crucial for CO₂ electrocatalysis to mitigate energy shortages and to lower the global carbon footprint. Herein, we first report that carbon-coated Ni nanoparticles supported on N-doped carbon enable efficient electroreduction of CO₂ to CO. In contrast to most previously reported Ni metal catalysts that resulted in severe hydrogen evolution during CO₂ conversion, the Ni particle catalyst here presents an unprecedented CO faradaic efficiency of approximately 94% at an overpotential of 0.59 V, even comparable to that of the best single Ni sites. The catalyst also affords a high CO partial current density and a large CO turnover frequency, reaching 22.7 mA cm⁻² and 697 h⁻¹ at -1.1 V (versus the reversible hydrogen electrode), respectively. Experiments combined with density functional theory calculations showed that the carbon layer coated on Ni and N-dopants in carbon material both play important roles in improving catalytic activity for electrochemical CO₂ reduction to CO by stabilizing *COOH without affecting the easy *CO desorption ability of the catalyst.

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Introduction

Direct electrochemical reduction of CO₂ (ECR) powered by electricity from renewable sources provides a “clean” and efficient way to alleviate the greenhouse effect and to convert CO₂ into value-added fuels and chemicals.^{1–10} Despite the recent progress made in ECR,^{11–16} it still suffers from (1) a large overpotential, (2) sluggish electron transfer kinetics, (3) insufficient product selectivity, and (4) degradation of catalytic activity within short periods. Additionally, proton reduction to generate H₂ always takes place as a competitive reaction, especially in aqueous solutions, which lowers CO₂ reduction selectivity and efficiency. Extensive efforts are therefore being devoted to developing new electrocatalysts that can reduce CO₂ at high

rates with low overpotentials and large turnover frequencies (TOFs).

The reduction of CO₂ to CO [CO₂ + 2H⁺ + 2e⁻ → CO + H₂O, $E_{\text{redox}}^0 = -0.11$ V vs. the reversible hydrogen electrode (RHE)] proceeds through a two-electron (e⁻)/proton (H⁺) transfer pathway.⁷ A CO₂ molecule is first reduced to a carboxyl intermediate (*COOH) either by a concerted e⁻/H⁺ or by a decoupled e⁻ and H⁺ transfer that involves the formation of a CO₂^{•-} radical. Subsequently, a second e⁻/H⁺ attacks the oxygen atom (OH) in the *COOH to generate H₂O (l) and CO. Au,¹⁷ Ag,¹⁷ modified Pd,^{18,19} and bimetallic Cu²⁰ can tightly bind *COOH, which is further reduced to a *CO intermediate in aqueous media. The *CO is weakly bound to their surfaces, and CO desorbs from the metal electrodes as a major product. Despite their high CO₂-to-CO conversion, the high cost and scarcity of these metals are problematic for practical applications. Exploration of cheap and earth-abundant catalysts for efficient CO₂ electrocatalysis is thus desirable. Late transition metals such as Fe, Co, and Ni are promising alternatives to expensive noble metals. However, metallic Fe, Co, and Ni tend to promote the hydrogen evolution reaction (HER). They also possess strong bonding with adsorbed CO, dramatically limiting ECR. To solve this problem, construction of single metal sites has been demonstrated to enable engineering of the electronic properties of transition metals for enhanced ECR.^{21–26} It was speculated that charge transfer occurred between the metal atoms with delocalized electrons and the carbon 2p orbital in CO₂ to form a CO₂^{δ-} species, thereby reducing the energy barrier for ECR.

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Both XRD and XPS analyses confirmed the major form of metallic Ni rather than single Ni atoms in the resulting Ni catalysts.

Fig. 2a shows the X-ray absorption near edge structure (XANES) of Ni-NC_TPA@C and Ni-NC_ATPA@C as well as nickel foil and nickel oxide for comparison. The Ni absorption edge positions of Ni-NC_TPA@C and Ni-NC_ATPA@C are both consistent with that of the Ni metal standard (Fig. 2b). No Ni(I) or Ni(II) moieties were detectable, indicating that Ni was present in the metallic state rather than in the form of single Ni sites. Fourier transformed extended X-ray absorption fine structure (EXAFS) analysis also confirmed the predominant presence of Ni–Ni bonds and the absence of Ni–N bonds in the pyrolysis products, in agreement with the XRD and XPS results (Fig. 1a–c).

Aberration corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) observation (Fig. 3a and b) revealed the formation of Ni nanoparticles, with diameters ranging from 10 to 100 nm (inset of Fig. 3a). The brighter spots in the STEM images can be assigned to Ni particles because of the higher atomic number of Ni than C. The energy-dispersive X-ray spectroscopy (EDX) maps (Fig. 3c–f) along with the EDX spectrum (Fig. 3g) confirmed the presence of Ni within the N doped carbon matrix. However, no single Ni atoms or subnanometer Ni structures, which should appear as bright dots in HAADF images if present, were detected even after careful examination of different regions by HAADF-STEM. The sample exhibited strong ferromagnetic properties (Fig. S2†), providing additional evidence that single Ni atoms unlikely predominated. Combining the XRD, XPS, XANES, EXAFS, and HAADF-STEM results, we infer that Ni exists mainly in metallic nanoparticles instead of single sites. Most of the crystalline Ni particles were observed to be wrapped by carbon shells (Fig. 3h–j) and deposited on a graphitic support (Fig. 3k). This carbon shell likely prevents the Ni NPs from coming into direct contact with the aqueous electrolyte, thereby significantly suppressing the HER. The role of this shell in ECR will be discussed further in the following DFT part. A similar morphology has also been observed for Ni-NC_TPA@C.

The carbon supported Ni nanoparticle catalysts were subjected to electrochemical CO₂ reduction tests in a gas-tight three-electrode configuration cell. All potentials reported in

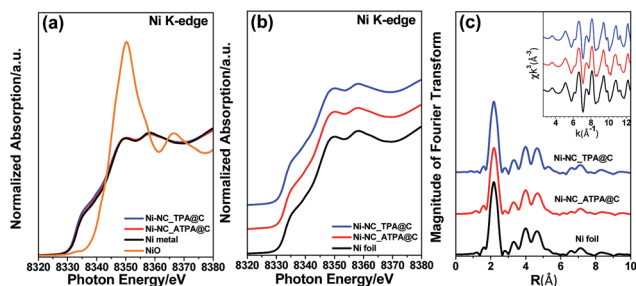


Fig. 2 (a) Ni K-edge X-ray absorption fine structure spectra of Ni-NC_TPA@C and Ni-NC_ATPA@C along with those of NiO and Ni foil as reference standards. (b) Enlarged XANES spectra and (c) Fourier transformed EXAFS spectra of the Ni K-edge for Ni-NC_TPA@C, Ni-NC_ATPA@C, and Ni foil.

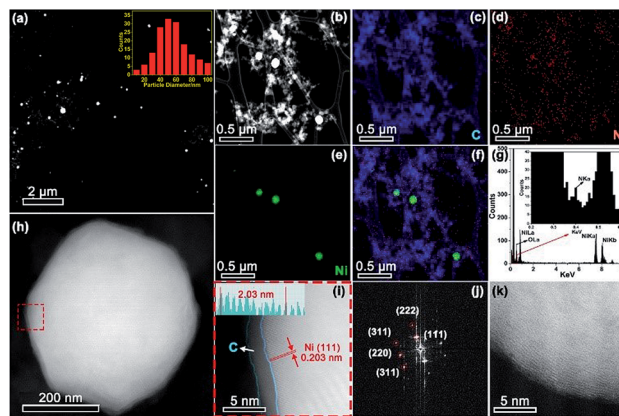


Fig. 3 (a and b) STEM images of Ni-NC_ATPA@C. Inset in (a): size distribution of Ni NPs. EDX maps of (c) C, (d) N and (e) Ni. (f) Overlay EDX map. (g) EDX spectrum of the region shown in (b). (h) STEM image of an individual Ni NP. (i) Enlarged STEM image of the area enclosed in the red dashed square in (h), manifesting an outer carbon layer around the crystalline Ni NP. (j) Fast Fourier transform (FFT) of the region shown in (i). (k) STEM image of the carbon support.

this work are with respect to the RHE scale unless specified otherwise. Shown in Fig. 4a are the linear sweep voltammetry (LSV) results of Ni-NC_TPA@C and Ni-NC_ATPA@C in 0.5 M aqueous KHCO₃ saturated with Ar or CO₂. A cathodic peak at about -0.6 V was observed in the LSV curves. The gaseous and liquid products were analyzed by gas chromatography (GC) and ¹H nuclear magnetic resonance (NMR). Only CO and/or H₂ were detectable, but no liquid products were detected under applied potentials in the range of -0.5 to -1.2 V in a CO₂-saturated 0.5 M KHCO₃ solution (pH 7.2) at room temperature and atmospheric pressure. As shown in Fig. 4b, CO₂-to-CO conversion starts from potentials ≥ -0.5 V and increases to a maximum CO FE at -0.7 V. The CO FE follows the trend of Ni-NC_ATPA@C > Ni-NC_TPA@C, which likely correlates with the trend of the content of overall N and pyrrolic N species. Both Ni samples dramatically outperform the N-doped carbon catalyst without metal (Fig. 4b and S3†). Notably, the maximum CO FE is up to 93.7% for the Ni-NC_ATPA@C, making it superior to previously reported carbon supported Ni NPs (maximum CO FE < 25%) and Ni single atoms derived from ZIF-8 (maximum CO FE = 71.9% at -0.9 V),¹² and even comparable to the best single Ni site catalysts (Table S1†).^{24,25,29–31} The competitive HER was substantially inhibited with H₂ FE less than 10.0%, in sharp contrast to the severe production of H₂ (H₂ FE $\geq 90\%$) over supported Ni nanoparticle catalysts as reported in the literature.³⁰ Both CO partial current density and mass activity increased as a function of overpotential with Ni-NC_ATPA@C outperforming Ni-NC_TPA@C (Fig. 4c and d), with the corresponding values above 13.2 mA cm⁻² and 527 mA mg_{Ni}⁻¹, respectively for Ni-NC_ATPA@C at potentials of -0.8 to -1.2 V. The maximum values of the two parameters reached as high as 22.7 mA cm⁻² and 910 mA mg_{Ni}⁻¹, respectively at -1.1 V.

The Tafel slope (Fig. 4e), an indication of the kinetics for CO formation, is ~ 122 mV dec⁻¹ for Ni-NC_ATPA@C, lower than 139 mV dec⁻¹ for Ni-NC_TPA@C. This suggests that the formation of the *COOH intermediate on the surface of both





Fig. 5 (a) Calculation models for Ni(111) and two graphene structures (bridge-top and fcc-top) for Gr/Ni(111). The free energy diagrams for (b) electrochemical CO₂ reduction to CO and (c) the HER on Ni(111), Gr/Ni(111), pristine graphene and Ni-N₄/Gr.

Pristine graphene shows a high reaction free energy for *COOH formation (2.31 eV), which is the first protonation step for electrochemical CO₂ reduction to CO. Interestingly, Gr/Ni(111) displays a significantly lowered free energy change for *COOH formation (0.58–0.66 eV), even lower than that of Ni-N₄/Gr (1.51 eV) reported previously as an efficient catalyst for the same reaction. Ni(111) shows a lower free energy change for *COOH formation. However, Ni(111) requires a large energy penalty for CO desorption (1.26 eV), indicating overall difficult CO production on the bulk Ni(111) surfaces. In contrast to Ni(111), CO desorption is exothermic on Gr/Ni(111), pristine graphene, and Ni-N₄/Gr. However, it is important to emphasize that, in Gr/Ni(111), Ni(111) plays an important role in improving catalytic activity by greatly stabilizing the *COOH adsorption on graphene but not affecting the easy CO desorption ability of graphene.

In the presence of N in the carbon support, the free energy change for *COOH formation increases in the order of pyrrolic N (−0.71 eV) < pyridinic N (−0.06 eV) < graphitic N (1.34 eV) (Fig. S10†). All of these reaction free energies are lower than that of pristine graphene (2.31 eV), indicating that N can facilitate stabilization of *COOH compared to pristine graphene. The free energy change for CO desorption is also lowered on pyrrolic N (0.79 eV) and graphitic N (−0.79 eV) compared to that of Ni(111) (1.26 eV), except for pyridinic N (1.69 eV). These results suggest that N-doping, particularly in the form of pyrrolic N and graphitic N, can indeed prompt electrochemical CO₂ reduction to CO on the carbon support material, consistent with experiments.

We also found that the hydrogen evolution reaction (HER), which is the most problematic yet dominant side reaction in ECR, can be suppressed on Gr/Ni(111) compared to Ni(111) (Fig. 5c). For the HER, we focused on the strength of H adsorbed on the surface (*H) since that determines the thermodynamic feasibility of the HER and, more importantly, acts as an active site to block ECR.³³ The free energy change for *H formation is highly negative on Ni(111) (−0.41 eV), indicating that *H covers the Ni(111) surface very easily. On the other hand, on

Gr/Ni(111), the free energy change for *H formation is much less favorable (0.10–0.20 eV), meaning that Gr/Ni(111) will be less covered by *H with the active sites made available for ECR.

Conclusions

In summary, we demonstrate that modification of metallic Ni by a combination of carbon coating and incorporation of a N-doped carbon support can effectively suppress the HER and significantly enhance the electroreduction of aqueous CO₂ to CO. This metallic Ni catalyst affords a high CO FE of up to approximately 94% (at −0.7 V vs. RHE) and a current density of 22.7 mA cm^{−2} (at −1.1 V), making it superior to all previous metallic Ni catalysts and even comparable to the best single Ni atom catalysts reported to date. Manipulation of the organic linker type and the addition of carbon black enable tuning of the catalytic properties of the resulting Ni nanoparticles. DFT calculations demonstrate that Ni greatly stabilizes the adsorption of *COOH on Gr/Ni(111) (increased activity) compared to pristine graphene without compromising the easy *CO desorption ability of pristine graphene (selectivity). Also, adding nitrogen-dopants (mainly graphitic N and pyrrolic N configurations) to the carbon support is shown to play an important role in improving catalytic activity by stabilizing *COOH. We believe that this work provides a new scheme to design low cost and active CO₂ reduction catalysts with high selectivity toward CO, which is of importance to both fundamental mechanism studies and technological applications in ECR.

Conflicts of interest

The authors of this manuscript have no conflicts of interest.

Author contributions

M. J., C. M. and H. T. prepared the samples and conducted electrocatalytic tests. M. J., Q. F. and S. L. performed XRD, XPS, FTIR, and SEM characterization experiments. C. C. and Y. J. performed DFT calculations. S. H. performed STEM measurements. T. W. and Y. S. performed EXAFS tests. P. K. and J. Q. helped with discussions on the electrocatalytic results. Z. S. supervised the project and wrote the manuscript. All authors discussed the results and commented on the manuscript.

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