Metal-Nitrogen-Doped Carbon Materials as Highly Efficient Catalysts: Progress and Rational Design

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As a typical class of single-atom catalysts (SACs) possessing prominent advantages of high reactivity, high selectivity, high stability, and maximized atomic utilization, emerging metal-nitrogen-doped carbon (M-N-C) materials, wherein dispersive metal atoms are coordinated to nitrogen atoms doped in carbon nanomaterials, have presented a high promise to replace the conventional metal or metal oxides-based catalysts. In this work, recent progress in M-N-C-based materials achieved in both theoretical and experimental investigations is summarized and general principles for novel catalysts design from electronic structure modulating are provided. Firstly, the applications and mechanisms on the advantages and challenges of M-N-C-based materials for a variety of sustainable fuel generation and bioinspired reactions, including the oxygen reduction reaction (ORR), oxygen evolution reaction (OER), hydrogen evolution reaction (HER), carbon dioxide reduction reaction (CO₂RR), nitrogen reduction reaction (NRR), and nanozyme reactions are reviewed. Then, strategies toward enhancing the catalytic performance by engineering the nature of metal ion centers, coordinative environment of active centers, carbon support, and their synergetic cooperation, are proposed. Finally, prospects for the rational design of next generation high-performance M-N-C-based catalysts are outlined. It is expected that this work will provide insights into high-performance catalysts innovation for sustainable and environmental technologies.

1. Introduction

Ubiquitous chemical reactions play an imperative role in the survival and development of human society and they have been widely applied in the industrial, medical, and biological fields. The chemical processes especially those involving energy conversion and storage, however, usually suffer from sluggish kinetics and low efficiency. Therefore, the search for an efficient catalyst, which can accelerate the reaction rate with a low energy inputs and possess a high selectivity toward targeted products, has been a vital task in both academic and industry communities. Traditional heterogeneous catalysts, particularly noble-metal-based catalysts (e.g., Pt, IrO₂, and RuO₂), show advantages of high activity and efficiency as well as high stability and good recyclability. Nevertheless, such catalysts suffer from shortcomings of low atom-utilization efficiency and poor selectivity, since they contain metal particles with a range of sizes and only some of them are involved in catalysis. On the contrary, homogeneous catalysts deliver excellent activity and exclusive selectivity toward a specific reaction due to the homogeneity of their active sites. The major issues of poor stability and bad reusability, however, have impeded their further applications. In order to promote a wider commercialization, it is critical to construct the catalyst that can bridge the gap between the heterogeneous and homogeneous catalysis.

Since the discovery of single platinum atoms dispersed on FeOₓ with high CO oxidation activity in 2011, single-atom catalysts (SACs) with isolated single atoms anchored on supports, have been emerging to inherit the merits of both heterogeneous and homogeneous catalysts. On account of maximum atom utilization efficiency, the catalytic performance is greatly enhanced and the reduction in cost of metal is particularly important for precious metal catalysts. Moreover, the well-defined and uniform active centers endow SACs with excellent selectivity. Meanwhile, SACs possess advantages of high stability and good reusability from heterogeneous catalysts. Unfortunately, these low-coordination single atoms possess extremely high surface energy and tend to aggregate during the synthesis process. The supports are thus necessary for SACs to stabilize those isolated single atoms against migration and agglomeration through
strong metal-support interactions. The metal-support interactions can simultaneously induce charge transfer between metal and associated interface, thereby to optimize the intrinsic activity of active sites.\textsuperscript{[17,18]}

Toward this end, various types of supports have been developed, including metals,\textsuperscript{[19]} metal oxides,\textsuperscript{[20]} carbon,\textsuperscript{[21]} and its derivatives.\textsuperscript{[22]} Intriguingly, in addition to the strong interaction between N atoms in carbon and single atom catalysts, nitrogen-doped carbon (NC) has been considered as an appealing substrate for SACs due to the characteristics of good mechanical properties, large specific surface area, excellent electronic conductivity, structural flexibility beyond atomic scale, low cost, and ideal stability in acidic/alkaline condition. All these characters as well as non-noble-metal catalysts (M = Co, Fe, Ni, Cu, Zn, Mo, etc.) make M-N-C nanomaterials promising in a diverse set of catalysis.\textsuperscript{[23,24]}

Although the catalytic superiority of pristine M-N-C catalysts to conventional benchmarks for the critical chemical reactions in industrial, medical, and biological fields has been demonstrated in past years,\textsuperscript{[25,26]} there is still a plenty room for developing higher-performance M-N-C-based catalysts and rational principles more than trial-and-error approaches for experimental design and computational screening. In theory, deterministic control of extrinsic and intrinsic factors associated with active centers is essential for highly efficient M-N-C catalysts with optimal electronic and geometric structures.\textsuperscript{[27]} As for extrinsic factors, which are related to the abundance of accessible metal catalysts,\textsuperscript{[28]} the mainstream design strategy is to tune the morphology of carbon support, and the construction of 3D hierarchical porous structure not only provides a large specific surface area to populate and stabilize more single-atom active sites but facilitates the diffusion of reactants, ions, and products.\textsuperscript{[29,30]} On the basis of pristine M-N-C catalyst, the intrinsic factors such as dopants and defects can interact with active centers by charge transfer effect and correspondingly alter the electronic structure of active centers.\textsuperscript{[31]}

Meanwhile, the unit activity of metal catalysts is intrinsically sensitive to their electronic structure (e.g., work function, d-band center, Fermi level, etc.), especially the d-band center of metal species.\textsuperscript{[32]}

Applausive achievements on theoretical understanding of the roles of electronic structure of M-N-C SACs have been reached to date. First, the occupation states of the orbitals strongly influence the adsorption of reactants and intermediates during catalysis reactions. The higher the d-band center of metal active site, the more obvious interaction with the Lowest Unoccupied Molecular Orbital (LUMO) of reactants, which is usually an antibonding orbital, leads to a strong adsorption and activation of molecules,\textsuperscript{[33]} but a high intermediate desorption energy barrier which is attributed to the less occupied antibonding orbital after the hybridization between d band of metal catalyst and s/p band of adsorbates.\textsuperscript{[34]} In contrast, the lower d-band center implies a high dissociation barrier of reactant but an easy desorption of intermediates during the catalytic reactions. Such relation between the activation of reactant and the desorption of intermediate is restricted by the Br\textsuperscript{-}nsted–Evans–Polanyi (BEP) principle. Thus, the optimal d-band center of M-N-C catalyst to climb the top of volcano plot must have a balanced adsorption energy of reactants and intermediates toward specific reaction.\textsuperscript{[35,36]} Second, following the above principle, intrinsic factors that can optimally modify the d-band center have been put forward to enhance the catalytic activities. For example, dopants as well as molecules either in carbon support or coordinating the metal catalyst are able to act as electron donor or acceptor, inducing electron redistribution around the metal active sites, and altering the density of states (DOS) of d band near the Fermi level.\textsuperscript{[17,18]} Likewise, metal cluster embedded in carbon support not only provides more active sites but also modulates the d-band center with the charge transfer between metal cluster and single metal site.\textsuperscript{[39]} Either defects in carbon support or the change in the coordination number/type of active center that break the symmetry of catalyst and shift the energy level of d-band center of metal atom, is another effective way to modulate the catalytic activity.\textsuperscript{[40,41]} Third, in addition to the charge transfer in M-N-C catalysts induced by hybridizing with other 2D materials, strong synergistic effect originated from the valence electron interactions between hybrids’ active centers may be introduced to enhance the activity and selectivity toward some specific reactions. Additionally, the dopant in the carbon support itself can be an active site and bring in the beneficial synergistic effect to enhance the activity and selectivity of pristine M-N-C catalyst.\textsuperscript{[41]} Similarly, the synergistic effect happens between active centers when the metal loadings are highly increased.\textsuperscript{[44]} A typical example is the polynary M-N-C catalysts with active centers adjacent to each other, which have
been proved to achieve a more balanced binding to the reactants and intermediates than the single metallic M-N-C catalysts. In a word, besides the extrinsic and intrinsic factors that directly enhance the catalytic performance, the synergistic effects between metal ion centers or between metal ion center and other active site, which are induced by extrinsic and intrinsic factors, also play an important role in boosting the catalytic performance. Even though significant progress has been achieved in the understanding of M-N-C catalysts for sustainable fuel generation and biological reactions, a critical review which provides insights in rational design of high-performance catalysts based on both the theoretical and experimental progress has yet to be proposed.

In this review, as shown in Figure 1, we overview recent progress in the catalytic applications of oxygen reduction reaction (ORR), oxygen evolution reaction (OER), hydrogen evolution reaction (HER), carbon dioxide reduction reaction (CO₂RR), nitrogen reduction reaction (NRR), nanozymes, and other applications from both theoretical and experimental perspectives, aiming at putting forward approachable strategies for rationally designing highly efficient M-N-C-based catalysts and beyond. Herein, we first introduce the significance and advantages of the application of M-N-C nanocatalysts toward the typical sustainable fuel generation and biological reactions. Based on the achieved progress, some general principles or strategies for enhancing the activity, selectivity, and stability of pristine M-N-C catalysts through rational engineering of metal ion centers, coordinative environment, and carbon support are extracted. Particularly, we pay special focus on how the extrinsic and intrinsic factors affect the activity and selectivity of M-N-C-based catalysts in terms of population/accessibility of active centers, electronic structure of active centers, and synergistic effect between active centers. Finally, according to the comprehensive understanding, prospects of developing novel strategies are outlined.

2. Catalytic Applications of M-N-C SACs for Sustainable Fuel Generation and Biological Reactions

M-N-C-based materials combine the merits of each constituent of SACs, such as high activity, selectivity, maximum atomic utilization, good recyclability, and of the NC support including low cost, excellent electrical conductivity, robust chemical stability in acidic/alkaline medium, and large specific surface area, etc. Additionally, M-N-C-based materials are also

Figure 1. Schematic overview of extrinsic and intrinsic factors to enhance the catalytic performance of M-N-C-based materials.
characterized by high stability against thermal aggregation, and leaching, which is benefited from the strong coordination between the doped N atoms and transition metal atoms.[48] The usage of cost-effective transition metals (e.g., Fe, Co, and Ni) in M-N-C materials also justifies a promising potential to replace the precious-metal-group (PMG) materials in a variety of application fields, such as electrocatalysis, photocatalysis, and thermocatalysis, etc.[49,50] Due to the electronic, geometric, and chemical similarity between the M-N active centers and the nature metalloenzymes,[51] M-N-C catalysts also hold great promise to act as biocatalysts.[52] In the following sections, the progresses in the catalytical performances for typical catalytic reactions, including ORR, OER, HER, CO2RR, NRR, bioinspired enzyme catalysis reactions, and other applications, which have been made by effective strategies on engineering metal ion centers, coordinative environment, and carbon support of M-N-C-based catalysts, are reviewed.

2.1. M-N-C for Oxygen Reduction Reaction (ORR)

The ever-increasing energy demands and environmental concerns caused by the use of fossil fuels have stimulated enormous interests to develop environment-friendly energy storage, transport, and conversion technologies, including fuel cells, metal-air batteries, water splitting, and etc.[53–57] Among these devices, electrocatalytic oxygen reduction reaction (ORR) plays a crucial role on their overall performance.[58,59] In aqueous solution, the ORR proceeds either via a two-step pathway to generate an intermediate H2O2 (e.g., O2 + 2H+ + 2e− → H2O2), or through a four-electron pathway to form the final product 2H2O (e.g., O2 + 4H+ + 4e− → 2H2O).[60] However, these multiple e−/H+ processes always suffer from sluggish kinetics resulting from O=O bond breaking, and instability of catalysts in corrosive electrolytes, which become a challenge for the commercialization of these energy technologies.[61] It is well documented that platinum-based catalysts are the most active catalysts for oxygen reduction reactions,[62] whereas their limited world reserve, prohibitive cost, and vulnerability to poison species (methanol crossover, carbon monoxide poisoning, etc.) restrict their practical applications.[63] In this context, the exploration of alternative Pt-free materials with low cost, abundant source, and high ORR activity and stability is extremely imperative and has triggered tremendous research interests.[64] Among the non-precious-metal-based ORR catalysts studied so far,[65,66] transition-metal (TM) M-N-C materials have been emerging as the most appealing platinum-free candidates.[67,68]

In particular Fe–N–C and Co–N–C nanomaterials have been recognized as the most promising non-precious ORR catalysts with higher electrochemical activities in both acidic and alkaline media, as shown in Table 1, compared to other TM M-N-C materials.[69,70] It is clear that, although M-N-C materials show a high catalytic promise, some barriers still exist, such as sluggish O=O bond breaking, undesirable metal loadings, easy stacking of 2D carbon support, and inferior ORR performance to Pt/C catalyst in acidic electrolyte, which significantly impede the practical application of this class of materials. To address these issues, considerable efforts have been devoted to boosting the catalytic ORR performances of M-N-C materials recently.

One approach to enhance the catalytic performance of M-N-C materials is to increase the accessible number of active centers in catalysts. The construction of 3D nanoporous (micropores, mesopores, and macropores) M-N-C-based catalysts with high surface-to-volume ratios turns out to be an effective way to maximize the expose of active sites.[102] In addition to minimizing the support stacking, facilitating the mass transport during reaction, and stabilizing the single catalyst against sintering,[103] which all in turn help to enhance the overall catalytic activity and stability. For example, Qiu et al. have prepared a 3D graphene hollow nanosphere (GHSs) containing isolated Fe single atomic sites (Fe ISAs/GHSs). In addition to the inherent advantages of 2D graphene support, the homogeneity of active centers, and high porosity in 3D nanopore structure all helped to improve the sluggish reaction kinetics and contributed to an exceptional ORR performance with a high onset potential (E_onset = 1.05 V), a high half-wave potential (E_1/2 = 0.87 V), a high stability, and a high tolerance to poison species (methanol, SO2, and NOx).[76] Using the same strategy, Chen et al. synthesized atomically dispersed Fe catalysts anchoring on N-doped carbon nanospheres (Fe–N–C HNSs) with 3D hollow inner-connected architecture, which benefited to the accessibility of active single metal sites, and the mass transfer during the reaction process.[80] The ORR activity of Fe–N–C HNSs (E_onset = 1.046 V and E_1/2 = 0.87 V) in alkaline medium exceeded that of commercial Pt/C catalysts (E_onset = 1.03 V and E_1/2 = 0.84 V), other than their superior stability and resistance to methanol crossover. Due to the high chemical stability against acid etching as well as other advantages of carbon support, M-N-C catalysts hold a promise to replace the Pt/C catalysts for the ORR application in acidic medium. Even though M-N-C-based materials lack sufficient intrinsic activity in terms of half-wave potential,[104] they can outperform Pt/C catalysts on other aspects of performance via morphology engineering on the carbon support. Qian et al. have proposed a 3D catalysts using highly conductive nitrogen-doped carbon network to host Fe atoms (SA-3DNC).[85] SA-3DNC catalyst exhibited an onset potential of 0.906 V for ORR, about 30 mV than that of commercial Pt/C, in addition to its superior stability. This result can be attributed to its highly micro-macroporous hierarchical morphology which prohibited the stacking of carbon support, improved the expose of the Fe-Nx active sites, and provided sufficient channels for mass transport.

Assuming a full exposure of active sites, to increase the loading of active sites without aggregation is an effective strategy to enhance the ORR performance, which can lead to an enhanced current density and a synergistic cooperation between the neighboring active sites.[100] For instance, Ye et al. have prepared a iron-nitrogen-doped porous carbon (Fe–N–C) catalyst with a high loading of atomically dispersed Fe (5.86 wt%).[90] Since the number of active sites boosted the energy density during the reaction process, the Fe–N/C catalyst showed a high half-potential of 0.85 V and a high current density of 6.0 mA cm−2. In alkaline medium, a Fe–N/C catalyst characterized by a high metal loading up to 12.1 wt% at 350 °C.[88] A sequential protecting strategy was utilized to prohibit the sintering of dense Fe ion centers when Fe–N bonding happened over 600 °C, which was promising for massive application. As a result, the Fe–N–C catalyst exhibited
| Catalyst                  | Alkaline condition | Acidic condition | Ref. |
|---------------------------|--------------------|------------------|------|
|                           | Electrolyte        | Half-wave potential/V (vs. RHE) | Onset potential/V (vs. RHE) | Electrolyte | Half-wave potential/V (vs. RHE) | Onset potential/V (vs. RHE) |      |
| Zn-N-C-1                  | 0.1 M KOH          | 0.873            | -    | 0.5 M H_2SO_4 | 0.72         | 0.82         | [70] |
| Sc@NG-750                | 0.1 M KOH          | 0.89             | 0.99 | 0.1 M HClO_4 | 0.811        | -            | [71] |
| CoTMP-700                | 0.1 M KOH          | 0.81             | 0.92 | 0.1 M HClO_4 | 0.81         | 0.95         | [72] |
| FeFe(CN)_3               | 0.1 M KOH          | 0.91             | -    | 0.1 M HClO_4 | 0.78         | -            | [73] |
| Fe-N-C                   | 0.1 M KOH          | 0.90             | 1.0  | 0.1 M HClO_4 | 0.82         | -            | [74] |
| Fe@NMC-1                 | 0.1 M KOH          | 0.88             | 1.01 | 0.1 M HClO_4 | 0.78         | -            | [75] |
| Fe ISAs/GHs              | 0.1 M KOH          | 0.87             | 1.05 | -              |              |              | [76] |
| Co-N_x-C                 | 0.1 M KOH          | 0.83             | -    | 0.5 M H_2SO_4 | 0.823        | -            | [77] |
| TPI@Zr(SiO_2)-650-C      | -                  | -                | -    | 0.1 M H_2SO_4 | 0.78         | -            | [78] |
| Fe 5As/N-C               | 0.1 M KOH          | 0.91             | -    | 0.1 M HClO_4 | 0.798        | -            | [79] |
| Fe-N-C HN5s              | 0.1 M KOH          | 0.87             | 1.045| 0.1 M HClO_4 | 0.82         | -            | [80] |
| Fe-NC NWs                | 0.1 M KOH          | 0.91             | -    | 0.1 M HClO_4 | 0.82         | -            | [81] |
| Fe-N_x-C                 | 0.1 M KOH          | 0.83             | -    | 0.5 M H_2SO_4 | 0.785        | 0.89         | [82] |
| 1.6%CoNC@ArNH_3          | -                  | -                | -    | 0.1 M HClO_4 | 0.729        | 0.906        | [83] |
| Fe-SilkPNC               | 0.1 M KOH          | 0.853            | -    | 0.5 M HClO_4 | 0.82         | -            | [84] |
| SA-3DNC                  | -                  | -                | -    | 0.5 M H_2SO_4 | 0.78         | -            | [85] |
| Fe-N-C                   | -                  | -                | -    | 0.5 M HClO_4 | 0.84         | -            | [86] |
| Co-N-C@F127              | -                  | -                | -    | 0.5 M H_2SO_4 | 0.84         | -            | [87] |
| Fe-NC SAC                | 0.1 M KOH          | 0.90             | 0.98 | -              |              |              | [88] |
| CNT-Fe/NHCNS             | -                  | -                | -    | 0.1 M HClO_4 | 0.84         | -            | [89] |
| Fe-N/C                   | 0.1 M KOH          | 0.85             | -    | 0.5 M HClO_4 | 0.84         | -            | [90] |
| H-Fe-N_x-C               | -                  | -                | -    | 0.1 M HClO_4 | 0.77         | 0.950        | [91] |
| MgO@Phen-Fe-800-3/1      | -                  | -                | -    | 0.5 M H_2SO_4 | 0.84         | -            | [92] |
| WN_x-1                   | 0.1 M KOH          | 0.88             | 1.01 | 0.1 M HClO_4 | 0.77         | 0.87         | [93] |
| Fe SAC/N-C               | 0.1 M KOH          | 0.89             | -    | -              |              |              | [94] |
| Fe-NPC                   | 0.1 M KOH          | 0.83             | 1.089| -              |              |              | [95] |
| Fe-NPC                   | 0.1 M KOH          | 0.88             | 1.03 | -              |              |              | [96] |
| Fe-N-S CNN               | 0.1 M KOH          | 0.91             | -    | 0.5 M H_2SO_4 | 0.78         | -            | [97] |
| Cu-SA/NPSC               | 0.1 M KOH          | 0.84             | -    | 0.5 M H_2SO_4 | 0.84         | -            | [98] |
| AC@-FeFeCoNC900          | 0.1 M KOH          | 0.89             | 1.05 | 0.1 M HClO_4 | 0.81         | 0.87         | [99] |
| CuCo@NCNT-700            | 0.1 M KOH          | 0.844            | 0.964| -              |              |              | [100]|
| Zn/Co-N_x-C-Sy           | 0.1 M KOH          | 0.893            | 1.07 | -              |              |              | [101]|
a superior ORR electrocatalytic activity with regard to the half-wave potential of 0.9 V and the kinetic current of 100.7 A g$^{-1}$ at 0.9 V, 50 mV and 65 A g$^{-1}$ higher than that of the commercial 20% Pt/C catalyst.

It is worth noting that apart from the increased loading of active sites multi-metallic M-N-C materials featured with an extensive synergistic cooperation among the dissimilar active sites can facilitate the ORR performance compared with single-metallic M-N-C materials. Zhang et al. have developed a formamide-converted transition metal-nitrogen-carbon electrocatalyst containing isolated Fe-Co dimers (f-FeCoNC900). This material not only exhibited a superior catalytic performance in alkaline medium due to the cooperation between Co and Fe active sites, and in addition its ORR activity in acidic medium was also excellent with a half-wave potential of 0.81 V, around 20 mV higher than that of commercial 20 wt% Pt/C catalyst. The introduction of multi-metal in M-N-C catalysts even overcame the inferior ORR performance of single-metal involved M-N-C catalysts in acidic solution. [99] This result also impels the exploration of possible combinations of metallic components to develop high performance bimetallic and trimetallic M-N-C catalysts that can induce beneficial synergistic effect.

It has been demonstrated that improving the intrinsic activity of catalytic site by regulating its coordinative environment, which can optimize the electronic structure of metal active site to reach a balanced activation of molecules and adsorption of key intermediate, is also an effective approach to obtain high ORR performance. Given that the rate determining step (RDS) for single Fe catalyst coordinated by four pyridine ligands (Fe-4pN) in ORR was the desorption of OH$^*$ intermediate, the coordination of pyridine ligand or hydroxyl group to the central Fe ion of Fe-N$_2$-C catalysts aimed to remove electrons from Fe ion centers and to shift the d-band to a lower energy level correspondingly, thereby to reduce the adsorption energy of ORR intermediates with compromising the activation of O$_2$ molecule based on BEP principle. [94] For Fe-4pN with pyridine ligand coordinated in particular, the partial Bade charge (+1.12 |e|) on the active Fe ion was more reasonable compared to Fe-4pN with no molecular ligand and Fe-4pN-OH (+1.22 |e|) with hydroxyl group coordinated, indicating a more optimized activity toward the activation of O$_2$ molecule and the adsorption of OH$^*$ intermediate. The calculated energy barrier for rate determining step (OH$^*$ + 3OH$^-$ + e$^-$ $\rightarrow$ 4OH$^-$) was remarkably reduced to 0.11 eV after the pyridine ligand was introduced, compared to 0.35 eV for ligand-free catalyst (Figure 2b). As a result, the pyridine ligand coordinated Fe single catalysts doped in carbon matrix (Fe SAC/N-C) with less electrons on ion site showed a superior catalysis on ORR reaction at a half-wave potential of 0.89 V in alkaline solution (Figure 2a), around 40 mV higher than that of the commercial Pt/C catalyst.

The functional groups onto the carbon support are able to either modulate the charge density around the metal sites, or act as active sites themselves and lead to a synergistic cooperation with the existing metal sites during the catalytic processes. Co-N$_2$-C was a highly efficient ORR catalyst but had a low selectivity toward H$_2$O$_2$ intermediate. OFGs had a high selectivity toward H$_2$O$_2$ but suffered from the sluggish kinetics in ORR catalytic reaction. Li et al. have introduced OFGs into Co-N$_2$-C to form a
new Co-POC-O catalyst, which successfully combined the merits of Co-N₃-C and OFGs via their synergistic cooperation. The as-prepared Co-POC-O catalyst exhibited a high selectivity over 80% toward H₂O₂, a high activity with a potential of 0.79 V at 1 mA cm⁻², and a remarkable stability for 10.0 h.[106]

### 2.2. M-N-C for Oxygen Evolution Reaction (OER)

Oxygen evolution reaction (OER),[107] as one of the half reaction of water splitting (2H₂O → 2H₂ + O₂)[108–110] is vital to renewable energy conversion technologies, such as water electrolyzers and rechargeable metal-air batteries[111,112] where the OER is driven on the cathode surface during the charging process.[113] The four proton-coupled electron transfer processes (Acidic conditions: 2H₂O → O₂(g) + 4H⁺ + 4e⁻; Alkaline conditions: 4OH⁻ → O₂ + 2H₂O + 4e⁻) indicate an intrinsic sluggish kinetics, which require a high over-potential to break O–H bonds and form O=O bonds.[114] To date, Ir/Ru-based materials are commonly used as electrocatalysts toward OER, whereas their high cost and scarcity severely hinder their widespread applications.[115] It is hence critically important to develop cost-effective, efficient, and highly durable nonprecious-metal-based electrocatalysts to replace noble-metal-based materials. M-N-C-based catalysts, earth-abundant 3d transition-metal (TM) metals involved in particular, have been considered as promising catalysts used in electrocatalytic OER applications (Table 2).[116] Similar to the application of M-N-C in ORR, there are also challenges for the high-performance application in OER, such as high driving force over 1.23 V, undesirable metal loadings, and support stacking, which can be addressed by the strategies of doping, molecular ligand, morphology engineering and etc.

The construction of highly dense M-N active centers without agglomeration in the carbon-based materials is a strategy to attain a remarkable OER performance, which is comparable or even outperform that of Ir/Ru-based materials.[127] Single cobalt atoms anchored on the nitrogen-doped graphene-like carbon support (SCoNC) have been developed by Wu et al., where the Co loadings reached as high as around 15.3%. The SCoNC catalyst exhibited a better OER performance with a smaller potential of 1.54 V at a current density of 10 mA cm⁻² compared to the benchmark IrO₂, (Eₗ₁₀ = 1.62 V), which was attributed to the high density of monodispersed Co-N₄ units as well as the enhanced synergistic cooperation between them.[117] The overpotential of OER on SCoNC materials calculated from Density Functional Theory (DFT) was as low as 0.338 V, which outperformed the IrO₂ catalyst. 3D nanoporous graphene (np-graphene) with large specific surface area provided a practical way to increase the dispersed number of Ni-N₄ active centers (denoted as Ni, N codoped np-graphene), where the loading amount approached 23 wt%.[119] The C atoms adjacent to N ligand became active sites themselves to be involved in stabilizing the O* intermediate in addition to Ni active sites. The free energy difference between O* and *OH intermediates was reduced due to the fact that the interdependence of intermediate adsorption on Ni atoms only was broken, and as a result, the Ni, N codoped np-graphene catalyst achieved a high OER activity of Eₗ₁₀ = 1.45 V and Eₗ₁₀ = 1.50 V.

The selective doping of heteroatom which can modulate the coordination environment and electronic structure of active metal sites, is practical to change the adsorption behavior of OER intermediates, thereby improving the ultimate performance. For instance, Hou et al. have doped S atoms into Ni-N₄ moieties (S[NiN₄] embedded in the porous carbon (PC) nanosheets, which were synthesized from graphene (EG) foil (S[NiN₄]-PC/EG).[105] As shown in Figure 2c, an excellent OER performance was achieved for this material with a smaller potential (Eₗ₁₀ = 1.51 V) and a higher current density at the full potential range compared to commercialized Ir/C in use. The uneven electron distribution on the Ni-NₓS active sites (Figure 1f) was the major reason to boost the OER performance of S[NiN₄]-PC/EG based on DFT calculations, and as shown in Figure 2d the over-potential for overall evolution of O₂ is only 0.346 V. In addition to in alkaline media, the efforts on pursing promising OER catalyst with high catalytic performance and durability in acidic conditions have become the focus of attention recently, due to the high chemical stability of

| Catalyst        | Reaction | Electrolyte | Onset potential (V vs. RHE) | Overpotential @10mA/cm⁻² [V] | Ref. |
|-----------------|----------|-------------|-----------------------------|------------------------------|-----|
| SiNi₄-PC/EG     | OER      | 1.0 M KOH   | 1.50                        | 1.51                         | [105]|
| SCoNC           | OER      | 1.0 M KOH   | 1.46                        | 1.54                         | [117]|
| HNC-Co          | OER      | 0.5 M H₂SO₄ | 1.28                        | 1.495                        | [118]|
| co-doped np-graphene | OER      | 1.0 M KOH   | 1.45                        | 1.50                         | [119]|
| Fe-NSDC         | OER      | 0.1 M KOH   | -                          | 1.64                         | [120]|
| Pt₁ SAC/VNGNMA  | HER      | 0.5 M H₂SO₄ | 0                          | 0.015                        | [121]|
| Ru@Co-SA5/N-C   | HER      | 1 M KOH     | 0                          | 0.007                        | [122]|
| Ru@Co-SA5/N-C   | HER      | 0.5 M H₂SO₄ | -                          | 0.057                        | [122]|
| Ru@Co-SA5/N-C   | HER      | 1 M PBS     | -                          | 0.055                        | [122]|
| Co@NG-750       | HER      | 0.1 M KOH   | -                          | 0.172                        | [123]|
| Co@NG-750       | HER      | 0.5 M H₂SO₄ | -                          | 0.182                        | [123]|
| Ru-NC-700       | HER      | 0.1 M KOH   | -                          | 0.047                        | [124]|
| Co-SAC          | HER      | 0.5 M H₂SO₄ | -                          | 0.23                         | [125]|
| Ni NP[Ni-N-C]   | HER      | 1 M KOH     | 0.046                       | 0.147                        | [126]|

Table 2. Summary of recently reported M-N-C-based catalysts for OER and HER in acidic, alkaline, and neutral electrolyte.
nitrogen-doped carbon support. Su et al. have coordinated four N atoms and one amino-N ligand with single Co atoms embedded in the carbon substrates to design a HNC-Co heterostructure. This HNC-Co heterostructure can catalyze the evolution of oxygen molecules with a low over-potential of 265 mV at 10 mA cm⁻², around 60 mV lower than that of IrO₂.

2.3. M-N-C for Hydrogen Evolution Reaction (HER)

Hydrogen evolution reaction (HER) is of great practical significance to produce clean and sustainable hydrogen energy during electrochemical water splitting. This process involves a two-electron-transfer reaction, through either Volmer–Heyrovsky mechanism (H⁺ + e⁻ → H_ads, H_ads + H⁺ + e⁻ → H₂) or Volmer–Tafel mechanism (H⁺ + e⁻ → H_ads, H_ads + H_ads → H₂). The kinetics of these two pathways are determined by the free energy of hydrogen adsorption ΔG_H₂/[129] The electrocatalyst with a ΔG_H₂ close to 0 eV, which means the adsorbed H can assist an easy charge transfer and hence desorb as hydrogen,[130] is urgently required. Precious-metal (Pt, Ru, etc.) based catalysts are ideal for HER with a small absolute ΔG_H₂ value. But the high cost and scarcity hamper their extensive applications. M-N-C catalysts, from a perspective of 100% utilization of either noble metal atoms or low cost earth-abundant transition metals, become one of the most promising candidates for HER (Table 2). Recently, Hossain et al. have calculated the catalytic performance of a series of transition-metal-based M-N-C materials toward HER based on DFT modelling. Co–N–C turned out to be the most promising one with the highest HER activity of 0.13 eV.[125] In acidic solution, the overpotential for HER was only 230 mV at a current density of 10 mA cm⁻².

\[
\begin{align*}
H_2O + e^- & \rightarrow H_{ads} + OH^-; & H_{ads} + H_2O + e^- & \rightarrow H_2 + OH^- (1) \\
H_2O + e^- & \rightarrow H_{ads} + OH^-; & 2H_{ads} & \rightarrow H_2 (2)
\end{align*}
\]

Given that the acidic reaction conditions are not favorable for the stability of metal-based materials, the development of low-cost and high-performance electrocatalysts to work in alkaline media has attracted significant attention. Under alkaline condition, the energy barrier for water dissociation[131] along either the Volmer–Heyrovsky (Equation (1)) or Volmer–Tafel pathway (Equation (2)) becomes the rate-determining step in hydrogen evolution reactions. The HER kinetics therefore show diminishing efficiency in alkaline media.[132] To achieve a high HER activity in alkaline solution, one principle method is to engineer the d orbitals of the metal ion centers to hybridize with the Lowest Unoccupied Molecular Orbital (LUMO) of H₂O molecule, and hence to reduce the energy barrier for water dissociation reactions. Following this principle, in Ru, N-codoped carbon nanowires (RuC₃N₄), the RuC₃N₄ moieties (RuC₃N₄-1) with the most optimized d-band center showed an ideal hydrogen adsorption free energy ΔG_H₂ close to zero, compared to RuN₄ and other configurations, and had a low energy barrier for H₂O dissociation (0.59 eV). The overall HER performance of RuC₃N₄-1 catalyst was much superior to the commercial Pt/C in alkaline media, with an overpotential almost near zero (0.047 V).[124]

The metal clusters embedded into M-N-C materials can provide more active sites, modulate the electronic structure of active centers, and boost the HER performance as well. Lei et al. introduced Ni nanoparticles (Ni NP) near the Ni-N₄ moieties in porous carbon matrix (denoted as Ni NP[Ni-N₄-C] as shown in Figure 3a.[126] The electronic coupling between Ni NP and Ni-N₄ moieties increased the d-dominated electron density below the Fermi level (Figure 3b), which was beneficial for the activation of H₂O molecule, and greatly lowered the energy barrier of water dissociation to 0.34 eV (Figure 3c). However, the d-band center at a high energy level also led to a strong adsorption of intermediates and a high energy barrier for H₂* desorption. As a consequence, the Ni NP[Ni-N₄-C] catalyst achieved an improved performance (E₁₀₀₅0 = 46 mV and E₁₀ = 147 mV) toward HER, as shown in Figure 3d, which succeeded to narrow the gap with Pt/C catalyst. The same strategy was also performed in the hybrid Co-SAs/N-C electrocatalyst where metal clusters (Ru, Pt, Pd etc.) were involved.[127] The synergistic interaction between Ru and Co active sites promoted the dissociation of H₂O molecule with a reduced energy barrier compared to the pristine Co-SAs/N-C catalyst. Meanwhile, the Ru active sites facilitated the adsorption of H* intermediate. The overpotentials tested for hydrogen evolution over a full pH range were recorded as 0, 57, and 55 mV in alkaline, acidic, and neutral electrolyte, respectively.

2.4. M-N-C for CO₂ Reduction Reaction (CO₂RR)

The consumption of fossil fuels leads to an increasing CO₂ in the atmosphere and global warming, which has thus imposed a threat on the sustainable development of human society.[133] To alleviate the energy crisis and solve the environmental issues, the conversion of CO₂ molecules into high-value carbon-based products, including carbon monoxide (CO), formic acid (HCOOH), formaldehyde (HCHO), methanol (CH₃OH), methane (CH₄), ethylene (C₂H₄), ethanol (C₂H₅OH), ethane (C₂H₆), and n-propanol (C₃H₇OH), etc., via electrochemical CO₂ reduction reaction (CO₂RR) is becoming a promising technical approach.[134] However, the breach of thermodynamically stable C=O bond in CO₂ needs a high energy cost (806 kJ mol⁻¹), which restricts the efficiency of CO₂RR. Besides, the reduction of CO₂ has a poor selectivity toward high valuable chemicals due to the similar redox potentials. When CO₂RR occurs, the fast kinetics of hydrogen evolution reaction also degrades the CO₂ conversion.[135] Cost-effective CO₂RR catalysts with high intrinsic activity and selectivity, to replace silver[136] and gold-based catalysts[137] are therefore highly desired.[138] M-N-C materials as a promising candidate have opened a great prospect to selectively catalyze CO₂ into CO[139] and other chemicals beyond CO[140] (Table 3). Recently, there are intrinsic factors such as hybrids, polynary M-N-C, defects, and N ligand type/number proposed to improve the selectivity for CO₂RR over HER by enhancing the activation of CO₂ and suppressing the HER, and facilitate the reaction kinetics by lowering the energy barrier of CO desorption.

Möller et al. have explored the inherent CO₂RR performance of pristine Fe–N–C and Ni–N–C catalysts compared to the benchmark of AgO₂.[141] As shown in Figure 4c and 4d, Fe–N–C...
Figure 3. a) Atomic structure of Ni metal cluster loading on Ni-N₄-C. b) Density of states for NiN₄, NiN₄NP₂, and NiN₄NP₂. c) Free-energy diagrams for water dissociation on NiN₄, NiN₄NP₁, NiN₄NP₂, and NiN₄NP₃. d) Polarization curves for HER on EG, Ni NP/EG, Ni-N-C/EG, physical mixture/EG, Ni NP|Ni-N-C/EG, and Pt/C. a–d) Reproduced with permission. [126] Copyright 2019, Royal Society of Chemistry.

Table 3. Summary of recently reported M-N-C-based catalysts for CO₂RR and NRR in acidic, alkaline, and neutral electrolyte.

| Catalyst                  | Electrolyte | Product | Faradaic efficiency | Current density [mA cm⁻²] | Yield rate [μg mg⁻¹ h⁻¹] |
|---------------------------|-------------|---------|---------------------|---------------------------|--------------------------|
| Fe–N–PC                   | 0.5 M KHCO₃| CO      | 90% @ −0.49 V       | 11.44 @ −0.49 V           |                          |
| Ni–SA–NCs                 | 0.5 M KHCO₃| CO      | 99% @ −0.8 V        | 50 @ −1.0 V               |                          |
| Ni–N–C                    | 0.1 M KHCO₃| CO      | 85% @ −0.9 V        | 12 @ −0.85 V              |                          |
| Fe–N–C                   | 0.5 M KHCO₃| CO      | 93.5% @ −0.5 V      | –                         |                          |
| Co₃Pc©Fe–N–C              | 0.5 M KOH   | CO      | 93% @ −0.84 V       | 275.6 @ −0.84 V           |                          |
| Ni/Fe–N–C                 | 0.5 M KHCO₃| CO      | 98% @ −0.7 V        | 23.7 @ −1.0 V             |                          |
| Ni–N₂–V                  | 0.5 M KHCO₃| CO      | 94% @ −0.8 V        | 48 @ −0.8 V               |                          |
| Fe³⁺–N–C                 | 0.5 M KHCO₃| CO      | 90% @ −0.45 V       | 94 @ −0.45 V              |                          |
| Ni SAs/NCNTs             | 0.5 M KHCO₃| CO      | 97% @ −0.9 V        | 41.3 @ −0.9 V             |                          |
| Ni–NCB                   | 0.5 M KHCO₃| CO      | 99% @ −0.68 V       | 6.8 @ −0.68 V             |                          |
| SA-Mo/NPC                | 0.1 M KOH   | NH₃     | 14.6 ± 1.6% @ −0.3 V| 34.0 ± 3.6 @ −0.3 V       |                          |
| SA-Mo/NPC                | 0.1 M HCl   | NH₃     | 6.8 ± 0.3% @ −0.25 V| 31.5 ± 1.2 @ −0.25 V      |                          |
| iSAS-Fe₂/NC              | 0.1 M PBS   | NH₃     | 18.6 ± 0.8% @ −0.4 V| 62.9 ± 2.7 @ −0.25 V      |                          |
| Fe₃₋₄A–N–C              | 0.1 M KOH   | NH₃     | 56.55 ± 0V          | 7.48 @ 0 V                |                          |
catalyst had a more balanced activity toward CO2 molecule activation and *CO desorption compared to Ni–N–C and AgOx catalysts, indicating a less driving force was required to produce CO (Figure 4a,b). Although the similar free energy difference was observed between the first protonation of *CO2 and *H adsorption in Fe–N–C, and Ni–N–C catalysts which theoretically indicated a close value of initial FECO, the relatively superior HER performance and the strong *CO binding on Fe–N–C catalyst led to inferior selectivity (FECO) and a sluggish reaction kinetics. The *CO poison issue for pristine Fe–N–C is not beneficial for the CO production, but on the other hand, it will help the CO2RR toward products beyond CO. On contrary, due to the relatively weaker *H binding and easier *CO desorption, Ni–N–C exhibited a comparable or superior performance to AgOx catalyst, although a large potential was needed to adsorb and activate CO2 molecule. In order to achieve a more balanced CO2 activation and CO intermediate desorption on metal ion centers, some novel strategies have been developed to modulate the electronic structure of metal ion centers or to introduce the synergistic cooperation between active centers.

The effect of N coordination number on the activation of CO2 can be explained by catalytic activity-d-band center relationship, as shown in Figure 4e,f. Due to the electronegativity difference between N (3.04), C (2.55), and Ni (1.91) atoms, the charge transfer Ni ion centers to the neighboring atoms was reduced accordingly with the decreasing N ligand number, indicating an upward shift of Ni d-band center to a higher energy level and an easier activation of CO2 molecule. However, simply shifting up the d-band center of Ni ion center to enhance the activation of CO2 needs to compromise the selectivity for CO2RR since the HER could also be boosted. In addition to the modulation of N coordination number, changing the coordination type of N ligand in M-N-C materials is also an effective strategy to modulate the electronic structure of single metal atoms, and then...
to achieve an optimal catalytic performance for CO\textsubscript{2}RR.\cite{154} Gu et al. have incorporated different types of N ligands to form a variety of Fe–N–C materials where the electronic structure of Fe ions was regulated accordingly to change the final CO\textsubscript{2} electro-
reduction performance.\cite{148} In 0.5 M KHCO\textsubscript{3}, Fe\textsuperscript{3+}–N–C kinetically adsorbed the CO\textsubscript{2} molecules and achieved a FE\textsubscript{CO} over 90% at −0.45 V. The weak binding of *CO to the Fe\textsuperscript{2+} site coordinated by pyridinic N atoms, which was induced by the downward shift of Fe d-band center to a lower energy level compared to Fe\textsuperscript{3+}–N–C containing pyridinic N ligands, brought about a very high current density of 94 mA cm\textsuperscript{−2} at −0.45 V. Shifting down the d-band center of Fe ion center to lower the energy barrier of CO\textsuperscript{*} intermediate desorption can also degrade the HER performance, which is capable of improving both the activity and selectivity toward CO\textsubscript{2} RR.

The hosting environment of Fe–N\textsubscript{4} moieties is also a factor that can be adjusted to modulate the electronic structure of metal catalyst and optimize the electro-catalytic conversion efficiency of CO\textsubscript{2}to-CO.\cite{144} Qin et al. have reported that the synthesized Fe–N\textsubscript{4}pore materials (Figure 12d) were characterized by synergistically interacted Fe–N\textsubscript{4} moiety and defective graphitic layer with nanopores. The defects in the carbon support brought down the d-band center of Fe ion to a lower electronic energy range, and weakened the binding energy of *CO intermediate to Fe active site, which successfully avoided the *CO poison on Fe–N\textsubscript{4} and exhibited a maximum FE of 93.5% and an ultralow overpotential of 90 mV.

Considering the merits of a strong activation of CO\textsubscript{2} on Fe–N–C and an easy desorption of CO\textsuperscript{*} from Ni–N–C (Figure 5c), it was hypothesized that the synergistic cooperation between Fe and Ni ion centers can result in an enhanced CO\textsubscript{2}RR performance. Lin et al. have prepared a catalyst containing isolated diatomic Ni–Fe sites which were anchored on nitrogen-doped carbon materials (Ni/Fe–N–C).\cite{146} As shown in Figure 5c, a post-adsorption mechanism\cite{155} was proposed to occur on the bare Ni/Fe–N–C catalyst due to the *CO poison on Fe ion center (−0.65 eV). Once CO was adsorbed, the following activation of CO\textsubscript{2} molecule and the desorption of CO\textsuperscript{*} intermediate can proceed more smoothly. The Ni/Fe-N-C catalyst with CO\textsuperscript{*} can considerably decrease the free energy barrier of CO\textsuperscript{*} → CO(g) on Fe ion center with less compromise of CO\textsubscript{2} activation, which can greatly reduce the over-potential for CO production and reach a current density of 23.7 mA cm\textsuperscript{−2} at −1.0 V in 0.5 M KHCO\textsubscript{3} (Figure 5b). Differing from Fe–N–C, the less negative energy difference between the RDSs of CO\textsubscript{2}RR (U\textsubscript{R} (CO\textsubscript{2})) and HER (U\textsubscript{R} (H\textsubscript{2})) on Ni/Fe–N–C catalyst also improved the selectivity of CO-adsorbed Ni/Fe–N–C with a high FE\textsubscript{CO} of 98% at −0.7 V (Figure 5a).

The construction of a heterojunction of M-N-C with other 2D materials can modulate the electronic structure of metal active sites in M-N-C by charge transfer along with introducing strong synergistic effect, and alter the ultimate CO\textsubscript{2}RR performance. Lin et al. have hybridized the Fe–N–C catalyst with cobalt phthalocyanine molecule (CoPc©Fe–N–C) through van de Waals interaction, in order to improve the CO\textsubscript{2}RR performance on Fe ion centers.\cite{143} As shown in Figure 5f, the Co active site in the CoPc molecule had a high activity toward activating CO\textsubscript{2} with a ΔG\textsubscript{COOH} close to 0 eV. The relatively more positive limiting potential difference (U\textsubscript{R} (CO\textsubscript{2}) − U\textsubscript{R} (H\textsubscript{2})) led to a high selectivity for CO\textsubscript{2} conversion over HER. Moreover, the energy barrier for *CO desorption on CoPc (0.25 eV), was much smaller than that on Fe–N–C catalyst (1.08 eV), indicating a high reaction rate in the former. The beneficial synergistic cooperation of strong CO\textsubscript{2} activation on Fe active site and a high selectivity toward CO\textsubscript{2}RR on Co active site in the CoPc©Fe-N-C heterojunction resulted a high FE\textsubscript{CO} of 93% at −0.84 V (Figure 5d).

Meanwhile, due to that the electrons transferred from Co active sites helped to remove the *CO poison on Fe ion centers in CoPc©Fe–N–C catalyst, so a maximum CO current density of 275.6 mA cm\textsuperscript{−2} at −0.84 V was achieved (Figure 5e). Therefore, hybrids making the best of synergistic effect are an effective way to enhance both activity and selectivity toward a specific reaction.

### 2.5. M-N-C for Nitrogen Reduction Reaction (NRR)

The production of ammonia (NH\textsubscript{3}) is of great importance to global agriculture, chemical industries, and energy storage.\cite{156} However, the strong triple bond and the large energy gap (10.82 eV) to activate N\textsubscript{2} molecule (Figure 6a),\cite{157} prohibit a large production of NH\textsubscript{3}. The production of NH\textsubscript{3} needs extremely harsh conditions (400–600 °C, 20–40 MPa) by first cleaving the triple N≡N bond completely and then hydrogenating the single adsorbed N atom to form NH\textsubscript{3}, which also leads to CO\textsubscript{2} pollution.\cite{158} Inspired from the fact that nitrogen in bacteria can be electro-reduced under ambient conditions with the help of enzyme nitrogenase, the electrochemical reduction of nitrogen to form NH\textsubscript{3} via a six-proton-electron process (N\textsubscript{2} (g) + 6H\textsuperscript{+} + 6e\textsuperscript{−} → 2NH\textsubscript{3}(g)) becomes a prospective alternative to the conventional Haber–Bosch process (Figure 6d).\cite{159} Nevertheless, the first protonation of adsorbed N\textsubscript{2} ( *N\textsubscript{2} + H\textsuperscript{+} + e\textsuperscript{−} → *NNH) is the potential-determining step due to the inherent nature of strong N≡N bonds. At a similar potential, nitrogen reduction reactions become incompetent with the hydrogen evolution reactions as the active metal sites prefer to evolve hydrogen rather than to protonate the adsorbed dinitrogen.\cite{160} Both these factors lead to a poor selectivity for NRR, inferior faradaic efficiency (FE), and low NH\textsubscript{3} yield rate.\cite{161} To overcome these shortcomings, as shown in Table 3, non-precious-metal-based M-N-C catalyst is a superior candidate with a relatively high selectivity and yield rate toward NRR.\cite{162} Currently, research mainly focuses on the exploration of pristine M-N-C catalysts to strongly activate N\textsubscript{2} molecule over HER for a progressive selectivity and production toward NH\textsubscript{3} in acidic, alkaline, and neutral electrolyte, which inherently depends on the nature of metal ion centers.

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As shown in Figure 6b, Han et al. have fabricated N-doped porous carbon with dispersed Mo single atoms (SA-Mo/NPC).\cite{151} The loading density of Mo-N\textsubscript{4} active sites in SA-Mo/NPC was as high as 9.54 wt%. Due to the intrinsically high activity of Mo active center toward N\textsubscript{2} activation, the high density of atomically dispersed Mo active sites in SA-Mo/NPC, in addition to the hierarchically porous morphology that guaranteed the homogeneity of activity and selectivity and promoted the mass.
Figure 5. a) CO faradaic efficiency (FE CO) and b) CO partial current density (i CO) on Ni/Fe–N–C, Ni–N–C, and Fe–N–C. c) Free energy profiles for CO 2RR on Ni–N–C, Fe–N–C, Ni/Fe–N–C, and Ni/Fe–N–C with CO*. a–c) Reproduced with permission.[146] Copyright 2019, Wiley-VCH. d) j CO and e) FE CO on CoPc©Fe–N–C, CoPc©Zn–N–C, Fe–N–C, Zn–N–C, and Co/Fe–N–C. f) Free energy profiles for the CO 2RR to CO at U = −0.7 V versus RHE on the Fe site in CoPc©Fe–N–C, Fe site in Fe–N–C, Co site in CoPc©N–C, and Zn site in CoPc©Zn–N–C, respectively. d–f) Reproduced with permission.[145] Copyright 2019, Wiley-VCH.

transfer during the reaction, SA-Mo/NPC catalyst gave rise to a high NH3 yield rate of 34 ± 3.6 μgNH3 h−1 mg−1 cat. and faradaic efficiency of 14.6 ± 1.6% at −0.3 V in 0.1 M KOH (Figure 6c), which were comparable to or outperform that of Au/Ru-based catalysts.[163,164]

To elucidate the intrinsic superiority of Mo–N–C catalyst, the first protonation of N2 on Mo–N–C catalyst (RDS) was calculated based on DFT methods. The energy barrier of RDS was small at 0.50 eV[163] and the calculated energy difference between ΔG*NNH and ΔG*H was 0.01 eV. The final NRR selectivity was about 40% toward the first protonation of di-nitrogen on Mo-N-C catalyst according to Equation (3). Theoretical calculation also predicted that the energy difference (ΔG*NNH − ΔG*H) on Cr–N–C catalyst was −0.35 eV, corresponding to a nearly 100% NRR selectivity over HER at room temperature. Cr–N–C can be regarded as a promising non-precious-metal-based candidate to replace the Au/Ru-based catalyst toward NRR.

In addition to promoting the intrinsic selectivity and activity on catalyzing N2, to suppress the side reaction on M-N-C catalyst has become another way to improve the faradaic efficiency of N2 conversion. Li et al. have prepared single-atom dispersed Fe–N–C (FeSA–N–C) catalyst, and in alkaline medium, due to a high energy barrier (2.91 eV) of water dissociation, protons hardly involved in the adsorption on Fe–N–C catalyst. Moreover, the HER efficiency was further diminished because of the energy barrier of H* intermediate desorption. In contrast, the N2 activation was greatly promoted in alkaline solution, when the N2 adsorption on Fe–N–C catalyst was thermodynamically activated (−0.28 eV). As
Figure 6. a) N$_2$ molecular orbital. Reproduced with permission.$^{[157]}$ Copyright 2014, Royal Society of Chemistry. b) The atomic structure of Mo-N$_3$-C catalyst in porous architecture. c) NH$_3$ yield rate (red) and FE (blue) at each given potential. Reproduced with permission.$^{[151]}$ Copyright 2019, Wiley-VCH. d) Schematic depiction of distal, alternating, and enzymatic pathways for NRR. Reproduced with permission.$^{[159]}$ Copyright 2018, Wiley-VCH.

a result, Fe$_{3-x}$N–C demonstrated a superior faradaic efficiency of 56.55% and a desirable ammonia yield rate of 7.48 $\mu$g h$^{-1}$ mg$^{-1}$ at 0 V in alkaline solution.$^{[153]}$

2.6. M-N-C-Based Materials for Bioinspired Enzyme Catalysis Reactions

Nanozymes, with advantageous and intrinsic enzyme-like characteristics, are promising alternatives to natural enzymes.$^{[168]}$ Given the resemblance between the homogeneous MN$_x$ sites in M-N-C SACs and natural metalloenzymes, especially in terms of their electronic, geometric, and chemical structures (Figure 7),$^{[169]}$ it is hypothesized that M-N-C SACs can mimic natural enzymes to act as single-atom-based enzymes (SAzymes) for both biological and engineering applications. Most importantly, the atomically dispersed metal sites in SAzymes can be easily realized and characterized, which helps to shed light on fundamental science and mechanism toward the understanding of structure–activity relationship of nanozymes. To data, M-N-C-based biocatalysts, featured with either oxidative-like activities by forming reactive oxygen species (ROS) or anti-oxidative behaviors for ROS scavenging, have been synthesized. The applications of the bioinspired M-N-C nanozymes, including sensing, environmental protection, cancer treatment, wound healing, and cytoprotection, have been explored (Table 4). It is not difficult to forecast that bioinspired M-N-C nanozymes will be an emerging class of high-performance catalysts for biocatalysis.

2.6.1. M-N-C-Based Nanozymes for Environmental Protection

With growing concerns about the pollution to environment, effective control and degradation of the organic pollutants in wastewater, such as biodegradation treatment using natural enzymes, have become an urgent requirement.$^{[179]}$ The reactive oxygen species (ROSs) generated from natural enzymes, such as hydroxyl ($\bullet$OH) and superoxide ion radicals (O$_2^-$) which possess high redox potentials, can degrade many organic pollutants into insoluble precipitated products, and even CO$_2$ and H$_2$O through advanced oxidative processes (AOPs)$^{[180,181]}$. The limitations of natural enzymes, however, are obvious, such as easy deactivation, high cost, and non-cyclability. Bioinspired nanozymes with similar active sites and selectivity to natural enzymes have the potential to become an ideal replacement for natural enzymes in engineering applications, due to their catalytic activities, long-term stability, low cost, and recycling capabilities. One typical example is that M-N-C-based ROS generator has showed higher catalytic efficiency compared with conventional nanozymes.$^{[43]}$

Zhao et al. have proposed single Fe atoms on N-doped carbon nanomaterials (Fe SAEs) to mimic heme-containing natural enzymes. This material exhibited an excellent peroxidase-like activ-
ity to spontaneously dissociate H$_2$O$_2$ and generate hydroxyl radical (\(\cdot\)OH) species\[^{166}\]. The aggressive \(\cdot\)OH radical was able to extract hydrogen from stubborn organic pollutants and degrade them, which was extremely useful in environmental protection. Based on DFT calculations, the whole process was thermodynamically favored with an energy change of $-2.80$ eV. Additionally, Fe SAEs also displayed remarkable oxidase and catalase enzyme-like activities. Wang et al. have synthesized a Fe-N$_5$/C-CNT nano-material which exhibited a high oxidase-like activity toward the adsorption of O$_2$ molecule ($-2.77$ eV).\[^{171}\] The O$_2^-$ radical, which was generated during the reaction process, can effectively oxidize organic substrates such as tetramethylbenzidine (TMB). When the N coordination number was 5, the single-atom nanozymes of carbon nanoframe-confined axial N-coordinated single-atom Fe (FeN$_5$ SA/CNF), can mimic the axial ligand-coordinated heme of cytochrome. Due to this structural similarity,\[^{182}\] the filling of anti-bonding $\pi^*$ orbital in O$_2$ molecule as a result of the electron push effect of the axial-coordinated N in MN$_5$ SA/CNF (M = Fe, Mn, Co) led to a strong adsorption of O$_2$ and dissociation of O=O bond. An outstanding oxidase-like activity can be attained.

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**Figure 7.** a) The active sites of natural enzymes, nanozymes, and Fe SAEs. Reproduced with permission.\[^{166}\] Copyright 2019, Royal Society of Chemistry. b) The active centers in cytochrome P450, horseradish peroxidase. Reproduced with permission.\[^{167}\] Copyright 2019, AAAS.
17 times higher than FeN4 catalyst and 70 times higher than commercial Pt/C.[167]

2.6.2. M-N-C-Based Nanozymes for Chemical Sensing

H2O2 Detection is of chemical and genetical importance in biology, medicine, food industry, and environmental protection.[185] By monitoring the production of the oxidized substrate, which is catalyzed by mimicking peroxidase, H2O2 can be measured. Horseradish peroxidase (HRP) is commonly used to detect H2O2 due to its excellent catalytic activity and selectivity, but its limit is also obvious as a natural enzyme. To date, nanozymes have been extensively explored as the alternatives to natural peroxidase.[184] For example, Fe3O4 nanozyme exhibited an intrinsic peroxidase-mimicking activity by oxidizing the substrate. H2O2 was detectable by observing the color change during the oxidation process.[185] However, the efficiency of Fe3O4 magnetic nanoparticles needed to be enhanced to be competitive with HRP.[186]

Owing to the superior peroxidase-like performance in acidic media, Fe–N–C supported on carbon nanotube (CNT/FeNC) can help to sense H2O2 once the color was changed from colorless to blue in TMB catalytic reaction (TMB [colorless] + H2O2 $\rightarrow$ oxidized product $\rightarrow$ oxidize target of interest (oxTMB [blue] $\rightarrow$ H2O2).[175]) If other oxidase, such as glucose oxidase, was involved, which can convert O2 into H2O (Glucose + O2 + H2O $\rightarrow$ Gluconic acid + H2O2), the corresponding oxidase substrate (Glucose) can thus be detected. Furthermore, by utilizing the oxidized product to oxidize targets of interest (oxTMB [blue] + AA $\rightarrow$ TMB [colorless] + dehydro AA), the SAzymes can also sense molecules like ascorbic acid (AA) and glutathione (GSH) from the color change.[176]

2.6.3. M-N-C-Based Nanozymes for Therapeutics

The reactive oxygen species (ROS) produced during the catalytic reaction can be utilized to combat bacteria. Recently, by catalyzing O2 molecule to form ROS, FeN4 SA/CNF[167] helped to induce oxidative damage to the membrane integrity of bacteria and then promote wound healing. Likewise, Zn–N–C SAC can inhibit the growth of *Pseudomonas aeruginosa* up to 99.87%. The extremely high anti-bacterial effect in Zn–N–C was attributed to the coordinatively unsaturated Zn–N4 active sites, which exhibited a high peroxidase-like performance to decompose hydrogen peroxide (H2O2) and form •OH radical by mimicking natural metalloenzymes.[170] During the whole reaction process, the energy barrier of rate-determining step was 0.24 eV, that can be easily realized under ambient conditions.

Similarly, ROS generated during catalytic reaction can induce cell apoptosis in tumor.[187] The lack of nanocatalysts which are able to generate sufficient toxic ROS has hindered the development of tumor therapy. Recently, Fe–N–C was employed to enhance the efficacy in tumor therapy by catalyzing the Fenton reaction, wherein the energy barrier of rate-determining step was only 0.31 eV in acidic medium, and hence H2O2 molecules were easily decomposed to produce abundant hydroxyl •OH.[172]

On the other hand, if ROS was abnormally elevated during cell metabolism, it will, to some extent, induce oxidative damage to cell. Therefore, to remove excess ROS and to maintain intracellular redox homeostasis, the catalase, glutathione peroxidase, and superoxide dismutase-like nanozymes can be imported.[188] Single iron atoms anchored on N-doped porous carbon (Fe SAs/N C) has turned out to be an efficient antioxidant for cytoprotection. On one hand it can implement superoxide dismutase-like activity to convert superoxide ion radicals (O2−) into H2O2 and O2, on the other hand mimic catalase to decompose H2O2 into H2O and O2. In this way, Fe SAs/N C acted as a bifunctional SAzyme to reduce the excessive ROS level in cell.[178]

2.7. M-N-C for Other Applications

Except for the applications mentioned above, M-N-C materials have been explored in CO oxidation,[189] selective organic reactions,[190] lithium–sulfur (Li–S) batteries,[191] and pollutant removal[192] due to their intrinsically high activity and selectivity as single atoms catalysts, high stability derived from the strong bonding between N ligand and metal ion centers, and advantages from carbon support including high chemical stability against acid corrosion, high specific surface area, and tunable mechanical and electronic characteristics.

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Table 4. Summary of recently reported M-N-C-based nanozymes for various biological applications.

| SAzyme | Mimicking activity | Application | Ref. |
|--------|--------------------|-------------|------|
| Zn–N–C | Peroxidase         | Wound healing | [150] |
| FeN4 SA/CNF | Oxidase           | Wound healing, environmental protection | [147] |
| Fe–N/C–CNT | Oxidase           | Environmental protection | [147] |
| Fe SAEs | Peroxidase, oxidase, catalase | Environmental protection | [146] |
| PSAF NCs | Fenton-like       | Tumor therapy | [172] |
| Fe–N+GO | Peroxidase         | H2O2 detection | [173] |
| Fe–N–C | Peroxidase         | H2O2 detection | [174] |
| CNT/FeNC | Peroxidase      | Molecules detection | [136] |
| Fe–N–C | Oxidase            | Cytoprotection | [137] |
| Fe–C   | Glutathione peroxidase, catalase | Cytoprotection | [147] |
| Fe–SAEs/NC | Superoxide dismutase, catalase | | [178] |
For instance, Du et al. have proposed the mono-dispersed Co catalysts anchored on a nitrogen-doped graphene (Co–N/G) as a cathode in Li–S batteries. The homogeneity of Co ion centers, which was inherently similar to homogeneous catalysts characterized by high activity and selectivity, can improve the kinetics of Li2S formation and decomposition in discharge and charge processes, respectively. The large surface area and high chemical stability of Co–N/G allow for a high S utilization even at an overwhelming S mass ratio of 90 wt%. Simultaneously, Co–N/G was energetically more favorable to adsorb Li2S8 rather than S, Li2S2, and Li2S, which can efficiently avoid the shuttling effect of Li polysulfides. The gravimetric Li capacity that can be delivered by S@Co-N/G composite was as high as 1210 mAh g\(^{-1}\). Zhou et al. have synthesized the mono-dispersed Pd atom catalysts on nitrogen-doped graphene (Pd1/N-graphene). Due to the 100% atomic utilization of Pd catalysts with high inherent hydrogenation activity, and selectivity, Pd1/N-graphene achieved a high acetylene (C2H2) conversion efficiency of 99% under photothermal heating. Moreover, the low adsorption energy (-0.26 eV) of ethylene and the high hydrogenation energy barrier (1.17 eV) of converting ethylene to ethanol facilitated the production of ethylene at a high selectivity of 93.5% at 125 °C.

3. General Material Design Strategies for M-N-C Catalysts

In light of recent theoretical and experimental progress for M-N-C-based catalysts in diverse fields, the main principle to design and further improve their catalytic performance lies in precisely controlling the extrinsic and intrinsic factors associated with active centers, which is correlated with population/accessibility of metal ion centers, electronic structure of metal ion centers, and the synergistic effect between active sites. In order to develop instructive strategies and perceptions for future design of high-performance M-N-C-based catalysts and other novel 2D catalysts, we focus on how the design strategies toward metal ion centers, coordinative environment, and carbon support enhance the catalytic performance in this section.

3.1. Rational Design of Metal Ion Centers

The intrinsic activity of a given catalyst is primarily governed by the nature of metal species, from where metal-dependent descriptors to interpret the relationship between the properties of active center and the catalytic activity have been developed. Most catalytic activities, including the reactant activation and intermediate adsorption, are intrinsically originated from the electronic coupling between the catalysts and adsorbates. Some theoretical parameters of metal catalysts such as d-band center, chemical potential filling, and valence band have thus been proposed for the scaling relation to the adsorption strength of reactants/intermediates on the metal surface.

As shown in Figure 8a, the d-band theory was used to explain the origin of electrochemical activity, the valence orbital of transition metal catalysts can split into bonding (σ) and antibonding (σ\(^*\)) orbitals.

Figure 8. a) The orbital hybridization between d band of metal catalyst and s band of hydrogen (σ = bonding, and σ\(^*\) = antibonding state orbital). b) The linear relationship between Gibbs free energy (ΔG\(_{\text{H}}\)) and antibonding state. c) The orbital hybridization of metal atom and OH adsorbate. E\(_F\) is the Fermi level. d) The descriptor \(\varphi\) versus ΔGOH and the center of anti-bonding orbital E\(_{\text{anti}}\).
antibonding ($\sigma^*$) orbitals after catalyst-hydrogen hybridization. The higher the d-band position of metal species, the higher the antibonding ($\sigma^*$) orbital was occupied by less electrons, which corresponded to a stronger hydrogen adsorption on active sites, and correspondingly, a smaller hydrogen adsorption free energy ($\Delta G^*_H$). Therefore, the energy of antibonding state ($E^*_j$), which was in a linear relation to $\Delta G^*_H$, became an efficient descriptor for the hydrogen evolution reaction (Figure 8b). From this scaling relationship, the best HER performance ($\Delta G^*_H = 0$) on volcano plot corresponded to the optimal d-band center of metal ion centers so that the hydrogen adsorption was neither too strong nor too weak.

Similarly, as shown in Figure 8c, the descriptor stemmed from d-band model was also applied to the coupling between metal atom catalyst and intermediate OH species, which was the key intermediate in ORR. With the downward shift of the energy level of d-band center, more electrons occupancy in the anti-bonding orbital as a result of catalyst-OH hybridization led to a reduced OH adsorption (Figure 6d). Hence some volcano plots associated with descriptors are developed to provide valuable guidance for efficient computational screening and experimental design. Moreover, Xu et al. have developed a universal descriptor, $\varphi$, which can directly connect the catalytic activities of ORR/OER/HER with the fundamental natures of active centers, such as, the electronegativity of metal atom, the number and types of coordinative atoms of active centers. It is critical for the selection and modulation of metal ion centers that the optimized electronic configuration is enabled in the active ion and it is able to approach or surpass the peak of volcano.

Nevertheless, volcano plots based on descriptors developed so far are limited to linear scaling relationships including linear free energy (LFER) relationships and Brønsted–Evans–Polanyi (BEP) relationships, wherein the adsorption free energies of reaction intermediates are involved. According to the Sabatier principle, the most optimal catalysts approaching the top of volcano curve indicate a binding energy to the key intermediates neither too strong nor too weak and hence have a balanced binding energies to reactants and key intermediates. However, the independence of adsorbrates makes it impossible to achieve an ideal catalyst to catalyze the reactions without driving force. To design the next generation of M-N-C based catalysts, main efforts can be exerted on breaking energy scaling relationships by simply optimizing the binding of one intermediate only without compromising the others, and surpassing the top of volcanoes.

One practical approach is to relay two active sites and divide the multiple proton/electron transfer reaction into two independent ones, thus in this way to bypass the scaling relations and optimize the catalytic performance. Fe–N–C catalyst was one instance out of this as nitrogen atoms can act as active sites to generate CO molecules, while Fe atoms contributed to CO re-adsorption and the formation of hydrocarbon. Another method is to adjust hydrogen redox potential to approach the equilibrium potential for target multiple proton–electron transfer reaction if hydrogen acceptor/donor functionality can be introduced in the vicinity of active site. The rate-determining step will then be avoided with an alternative mechanism and the limitations restricted by the linear scaling relations can be removed. For instance, Busch et al. have incorporated different organic donors (R–COOH, R–OH, and R–NH$_2$) near the active site of M-N-C catalysts. Due to the favorable redox potential of R–COOH (1.05 eV), the combination of MnN$_4$ and R–COOH presented the best ORR and OER performance to avoid the problematic step ($^* = O + H_2O \rightleftharpoons – \text{OOH} + H^+ + e^*$) by an alternate route ($^* = O + R – \text{COOH} + H_2O \rightleftharpoons \text{\text{~R–COOH} +} O_2 + H^+ + e^*$) and successfully achieved a lower overpotential than the 0.4 V limit.

The catalytic activity of catalysts is also correlated with the population of active sites accessible. For example, the current density, $j$, of an electrode made of catalyst can be written as:

$$j(U) = i(U) \cdot \frac{S \cdot m \cdot \zeta}{A}$$

where $U$ is the electrode potential, $\zeta$ is the number of exposed active sites, and $S$ is the specific surface area. It is clearly that the electrode current density can be promoted linearly by increasing the number of active units. Additionally, synergistic effect raised from the active sites and their neighbors is able to enhance the intrinsic activity of catalysts. As a typical example, the construction of bimetallic or multimetallic M-N-C not only increases the density of active sites, as shown in Figure 9a, where Fe and Ni both can be the active sites for CO$_2$ conversion, but induce synergistic effect between metal sites adjacent to each other, and thus facilitate chemical reactions. As shown in Figure 9b, the length of O=O bond was elongated by the synergistic effect, demonstrating a strong activation of O$_2$. As a result, this synergistic effect has contributed to a good balance between the activation of O$_2$ and the adsorption of intermediates compared to single metallic M-N-C catalysts, leading to a thermodynamically favoured reaction without driving force (Figure 9c).

Still, the loading of dispersive metal sites in nitrogen doped carbon synthesized in the labs is quite low compared to that in conventional noble metal-based catalysts, such as commercial Pd/C and Pt/C catalysts with 30 and 20 wt% respectively.
The limited loading available in M-N-C catalysts leads to an undesired power/current density for their commercial application in energy conversion and storage technologies. The precise controlling of synthetic conditions to achieve a high homogeneity and high loading of M-N active centers at a low cost and high yield therefore becomes critical. While increasing the number of active centers, the aggregation or the leaching of single atoms (SAs) in M-N-C catalysts is sensitive to temperature, pH, solvent, potential, etc., which poses another great challenge for current “bottom-up” or “top-down” synthetic methods. For example, Electrochemical potential (U), as one of the leading factors in driving the reaction processes on M-N-C catalysts, can be unfavorable to the thermodynamical stability of SAs. The aggregation of SAs to form nanoparticles or the leaching of metal ion centers from N-C support can take place spontaneously at potentials when the binding energy of metal atom to the support is lower than the cohesive energy of bulk metal or the free energy of leaching process becomes negative. Hence, aiming to increase the loaded metal centers, it is also crucial to develop novel synthetic methods to further thermodynamically stabilize the loaded single metal atoms and kinetically confine their migration at the same time through rationally designing the coordinative environment and carbon support, in addition to delicately tailoring the nature and reactivity of metal ion center.

Therefore, to enhance the catalytic activity of M-N-C materials, we should perform rational design on the metal ion centers to meet the design principles of: i) increasing the population of single metal ion centers and their accessibility as well that can extrinsically enhance the catalytic performance of M-N-C materials, and intrinsically boost the unit activity and selectivity through the synergistic cooperation between neighboring active sites; ii) selecting the metal species with optimal electronic structure that is able to stimulate the activation of reactant and the desorption of intermediates, and effectively suppress the side reaction; iii) constructing multi-metallic active centers wherein the charge transfer between the neighboring metal sites and their synergetic operation can be adjusted, and in this way to enhance the activity and selectivity of M-N-C materials.

3.2. Rational Design of Coordinative Metal Environment

M-N-C single-atom catalysts, wherein the metal species are surrounded by electronegative nitrogen atoms, are not only stabilized in this way against aggregation, and acid etching, but the chemical natures of the metal centers are crucially affected by charge transfer, and the overall catalytic performances are tuned in the end. Therefore, by changing the coordinative environment, such as the coordination number or the coordinative types of atoms, the affinity of catalysts for reactants and intermediates will be adjusted accordingly, so is the catalytic performance which can be optimized for any given reaction.

The electronic structure of metal atoms involved in catalytic activities can be modulated by the surrounding N number/type. Wang et al. have prepared two types of catalysts, Co-N₄ and Co-N₂. The d-band center in Co-N₄ catalyst with less N number has shifted upward compared to the case in Co-N₄, which was beneficial to the activation of CO₂, as shown in Figure 10a,b. However, as shown in Figure 10c, the reduced occupation of the antibonding orbital led to an unfavorable CO desorption. Contrary to d-band center model, p-band center (eₚ) of main group metals plays a key role in the catalytic performances of M-N-C catalysts. Taking Mg-N-C for example, after the coupling between p-band metal and OH species, the energy level of eₚ resonance state which was up to the eₚ, affected the adsorption of OH intermediate (Figure 10d). Through regulating the N coordination number as shown in Figure 10e, the Mg-Nₓ-C catalyst had the higher eₚ compared to Mg-Nₓ-C and Mg-Nₓ-C catalysts. As a result, the higher p-adsorbate resonance state in Mg-Nₓ-C-OH indicated a less stabilized Mg–OH bond and a weakened intermediate OH adsorption, indicating an easy desorption of OH⁺ species.

Heteroatom doping, which breaks the original balance of the electron density distribution among N atoms, the dopants, and the metal atoms due to their electronegativity difference, is also a practical strategy to alter the electronic structure and activity of metal ion centers and the overall catalytic performance of M-N-C catalysts. As shown in Figure 10f, the S atom doped into Ni–N₄ moieties (Ni–N₄S) acted as an electron donor derived from the electronegativity difference between N (3.04), S (2.58), and Ni (1.91) atoms. The electrons that were transferred from Ni atom the coordinative N atoms were reduced in Ni–N₄S (0.91 e⁻) compared to 1.08 e⁻ in Ni–N₄ model. In other words, the introduction of S dopants can shift up the energy level of Ni d-band center to a higher energy level compared to pure N ligand model (Figure 10g), which strengthened the adsorption of O intermediate and OH intermediate. The energy barrier of rate-determining step (ΔG_{O} − ΔG_{OH}) for OER reaction was reduced accordingly so was their overpotential (Figure 10h).

The electronic structures of M-N-C catalysts can also be manipulated by hybridizing molecular ligands on the metal ions, which will alter the charges transferred between the metal ion center and molecular ligands, regulate the d-band state of metal active site, and modulate the final catalytic activity. For instance, Su et al. have designed a HNC-Co catalyst by coordinating the Co-Nₓ moieties with amino-N ligand. It was noticed that there was an increase of density of states (DOSs) for the HNC-Co catalyst across the Fermi level as shown in Figure 10i, which was originated from the charge transfer from the adsorbed ligand to the Co active center, and in turn, the activation of H₂O molecule and the afterward adsorption of intermediates were both enhanced (Figure 10j). As a result, the free energy barrier (ΔG_{O}) of the aO intermediate formation (“OH → aO + H⁻ + e⁻”), which was the rate-determining step for OER, was reduced to 1.43 eV (Figure 10k).

Based on the above discussed cases, rational design of coordination metal environment is very critical. On the way to achieve an enhanced catalytic performances of M-N-C catalysts, we should follow the design strategies by engineering i) the coordination number of N atoms; ii) the nature of N atoms such as pyridinic/pyrrolic N; the types of iii) doped heteroatoms and iv) molecular ligand. The electronic structure of metal ion centers will be modulated accordingly by charge transfer, and ligand itself or/and carbon atoms modulated by ligand that can be active sites could induce beneficial cooperation effect with metal ion centers.
Figure 10. Total and projected DOS for a) Co–N₂ and b) Co–N₄. c) Free energy profiles for CO₂ RR on Co–N₂ and Co–N₄. a–c) Reproduced with permission.[214] Copyright 2018, Wiley-VCH. d) The orbital hybridization between OH molecular orbitals and p-band of Mg atoms. e) The Mg–N–C with different N number that tunes ϵ_p of Mg ion centers, and the corresponding DOS after orbital hybridization. d,e) Reproduced with permission.[215] Copyright 2020, Nature Publishing Group. f) Calculated population distributions for Ni–N₃S model. g) Calculated projected DOS for Ni–N₄, Ni–N₃S, and Fe₂O₃ models. h) The volcano plot of the overpotential η vs. the free energy difference (ΔG_O – ΔG_OH) for OER on N–S, Ni–S, Ni–N₄, and Ni–N₃S models. f–h) Reproduced with permission.[105] Copyright 2019, Nature Publishing Group. i) Calculated DOS for conductive carbon paper (CP) and HNC–Co. j) Adsorption energy of H₂O and formation energy of *O intermediate for CP, IrO₂, and HNC–Co. k) Free energy diagram for OER on HNC–Co. i–k) Reproduced with permission.[118] Copyright 2019, American Chemical Society.
3.3. Rational Design of Carbon Support

In addition to the metal ion centers and their coordinative environment, the modulation of either the morphology of the carbon support or the catalyst-support interaction also plays an important role in enhancing the catalytic performance of M-N-C materials. As the most popular platform for catalyst, graphene has a high electrical conductivity stemmed from its conjugated \( \pi \) orbitals, and a large specific surface area to allow for a high loading of exposed active centers, which is beneficial to the widespread application of single atom catalysts. Furthermore, graphene can be easily modified to tune the electronic coupling between the metal catalyst and the carbon support, and the electronic structure of metal active sites. Then the catalytic activity of the supported catalyst can be adjusted correspondingly.

Single layered graphene is promising as a catalyst support, but the irreversible stacking of 2D graphene as a result of \( \pi-\pi \) interaction would block the accessibility of the active sites and the mass transport, thus posing a negative impact on catalytic performance. To conquer this problem, 3D morphology of carbon-based support with abundant interconnected pores (macropore, mesopore, and micropore) is built to prevent the aggregation of active sites, to promote the adsorption of reactants, and to facilitate the diffusion of products, and in turn a high current density (Equation (4)) and fast reaction kinetics are accessible (Figure 11).

The incorporation of diverse functionalities, either as electron donor or acceptor is a practical way to modify the nature of delocalized \( \pi \)-band in the carbon support, so is the d-band center position of the metal atoms through support-catalyst interaction, which is intrinsically correlated with the kinetic activity of M-N-C catalysts (Figure 12a). For example, the thiophene-like S (C-S-C) functionality in carbon support supplied excessive electrons to the \( \pi \) orbitals of carbon, and furthermore lifted the d-band center of Fe-ion to a higher level, which led to a stronger adsorption of ORR intermediates compared to the pristine Fe–N–C catalyst. Hence the excess electrons from thiophene-like S functionality (C-S-C) despaired the ORR activity of Fe-N\(_x\) site. Conversely, the oxidized S functionality (C-SO\(_x\)) withdrew electrons from the carbon support, and in this way the d-band center of metal atoms shifted down to a lower energy level, which consequently enhanced the ORR activity (Figure 12b).

In addition to morphology and doping, defect engineering, which can produce under-saturated carbon atoms and induce charge redistribution in carbon support, alters the electronic structure of single metal catalyst and modulates the catalytic activity. In Figure 12c, the d-band center of the Fe-N\(_x\) catalyst has shifted downward after introduction of defective graphene support. Consequently, the adsorption of CO\(_2\) reactant and CO intermediate was reduced. The shortcoming of CO* species poison on bulk-Fe–N\(_x\) catalyst was overcome with compromising the activation of CO\(_2\) molecule on Fe–N\(_x\)-pore catalyst (Figure 12d).

Hybridizing carbon support with other 2D materials through van der Waals interaction also can modulate the d-band of metal active center, and optimize the catalytic performance of M-N-C by means of electronic scale synergistic cooperation. As shown in Figure 12e,f, the charge transfer between the CoPc molecule and Fe–N–C catalysts increased the charge density around Co and Fe active sites, and shifted up the d-band center of both Co and Fe ion centers to a higher energy level, which actually impaired the inherent activity toward the desorption of CO* and the intrinsic selectivity on both Co and Fe active centers, due to the enhanced adsorption of CO* and H* intermediates. However, the synergis-
tical cooperation of valence electron on Co and Fe active center promoted the CO$_2$RR performance. In detail, the Co-3d electrons in CoPc molecule were involved in reducing the energy barrier of CO release and suppressing other side reactions occurred on Fe active sites, and meanwhile the Fe-3d electrons played a dominative role on activating CO$_2$ molecule, which exhibited a clear synergistic cooperation to promote the CO$_2$RR performance with a high selectivity and a high current density.[145]

In general, an ideal carbon support should meet the design principles of i) guaranteeing the homogeneity of loaded active centers, allowing for the high density and expose of active sites, stabilizing the carbon support from stacking, and improving the mass transport during reaction process by morphology engineering; ii) engineering the intrinsic factors of carbon support, such as defects, functional dopants, metal cluster, and hybrids, to optimize the electronic structure of metal ion centers, so is their catalytic activity; iii) introducing new active site induced from engineering (ii) and inducing its synergistic cooperation with the metal ion centers.

4. Summary and Outlook

As a summary, M-N-C-based materials have exhibited exceptional performance towards diverse catalytic reactions including some typical sustainable fuel generation reactions, such as...
ORR, OER, HER, CO₂RR, NRR, and bioinspired enzyme catalysis reactions, and have become promising alternatives to conventional precious-metal or non-precious-metal-based catalysts. It is more applausive that the M-N-C-based catalysts can be engineered through properly modulating the nature of metal ion centers, the coordinative environment of monodispersed metal atoms, and the carbon support for significantly enhanced catalytic performances, such as enhanced activity, selectivity, and stability. In light of the recent progress of both theoretical and experimental investigations, some key principles that can help the design of next generation high-performance M-N-C catalysts and beyond are summarized as follows.

i) Design principle for metal ion centers: The nature of metal ion centers of the M-N-C-based materials, such as d-band center, $e_g$ filling, and valence band states, governs the performance of catalysts. In contrast to current trial-and-error approaches, appropriate descriptors and screening methods that are based on the descriptors beyond the volcano-like relation between the free energy of key adsorbate and catalytic activity are needed. A universal descriptor that can directly connect the catalytic activities with the fundamental natures of active centers, such as, the electronegativity of metal atom, the number and types of coordinative atoms of active centers, is more efficient to search the most optimized M-N-C catalysts on the peak of volcano plot. Generally, an efficient metal ion center should have increased populations and accessibility, an intrinsically high activity toward the balanced reactant activation and intermediates adsorption, and high selectivity for target reaction, which can be enhanced by effective charge transfer and synergistic effect between neighboring metal sites.

ii) Design principle for coordination environment: The coordination environment of active centers, including coordination number and types of ligands, plays a key role in modulating the affinity of catalysts toward reactants and intermediates, the selectivity toward target reaction, and thus the catalytic performance of the M-N-C-based materials. When design M-N-C catalysts, we should consider the surrounding N atoms number and type, the possible heteroatomic doping, the foreign ligands, which can alter the charge density distribution around metal ion centers, modulate the d-band state of metal sites, and possibly induce synergistic effect between metal ion center and active site caused by ligand. In view of abundance and diversity, molecular ligands especially organic ligands are expected to play an important role in boosting the catalytic performance along the volcano plot and beyond.

iii) Design principle for carbon support: Carbon support helps the high loading of homogeneous metal active centers. It should be with high specific surface area, non self-aggregation, chemical affinity with metal atoms, and high porosity that can promote the adsorption of reactants and facilitate the diffusion of products. Moreover, the imbalanced carbon support realized by doping, metal cluster, and defects has an altered localized electronic structure by charge transfer, and can modulate the catalytic activity and selectivity. In addition to charge transfer, synergistic effect between metal ion centers and active sites induced by these intrinsic factors could also contribute to an enhanced catalytic performance. Recently, carbon support hybridizing with other 2D materials through van de Waals force also demonstrated enhanced catalytic activity and selectivity, and could be a new approach for enhancing the performance of M-N-C catalysts.

iv) In addition to the design principles mentioned above in regards of modulating the internal nature of catalyst itself, the practical strategies can be extended to engineer external factors to break the linear scaling relationships and to enhance the catalytic performances. For example, strain engineering has been validated to be an effective approach for increasing the catalytic activity of catalysts.[231,232] The strain effect on M-N-C catalysts, however, has yet not been reported to date. The strain can be realized by mechanical loading or lattice mismatch through heterostructuring, which in turn can continuously modulate the d-band width and center of metal catalysts, and the molecule-surface interactions.[233,234] We expect these successful examples can be applied to the future study of M-N-C catalysts. It is also supposed to realize anisotropic modulation of the binding energy of different species on M-N-C catalysts via the application of biaxial or anisotropic strain, and thus change the adsorption/desorption behaviors of the reactants or intermediates on the catalysts. As alternatives, some external factors, including magnetic and electric fields, confinement effect, solvent effect, etc., have the capability to modulate the adsorption of intermediates on the catalysts at different levels, due to the difference of physical and/or chemical properties between adsorbates involved, which can also be useful to break the linear scaling relations and enhance the activity and selectivity toward target products.

The key to an ideal overall catalytic performance of a material is not a sole problem. The superior catalytic performances of M-N-C-based materials can only be achieved through combinations of series of design strategies, such as tuning the nature of metal ion centers, the coordinative environment of monodispersed metal atoms, and the carbon support, as discussed in this review. In addition, the theory-guided design by developing universally applicable descriptors beyond the linear scaling relationships and screening methods based on these descriptors is a complementary way to boost the discovery of novel catalysts. We hope that the design principles and the methodology proposed in this review will benefit the design of high-performance novel catalysts for the engineering application of emerging sustainable technologies and biotechnologies.

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Conflict of Interest

The authors declare no conflict of interest.

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biological reactions, catalytic activity-d-band center correlation, design strategies, metal-nitrogen-doped carbon materials, sustainable fuel generation, synergistic effects

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