Regulating the Coordination Environment of MOF-Templated Single-Atom Nickel Electrocatalysts for Boosting CO₂ Reduction

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Abstract: The general synthesis and control of the coordination environment of single-atom catalysts (SACs) remains a great challenge. Herein, a general host–guest cooperative protection strategy has been developed to construct SACs by introducing polypyrrole (PPy) into a bimetallic metal–organic framework. As an example, the introduction of Mg²⁺ in MgNi-MOF-74 extends the distance between adjacent Ni atoms; the PPy guests serve as a source to stabilize the isolated Ni atoms during pyrolysis. As a result, a series of single-atom Ni catalysts (named Niₓ₃₋ₓ-Ni-C) with different Ni coordination numbers have been fabricated by controlling the pyrolysis temperature. Significantly, the Niₓ₃₋ₓ-Ni-C catalyst, with the lowest Ni coordination number, achieves high CO Faradaic efficiency (98%) and turnover frequency (1622 h⁻¹), far superior to those of Niₓ₂₋ₓ-Ni-C and Niₓ-Ni-C, in electrocatalytic CO₂ reduction. Theoretical calculations reveal that the low Ni coordination number of single-atom Ni sites in Niₓ₃₋ₓ-Ni-C is favorable to the formation of COOH* intermediate and thus accounts for its superior activity.

Single-atom catalysts (SACs), featured with metal atoms dispersed at atomic level, can achieve a maximal utilization of metal atoms and have demonstrated excellent catalytic performance for various reactions. Combining the merits of both heterogeneous and homogenous catalysts, SACs have been regarded as a kind of unique heterogeneous catalysts to serve as an ideal model for the exploration of structure–property relationships during reaction processes. The atomically dispersed metal atoms of SACs are stabilized by the support through coordination interaction to minimize their surface energy. Therefore, the local coordination environment usually plays a significant role for both catalytic activity and selectivity of SACs. Although much work has been devoted in this field, to our knowledge, accurate control over the coordination environment of SACs at an atomic level remains a great challenge and has been rarely investigated.

Metal–organic frameworks (MOFs), a class of crystalline porous materials with well-defined structures and diverse compositions, not only exhibit great potentials for applications in diverse fields but also are promising precursors to produce desired materials for energy and catalysis. Particularly, MOFs have recently emerged as an ideal platform for the construction of SACs, as the targeted metal atoms in MOFs can be rationally and spatially separated in an atomically dispersed form. More specifically, because of the precisely designable and tailorable structures and components in MOFs, it is convenient to realize coordination environment regulation of SACs based on MOFs while great progress has been achieved, the currently available strategies towards MOF-based SACs are limited to MOFs involving abundant N atoms, such as ZIFs and porphyrinic MOFs. Given that N atoms are not involved in most MOFs, it is highly desired to develop a more general approach for the construction of SACs based on all kinds of MOFs, including non-nitrogenous MOFs. As a representative, the MOF-74 isomers, constructed by different divalent M²⁺ ions (for example, Mg²⁺, Ni²⁺, Co²⁺, etc.) and 2,5-dioxido-1,4-benzenedicarboxylate ligand, can be synthesized under similar conditions. This approach enables metal tunability, making it easy to regulate and control the dispersion/concentration of different metal species in MOF-74 via a mixed-metal synthetic strategy. In this respect, MOF-74...
is a promising candidate to spatially separate particular metal atoms in its M-oxo chains and to create favorable premise for the accurate construction of SACs.

With the above in mind, a bimetallic MgNi-MOF-74 has been synthesized, in which a large amount of Mg²⁺ helps to realize spatial isolation of Ni³⁺ in M-oxo chains. Polypyrrole (PPy) molecules as the nitrogenous guests are filled into the 1D channels of the MOF, yielding a PPy@MgNi-MOF-74 composite. Upon pyrolysis, the N atoms of PPy are incorporated into the porous carbon derived from the composite and serve as anchor sites to stabilize the Ni atoms, after MgO removal by etching. By means of such a host–guest cooperative protection strategy, single-atom (SA) Ni implanted N-doped carbon catalysts (Ni₃S₄-Nₓ-C) with controlled Ni–N coordination number from 4 to 2 are obtained (Scheme 1). In addition, Fe and Co SACs can also be obtained following the same strategy, demonstrating its universality. The optimal catalyst, Ni₃S₄-Nₓ-C, exhibits much higher activity and selectivity than other catalysts for the electrochemical reduction of CO₂ to CO. DFT calculations unveil that the reduced coordination of Ni₃S₄ by N atoms in Ni₃S₄-Nₓ-C favors the formation of a COOH⁺ intermediate and thus improves the activity towards CO₂ reduction reaction (CO₂RR). To our knowledge, this is the first report on the fabrication of SACs from non-nitrogenous MOFs.

On the basis of the isomorphism of Mg-MOF-74 and Ni-MOF-74, the bimetallic MgNi-MOF-74 was first prepared via a one-pot solvothermal reaction (Figure S1 in the Supporting Information). Then, pyrrole (Py) monomer was introduced into the MOF channels followed by in situ oxidative polymerization in the presence of I², producing polypyrrole (PPy) confined in the MOF (denoted PPy@MgNi-MOF-74), during which the crystalline MOF structure can be retained (Figure S1). The solid-state UV/Vis absorption spectrum shows the characteristic PPy absorption band, confirming the incorporation of PPy in MgNi-MOF-74 (Figure S2).[1][1]

The sharply reduced Brunauer–Emmett–Teller (BET) surface area (0.63 m² g⁻¹) compared with pristine MgNi-MOF-74 (931.6 m² g⁻¹) further approves the successful incorporation of PPy in the MOF channels (Figure S3). Upon pyrolysis at different temperatures in N₂ followed by MgO removal, PPy@MgNi-MOF-74 can be transformed to Ni-implanted N-doped porous carbons, namely Ni₃S₄-Nₓ-C, Ni₅S₆-Nₓ-C and Ni₅S₆-Nₓ-C, respectively, for the samples obtained at 600, 800 and 900°C, according to their actual nitrogen ratio (roughly 4:3:2, Table S1). Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis reveals similar Ni contents in all three samples (≈ 0.9 wt%, Table S1).

Taking Ni₃S₄-Nₓ-C as a representative, its powder X-ray diffraction (XRD) pattern shows two broad peaks in the ranges of 20–30° and 40–45° corresponding to the (002) and (101) planes of carbon, whereas no characteristic peak assigned to Ni crystals is observed (Figure S4). The Raman spectrum of Ni₃S₄-Nₓ-C displays two peaks at 1357 and 1596 cm⁻¹, assignable to disordered (D band) and graphitic carbon (G band), respectively. The corresponding intensity ratio of I_D/I_G is calculated to be 0.91, indicating a moderate degree of graphitization (Figure S5). The powder XRD and Raman data for Ni₅S₆-Nₓ-C and Ni₅S₆-Nₓ-C present similar results to those of Ni₅S₆-Nₓ-C (Figures S4, S5). In addition, Ni₅S₆-Nₓ-C possesses a high surface area (280.8 m² g⁻¹), comparable to Ni₅S₆-Nₓ-C (178.3 m² g⁻¹) and Ni₅S₆-Nₓ-C (322.1 m² g⁻¹). The hysteresis loops present in the N₂ sorption curves of all Ni₃S₄-Nₓ-C suggest the existence of abundant mesopores, which would be beneficial for the mass transfer during the catalytic process (Figure S6).

A transmission electron microscopy (TEM) image presents the porous structure of Ni₃S₄-Nₓ-C. No Ni nanoparticles (NPs) can be found (Figure 1a), in accordance with the above N₂ sorption and powder XRD results (Figures S4, S6). Aberration-corrected HAADF-STEM images clearly demonstrate the existence of isolated Ni atoms (Figure 1b, S7). Energy dispersive spectroscopy (EDS) mapping reveals the homogeneous distribution of Ni, N and C in Ni₃S₄-Nₓ-C (Figure 1c). To examine the existing situation of N and Ni elements, X-ray photoelectron spectroscopy (XPS) has been further conducted. The Ni 1s XPS spectra can be fitted to five
characteristic peaks, including pyridinic N (398.5 eV), Ni-N (399.8 eV), pyrrolic N (400.7 eV), graphitic N (401.5 eV) and oxidized N (402.9 eV), respectively, supporting the successful N doping and the formation of Ni-N sites (Figure 2a). The binding energy of Ni 2p3/2 in Ni3N2-C is located at 854.6 eV (Figure S8), which is in the range between metallic Ni0 (853.0 eV) and Ni2+ (857.5 eV), suggesting a weakly oxidated state of the Ni species in Ni3N2-C.

To elucidate the electronic and microstructural information of Ni atoms in Ni3N2-C (x = 2, 3, 4), X-ray absorption spectroscopy (XAS) was utilized to determine their valence states and coordination environments.

From the Ni K-edge X-ray absorption near-edge structure (XANES) spectra, the absorption edge of the three samples are all located between those of Ni foil and NiO, manifesting the positive valence of Ni atom situated between Ni0 and Ni2+ in accordance with the XPS results (Figure 2b, Figure S8). In the Fourier transform-extended X-ray absorption fine structure (FT-EXAFS) spectra, all three samples exhibit dominant peaks corresponding to the Ni–N (~1.36 Å) and Ni–C (~1.87 Å) scattering paths. Importantly, the peak related to Ni–Ni bond in Ni foil (~2.10 Å) is not observable in the profiles of Ni3N2-C (x = 2, 3, 4), verifying the formation of single Ni atoms in the samples (Figure 2c). To acquire more information on the chemical configuration, EXAFS fittings were performed (Figure 2d, Figure S9). The best fitting results reveal that, in addition to the 1 to 2 carbon atoms coordinated to each Ni atom, the Ni–N coordination numbers are 4.0, 3.4 and 2.0, respectively, for Ni3N2-C, Ni3N2-C and Ni3N2-C, which is in good agreement with the N ratios reflected by the elemental analysis (Tables S1 and S2). The results suggest that the introduction of abundant N source is crucial for stabilizing the single Ni atoms and avoiding their aggregation. Despite this, when the pyrolysis temperature increases to 1000°C, Ni NPs (~20 nm) can be clearly observed, demonstrating that 900°C is the upper limit temperature for the formation of SA Ni catalysts (Figure S10). In addition, the increased Ni content (to 1.5-fold) in MgNi-MOF-74 also led to the formation of Ni NPs by pyrolysis at 900°C, suggesting that the current Ni content in MgNi-MOF-74 is the optimal value (Figure S11).

For better comparison, PPy was also incorporated into monometallic Ni-MOF-74 followed by pyrolysis at 900°C. The resulting material shows the existence of Ni NPs in the N-doped carbon (denoted as NiPy-N-C) (Figure S12). This illustrates the important role of Mg for extending the spatial separation of Ni atoms in the MOF skeleton. Direct pyrolysis of MgNi-MOF-74 without PPy leads to the formation of NiO NPs loaded on porous carbon (NiO-n-C) (Figure S13), reflecting that the N atoms from PPy are of great significance for the stabilization of single Ni atoms. By means of this host (Mg)–guest (PPy) cooperative protection approach, Fe and Co SACs have been also achieved, validating the general applicability of this synthetic strategy (see details in the Supporting Information, Section 6, Figures S14–S21, Table S2), by which it is possible to extend the fabrication of SACs from the previous N-riched MOFs to all common MOFs.

Encouraged by the above results, electrocatalytic CO2 reduction over Ni3N2-C has been investigated to evaluate the influence of the Ni–N coordination environment on catalytic performance. From the linear sweep voltammetry (LSV) curves, the current densities of Ni3N2-C (x = 2, 3, 4) in CO2-saturated 0.5 M KHCO3 are much higher than in N2, indicating their activity in CO2 reduction (Figures S22–S24). Remarkably, Ni3N2-C possesses a higher current density than Ni3N2-C and Ni3N2-C in CO2-saturated 0.5 M KHCO3, manifesting the best activity of Ni3N2-C for CO2 reduction among all single-atom Ni catalysts (Figure 3a). Furthermore, the Faradaic efficiencies (FE) for CO2 reduction were examined in the potential range from −0.5 to −1.1 V (vs. RHE). As expected, Ni3N2-C affords a maximum CO FE of 98% at −0.8 V, which is the best FE among all measured SACs following a trend of Ni3N2-C > Ni3N2-C > Ni3N2-C (Figure 3b). The sums of FE for CO and H2 are...
The Gibbs free-energy calculations along with the electroreduction activity of single-atom Ni for electrocatalytic CO production were performed. Specifically, the optimal Ni activity is indicated to be 2.0 V, which is much higher than that of Ni$_{1-x}$N$_{2}$-C (1.09 eV) and Ni$_{3-x}$N$_{2}$-C (1.03 eV), suggesting the ease of CO$^*$ release from Ni$_{1-x}$N$_{2}$-C for CO production.

Figure 4a) Proposed reaction paths for CO$_2$RR with Ni$_{1-x}$N$_{2}$-C as a model. b) Free-energy diagram of CO$_2$ reduction to CO over Ni$_{1-x}$N$_{2}$-C catalysts.

**Conflict of interest**

The authors declare no conflict of interest.

**Keywords**: CO$_2$ electroreduction · coordination environment · metal–organic frameworks · single-atom catalysts

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