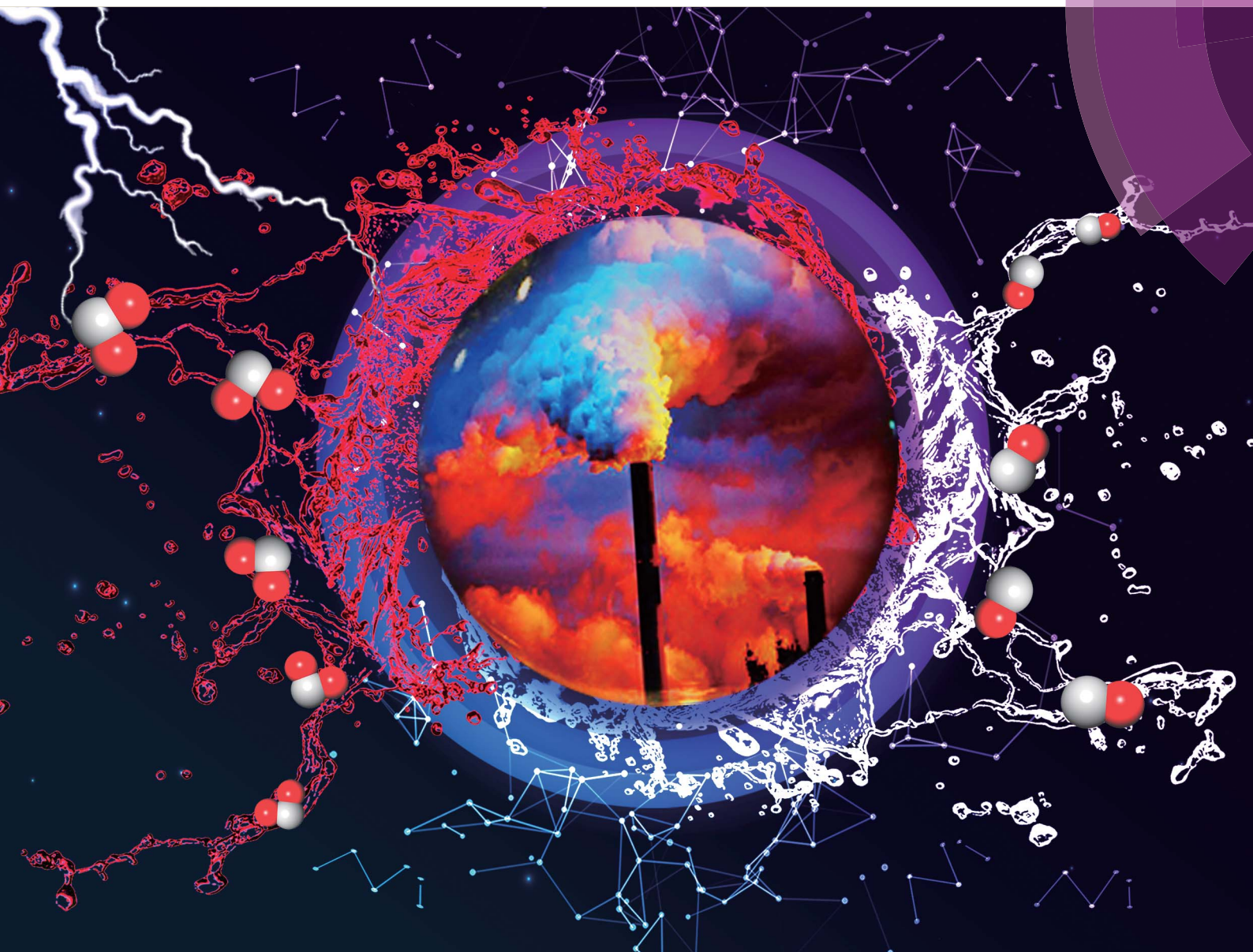


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Carbon-supported Ni nanoparticles for efficient CO₂ electroreduction†

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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_{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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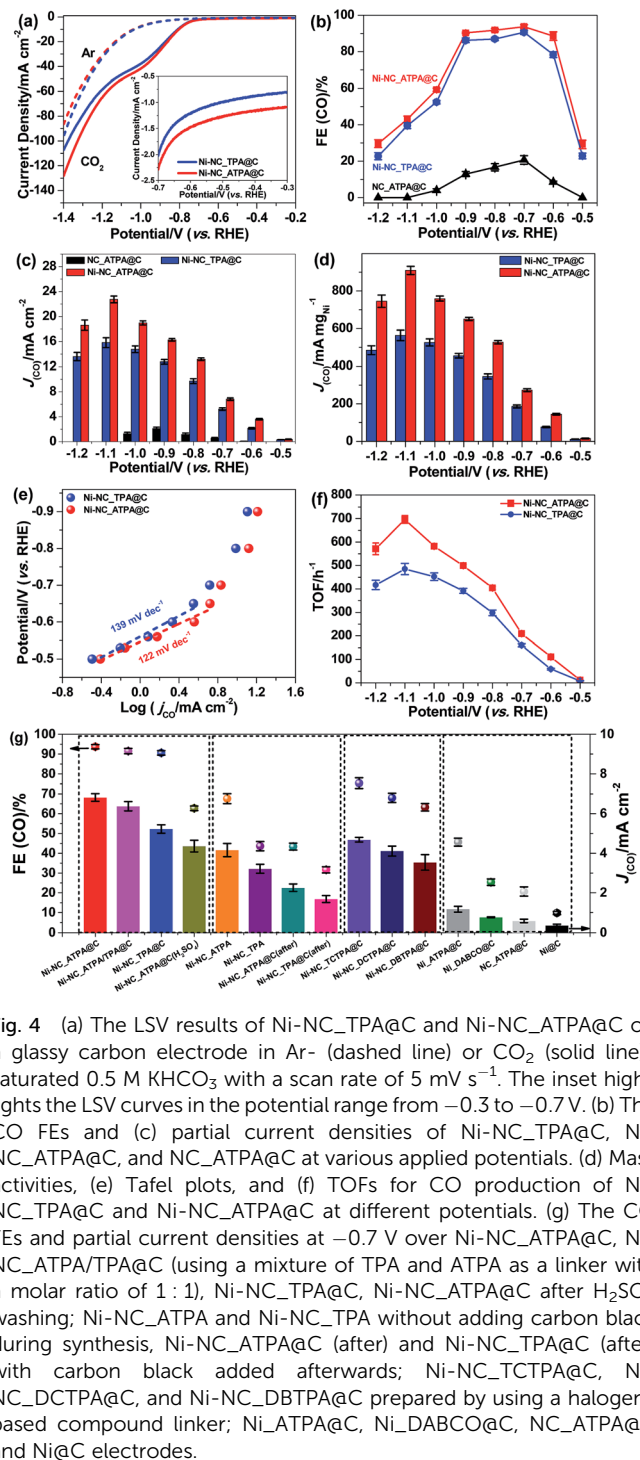


Fig. 4 (a) The LSV results of Ni-NC_TPA@C and Ni-NC_ATPA@C on a glassy carbon electrode in Ar- (dashed line) or CO₂ (solid line)-saturated 0.5 M KHCO₃ with a scan rate of 5 mV s⁻¹. The inset highlights the LSV curves in the potential range from -0.3 to -0.7 V. (b) The CO FEs and (c) partial current densities of Ni-NC_TPA@C, Ni-NC_ATPA@C, and NC_ATPA@C at various applied potentials. (d) Mass activities, (e) Tafel plots, and (f) TOFs for CO production of Ni-NC_TPA@C and Ni-NC_ATPA@C at different potentials. (g) The CO FEs and partial current densities at -0.7 V over Ni-NC_ATPA@C, Ni-NC_ATPA/TPA@C (using a mixture of TPA and ATPA as a linker with a molar ratio of 1 : 1), Ni-NC_TPA@C, Ni-NC_ATPA@C after H₂SO₄ washing; Ni-NC_ATPA and Ni-NC_TPA without adding carbon black during synthesis, Ni-NC_ATPA@C (after) and Ni-NC_TPA@C (after) with carbon black added afterwards; Ni-NC_TCTPA@C, Ni-NC_DCTPA@C, and Ni-NC_DBTPA@C prepared by using a halogen-based compound linker; Ni_ATPA@C, Ni_DABCO@C, NC_ATPA@C and Ni@C electrodes.

catalysts determines the reaction rate. But Ni-NC_ATPA@C has faster kinetics for CO₂ reduction than Ni-NC_TPA@C. Likewise, Ni-NC_ATPA@C exhibited larger CO formation TOFs than Ni-NC_TPA@C (Fig. 4f and S4†), and achieved 697 h⁻¹ at -1.1 V based on electrochemical surface area determination from double layer capacitance measurements. The Ni-NC_ATPA@C catalyst retained a stable current density over 6 mA cm⁻² and a CO FE of about 93% after electrolysis for 24 h at -0.7 V (Fig. S5†).

In order to probe the active centers in carbon supported Ni catalysts, control experiments were performed on different Ni catalysts that were produced with varying linkers, as displayed in Fig. 4g. It was found that N doped carbon in the absence of Ni (NC_ATPA@C) showed very low ECR activity toward CO generation (Fig. 4b, c, and g, and S3†), suggesting that Ni is responsible for efficient ECR. Nevertheless, Ni particles supported on carbon black without nitrogen modification (Ni@C) also exhibited poor ECR activity. This indicates that N doping plays an important role in facilitating CO₂-to-CO conversion. The ECR performance in terms of both CO FE and partial current density increased with N content. This can be evidenced by the significantly lower activity of the two Ni catalysts prepared by using only ATPA (Ni_ATPA@C) or DABCO (Ni_DABCO@C) without addition of another organic linker, which have lower N content as compared with Ni-NC_TPA@C, Ni-NC_TPA/ATPA@C, and Ni-NC_ATPA@C. We also made efforts to modify the carbon support with N and halogen (Cl or Br) atoms by using DCTPA, DBTPA, or TCTPA as a linker. However, the resultant Ni catalysts supported on N, Cl or Br co-doped carbon did not show improved ECR activity compared with Ni-NC_TPA@C. The Ni-NC_TPA and Ni-NC_ATPA without incorporation of carbon black, and Ni-NC_TPA@C (after) and Ni-NC_ATPA@C (after) with equivalent amounts of carbon black mixed afterwards all have lower CO FEs and partial current densities relative to the corresponding Ni catalysts with addition of carbon black during the preparation process. The pyrolysis temperature was observed to considerably influence the ECR performance of the catalyst as well, with 800 °C likely being the optimal reaction temperature (Fig. S6†). Furthermore, we found that acid treatment of Ni-NC_ATPA@C in 2 M H₂SO₄ for 1 h led to a pronounced decrease of the CO FE from ~93.7% to ~62.7%, highlighting that Ni NPs contribute to the ECR (Fig. 4g).

To investigate the effects of carbon coating on Ni nanoparticles and nitrogen content in carbon supports on the catalytic activity and selectivity of ECR, we performed DFT calculations. We considered a graphene (Gr) monolayer on a Ni(111) surface (Gr/Ni(111)) to model the carbon coating on Ni nanoparticles. Previous studies on graphene on Ni(111) by using high-resolution X-ray photoelectron spectroscopy (HR-XPS) combined with DFT calculations showed that the two different graphene structures (bridge-top and top-fcc) have almost identical energies and both structures are experimentally detected on Ni simultaneously.³² We also found that the energy difference between these two structures is 0.003 eV per C atom; thus, we considered both structures as well in a carbon coated model on Ni (Fig. 5a). For comparison, we also considered Ni(111), pristine graphene, and Ni-N₄ embedded graphene (Ni-N₄/Gr), which has been reported as an efficient Ni catalyst for ECR.^{24,25} Based on the XPS results (Fig. 1b), graphitic, pyridinic, and pyrrolic N were considered for investigating the effect of nitrogen content in carbon supports. The optimized structures of reaction models and intermediates are shown in the ESI (Fig. S7–S9†).

The free energy diagrams of electrochemical CO₂ reduction to CO (Fig. 5b) indicate improved catalytic activity of Gr/Ni(111) compared to the other catalysts under comparison here.



