Regulating the electrocatalytic performance for nitrogen reduction reaction by tuning the N contents in Fe$_3$@N$_x$C$_{20-x}$ ($x = 0$-$4$): a DFT exploration

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How to cite this article: Han B, Li F. Regulating the electrocatalytic performance for nitrogen reduction reaction by tuning the N contents in Fe$_3$@N$_x$C$_{20-x}$ ($x = 0$-$4$): a DFT exploration. J Mater Inf 2023;3:24. https://dx.doi.org/10.20517/jmi.2023.32

Received: 11 Sep 2023 First Decision: 28 Sep 2023 Revised: 20 Oct 2023 Accepted: 31 Oct 2023 Published: 3 Nov 2023

Abstract

The Haber-Bosch (H-B) process, which is widely used in industry to synthesize ammonia, leads to serious energy and environment-related issues. The electrochemical nitrogen reduction reaction (eNRR) is the most promising candidate to replace H-B processes because it is more energy-efficient and environmentally friendly. Atomic-level catalysts, such as single-atom and double-atom catalysts (SACs and DACs), are of great interest due to their high atomic utilization and activity. The synergy between the metal atoms and two-dimensional (2D) support not only modulates the local electronic structure of the catalyst but also controls the catalytic performance. In this article, we explored the eNRR performance of 2D Fe$_3$@N$_x$C$_{20-x}$ ($x = 0$-$4$), whose structure was based on the experimentally synthesized Ag$_3$@C$_{20}$ sheet, by means of density functional theory calculations. Through calculations, we found that the 2D Fe$_3$@N$_x$C$_{20-x}$ with Fe$_2$ site coordinated with four N is a promising eNRR catalyst: the limiting potential is as low as -0.45 V, and the competing hydrogen evolution reaction can be effectively suppressed. Our work not only confirms that the coordination environment of the metal site is crucial for the electrocatalytic activity but also provides a new guideline for designing low-cost eNRR catalysts with high efficiency.

Keywords: Electrochemical nitrogen reduction reaction, two dimensions, single-atom and double-atom catalysts, active site, coordination, density functional theory
INTRODUCTION

Ammonia is a raw material vital to the global economy because of its wide range to be converted into fertilizers, chemicals, future fuel substitutes, and hydrogen storage\cite{1}. The direct conversion of nitrogen in the air into ammonia is of paramount importance to both human beings and the planet’s ecosystem\cite{2}. Yet, the Haber-Bosch (H-B) process, the main traditional process for producing ammonia in industry, requires extremely demanding conditions, such as high temperatures and pressures\cite{3-5}. Furthermore, the hydrogen in the H-B process is derived from natural gas or methane\cite{6}, which means that the process will release large amounts of CO\textsubscript{2}. Electrocatalytic nitrogen reduction reactions (eNRR) have been attracting increasing interest because of the mild reaction conditions compared to those of the H-B process; the reaction can be carried out under ambient conditions with the assistance of renewable electricity\cite{7,8}. In addition, the source of hydrogen from water and the energy resource required for the eNRR process can be renewable, thus eliminating the negative impact of fossil fuels as the source of hydrogen and energy\cite{9}. However, eNRR is a complex reaction involving six electron transfer processes, which is kinetically and thermodynamically more difficult compared to the hydrogen evolution reaction (HER), thus making the protons and electrons on the electrocatalyst susceptible to the production of H\textsubscript{2} rather than NH\textsubscript{3}\cite{10,11}. Therefore, it is desirable to develop catalysts for eNRR with high conversion and effective HER inhibition\cite{11}.

Many candidates could be used as eNRR electrocatalysts, for example Chen et al. used plasma-etched Ti\textsubscript{3}O\textsubscript{4} (OV-Ti\textsubscript{3}O\textsubscript{4}) with oxygen vacancies to obtain maximum NH\textsubscript{3} yield up to 37.24 μg·h\textsuperscript{-1}·mg\textsubscript{cat}·h\textsuperscript{-1} in 0.1 M HCl\cite{12}, and they proposed a mixture of titanium dioxide and effusus-derived carbon microtubes with threedimensional cross-linked hollow tubular structures, which gave NH\textsubscript{3} yield as high as 20.03 μg·h\textsuperscript{-1}·mg\textsubscript{cat}·h\textsuperscript{-1} in 0.1 M Na\textsubscript{2}SO\textsubscript{4}\cite{13}. The single-atom catalysts (SACs)\cite{14}, which offer a new way to maximize the efficiency of metal atom use, have emerged as promising candidates\cite{15}. The localized structures of the metal atoms allow them to exhibit excellent electronic properties and catalytic performance in a variety of chemical reactions\cite{16}. However, the surface free energy of metals increases significantly with decreasing particle size, and metal atoms tend to aggregate\cite{17}. Additionally, the stability of SACs in practical reactions depends on the surface configuration, the substrate, the reactants, and the limited temperature/pressure, which are not well defined and vary from one system to another\cite{18}. The appropriate choice of substrates is a major (and in some cases a critical) factor in determining the catalytic performance of the catalyst, which should provide a large specific area to accommodate the metal sites and be able to modulate the local geometry and electronic structure of the metal atoms in the reaction, thus determining the overall catalytic performance\cite{19}. Two-dimensional (2D) carbon\cite{11,20}, N-doped carbon\cite{21-24}, etc.\cite{25-28}, used as substrates for metal atoms as atomic catalysts, exhibit excellent efficiency toward eNRR. As an extension of SACs, double-atom catalysts (DACs) became another research hotspot due to their higher metal loading than SACs\cite{29}. In terms of the overall reaction, DACs have multiple active sites (top and bridge) since their active centers are composed of two adjacent metal atoms, which can significantly improve the Faraday efficiency\cite{29}. The bridge-site adsorption behavior of metal-metal atoms was found to exhibit a strong synergistic effect of modulating the electronic structure and promoting adsorption\cite{30}. In addition, differences in surface states in different homonuclear or heteronuclear DACs can have an important impact on the selectivity and activity of the reactions\cite{31}. Thus, both SACs and DACs may be excellent electrocatalysts if the right substrate is chosen.

Previous studies revealed that excellent electrocatalytic performance for the nitrogen reduction reaction (NRR) can be obtained by loading iron onto different substrates, whether as monoatoms\cite{32-36}, dimers\cite{22,27-39}, or other sizes\cite{40-44}. In addition, given that the iron-molybdenum cofactor (FeMoco) is thought to be the site of dinitrogen reduction\cite{45}, we focused on Mo/Fe-containing catalysts. The chosen substrate was prompted by the recent experimental preparation of the 2D material Ag\textsubscript{3}C\textsubscript{20}\cite{46}, a planar structure with a rectangular lattice containing three Ag atoms and 20 C atoms. The three metal atoms in the lattice can be considered as

a single atom (M₁) and a bimetallic atom (M₂) site. In this work, we replaced the precious metal Ag atoms in Ag,[@C₂₀ with Mo/Fe atoms and obtained the Mo/Fe,[@C₂₀ monolayer. Through theoretical studies of the eNRR process, we found that Mo,[@C₂₀ is not suitable for eNRR due to its strong N₂ adsorption; in contrast, Fe,[@C₂₀ is a good eNRR catalyst (the limiting potential $U_\text{l} = -0.59 \text{ V}$). With the demonstration that Fe,[@C₂₀ can be used as an electrocatalyst for eNRR, we substituted the C bonded with Fe by N to tune the coordination environment of the metal sites in order to further improve the catalytic efficiency. The limiting potential was further changed to $-0.45 \text{ V}$ when the N doping of the Fe, site was the maximum; i.e., all the four C bonded with Fe, sites were replaced by N with the stoichiometry of Fe,[@NₓC₄₋ₓ.

**MATERIALS AND METHODS**

All density functional theory (DFT) calculations were carried out using the Vienna *ab initio* Simulation Package (VASP)\[^40\]. The Perdew, Burke, and Ernzerhof (PBE)\[^41\] parameterization of the generalized gradient approximation (GGA) was used to describe the exchange-correlation function. The DFT-D2 dispersion correction scheme was applied for van der Waals (vdW) interactions\[^42\]. A cut-off energy of 600 eV was used (convergence tests are shown in Supplementary Figure 1). The convergence parameters for force and energy were 0.02 eV/Å and $10^{-3}$ eV, respectively, and the convergence parameters were set the same as those in previous NRR calculations\[^43\]. The Brillouin zone was sampled using a Monkhorst-Pack k-point grid\[^31\] of $3 \times 5 \times 1$. The Bader charge analysis\[^32\] was employed to evaluate the charge transfer.

The adsorption energy of N₂ was calculated by $E_{\text{ads}} = E_{\text{tot}} \text{ - } E_{\text{N}_2}$, where $E_{\text{tot}}$, $E_{\text{N}_2}$ are the total energy of N₂ adsorbed on the catalyst, the clean catalyst, and free N₂, respectively. The free energy $G$ was obtained based on the computational hydrogen electrode (CHE) model proposed by Nørskov *et al.*\[^33\], with the formula:

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_U + \Delta G_{\text{pH}}$$

In the above equation, $E$ is the DFT energy, $E_{ZPE}$ and $S$ are the zero-point energy and entropy\[^34\], respectively, $E_{ZPE}$ and $T\Delta S$ can be obtained by VASPKIT post-processing program\[^55\], $\Delta G_U = -eU$, $\Delta G_{\text{pH}} = -k_B T\ln 10 \times pH$, $k_B$ is the Boltzmann constant, $T$ is 298.15 K\[^36\], and the pH is zero in this study. The corrected values of the gas molecules and intermediates were given in Supplementary Tables 1 and 2, respectively. The limiting potential ($U_\text{l}$) of the entire reduction process was determined by the potential limiting step and was computed by $U_\text{l} = -\Delta G_{\text{max}}/e$\[^37\].

We used the following equation for the formation energy of N doping:

$$E_f = E_{\text{Fe}_3@N_xC_{20-x}} - xE_N + xE_C$$

where $E_{\text{Fe}_3@N_xC_{20-x}}$ and $E_{\text{Fe}_3@C_{20}}$ are the energies of N-doped and pure Fe₃@C₂₀, respectively, $x$ is the number of N atoms, and $E_N$ and $E_C$ represent the energies of a free N/C atom. All the details of the calculations and the results of the energy difference calculations are presented in Supplementary Table 3.

**RESULTS AND DISCUSSION**

**The structure and the eNRR performance of the M₃@C₂₀ (M = Mo and Fe) monolayers**

After structural optimization, the structures are represented by the Fe₃@C₂₀ shown in Figure 1A with rectangular lattice constants of $a = 11.14$ Å and $b = 7.95$ Å, and $a = 11.59$ Å and $b = 8.45$ Å for Mo₃@C₂₀.
respectively. Due to the different loading positions of the metal atoms, they can be characterized as single-atom (M₁) and double-atom (M₂) sites (the Mo-Mo/Fe-Fe bond lengths at the diatomic sites are 2.85/2.22 Å, which also demonstrates the formation of metallic bonds in the M₂ sites). The results of the electron localization function (ELF: ELF values of 1.0 and 0.5, representing fully localized and free electron gases respectively, while ELF values close to 0 represent the low electron density region, Supplementary Figure 2) show that electron transfer from the Mo/Fe atoms to the C atoms, which is in line with the Bader charge analysis [Mo₁(Mo₂): 1.16 (1.46) |e| and Fe₁(Fe₂): 0.96 (1.34) |e|]. The covalent bond between C and C atoms (1.32~1.47 Å) can also be identified. The total density of states (TDOS) [Figure 1B and Supplementary Figure 3] reveals that there are electronic states crossing the Fermi energy level, indicating the metallicity of both Fe₃@C₂₀ and Mo₃@C₂₀, which is beneficial to electrocatalysis.

For the electrochemical synthesis of ammonia, the adsorption of N₂ on the catalyst surface is the first step in the process. We considered two possible N₂ adsorption configurations, i.e., the side-on and end-on structures, on both M₁ and M₂ sites, respectively. The results are displayed in Figure 2 and Supplementary Figure 4. After N₂ adsorption onto Mo@C₂₀, the distances between N₂ and Mo after structural optimization ranged from 1.95 to 2.25 Å. It is noteworthy that when N₂ adsorbs to the Mo₂ site in the side-on conformation, it will spontaneously shift to the end-on conformation; thus, we only considered the end-on adsorption structure. The N–N bond lengths of N₂ at the Mo₁(Mo₂) site in the side-on and end-on conformations are 1.21 and 1.14 (1.12) Å, respectively. The adsorption energies (E_ads) of N₂ at the Mo₁(Mo₂) sites are all larger than 5.00 eV; such strong adsorption is not conducive to subsequent reactions or nitride releasing, and therefore Mo₃@C₂₀ is not suitable for the eNRR. In contrast, the distances between N of N₂ and Fe range from 1.88 to 3.13 Å. The N–N bond lengths of the adsorbed N₂ adopting side-on and end-on configurations are 1.11 (1.18) and 1.13 (1.14) Å at the Fe₁(Fe₂) site, respectively, and the E_ads values of N₂ are -0.10 (-0.57) eV and -0.41 (-0.52) eV at the Fe₁(Fe₂) site, respectively. In comparison with the 1.11 Å of N–N length of an isolated N₂ molecule, the N–N length is elongated, and the adsorbed N₂ is activated (also indicated by the considerable adsorption strength), except for the case of N₂ adsorbing on the Fe₁ site with side-on structures. The Bader charge analysis showed that the number of electrons transferred from Fe₁(Fe₂) to the adsorbed N₂ with side-on and end-on configurations are 0.00 (0.49) and 0.16 (0.31) |e|, respectively, agreeing well with the adsorption strengths, which also suggests that the activation of N₂ at the Fe₂ site is more efficient than that at the Fe₁ site.

Before conducting the eNRR pathway test on the Fe₂ site, we evaluated the stability of Fe₃@C₂₀ by carrying out first-principles molecular dynamics (FPMD) simulations at 300 K for 5 ps (with a time step of 1 fs). The result showed that both the Fe₁ and Fe₂ moieties in the 2D structure were well preserved during the FPMD
Figure 2. Different adsorption structures of $\text{N}_2$ on Fe$_3$@C$_{20}$: (A) end-on and (B) side-on configurations at Fe$_1$ sites; and (C) end-on and (D) side-on configurations at Fe$_2$ sites, with the unit cells marked by black lines.

simulations [Supplementary Figure 5], which demonstrates that Fe$_3$@C$_{20}$ has good thermodynamic stability.

The two eNRR pathways on the Fe$_2$ site of Fe$_3$@C$_{20}$ to produce ammonia started from side-on (end-on) adsorption are shown in Figure 3A and B, which are the enzymatic (alternative) mechanism [$^*$ $\rightarrow$ $^*$N$_2$ $\rightarrow$ $^*$NNH $\rightarrow$ $^*$NH,NH $\rightarrow$ $^*$NH$_2$NH $\rightarrow$ $^*$NH$_2$NH$_2$ $\rightarrow$ $^*$N $\rightarrow$ $^*$NH$_2$ $\rightarrow$ $^*$NH$_3$ $\rightarrow$ NH$_3$(g)] and the consecutive (distal) mechanism [$^*$ $\rightarrow$ $^*$N$_2$ $\rightarrow$ $^*$NNH $\rightarrow$ $^*$NNH$_2$ $\rightarrow$ $^*$N $\rightarrow$ $^*$NH$_2$ $\rightarrow$ $^*$NH$_3$ $\rightarrow$ NH$_3$(g)], respectively. The main reasons for considering the above pathways can be assigned to the following two aspects: (1) N$_2$ has different adsorption configurations; (2) the proton-electron ($\text{H}^+$ + e$^-$) pairs attack N atoms in different manners [whether they attack one N atom consecutively first (consecutive/distal route) or attack the two N atoms alternatively (alternating/enzymatic path)].

Following the above mechanisms, the structural illustrations of each intermediate and free energy diagram are given in Figure 3. The results show that the change in free energy is preferred along the distal pathway. In detail, starting from the N$_2$ adsorbing with side-on configurations, the free energy change ($\Delta G$) follows the sequence of -0.09, 0.64, 0.00, -0.12, -0.04, -1.82, 0.07, and 0.53 (-0.09, 0.64, 0.50, -1.05, -0.57, -0.87, 0.07, and 0.53) eV for each elementary step along the enzymatic (consecutive) route; while starting from the end-on adsorption of N$_2$, $\Delta G$ goes through -0.09, 0.59, -0.06, -0.20, 0.14, -1.83, 0.08, and 0.53 (-0.09, 0.59, -0.04, -0.47, -0.57, -0.87, 0.08, and 0.53) eV for each elementary step, along the alternative (distal) path. The potential determining step (PDS) is the first hydrogenation step of N$_2$ ($^*$NN $\rightarrow$ $^*$NNH) in the four eNRR pathways with the largest $\Delta G$ of 0.64 or 0.59 eV, which is comparable to that over Fe$_3$@gra (0.60 eV)$^{[58]}$ and smaller than that on Fe-C,N (1.06 eV)$^{[21]}$. The free energy change of releasing NH$_3$ [$^*$NH$_3$ $\rightarrow$ NH$_3$(g), $\Delta G$ = 0.53 eV] is less than the $\Delta G$ of the first hydrogenating ($\Delta G$ = 0.64 or 0.59 eV), which is beneficial in facilitating the recovery of the catalyst.

The HER, requiring proton-electron pairs to proceed with the reaction, is the primary competitor against the eNRR. Therefore, we calculated the adsorption energy of $^*$H and found $E_{\text{ads}}$ of $^*$H (-0.30 eV) $>$ $E_{\text{ads}}$ of $^*$N$_2$ (-0.57/-0.52 eV) on the Fe$_1$ site. In addition, to exclude the possibility that the Fe$_1$ site may also proceed HER, lowering the selectivity towards eNRR, we also calculated $E_{\text{ads}}$ of $^*$H on the Fe$_2$ site (0.16 eV). All
results suggest that HER would be effectively suppressed over the Fe@C_{20}.

The geometry and the eNRR performance of the Fe@N_{x}C_{20-x} (x = 1~4)

Previous studies showed that the catalytic performance of catalysts is associated with the coordination environment of the active site. Thus, 2D Fe@N_{x}C_{20-x} (x ≤ 4) materials were constructed by replacing Fe_2-bonded C with N, and all the optimized structures remain well with the initial plane [Supplementary Figure 6]. The formation energy of Fe@N_{x}C_{20-x} decreases from -0.20 eV at x = 1 to -0.65 eV at x = 4 [Supplementary Table 3]. The lattice constants for these structures were given in Supplementary Table 4. Note that the N doping at x = 2 yields three structures, i.e., Fe@N_{2}C_{18}-I, Fe@N_{2}C_{18}-II and Fe@N_{2}C_{18}-III [Supplementary Figure 6B-D], with the lowest $E_f$ (-0.50 eV) of asymmetric substitution Fe@N_{2}C_{18}-II compared to the other two structures ($E_f$ = -0.22 eV for I and $E_f$ = -0.35 eV for III). The lattice constant $a/b$ decreases from 11.14/7.95 Å at x = 0 to 10.87/7.74 Å at x = 4, which can be understood by the smaller radius of N than that of C.

The adsorption energies of N$_2$ with side-on configurations on Fe$_2$ sites of most N-substituted monolayers are also stronger than those with end-on structures, and the adsorption strength decreases as the content of N increases, as demonstrated by the data in Supplementary Table 4: the $E_{ads}$ values of the side/end-on adsorption configurations on Fe$_2$ sites of 2D Fe@N$_x$C$_{20-x}$ (x ≤ 4) monolayers are -0.62/-0.55 eV for Fe@N$_1$C$_{19}$, -0.59/-0.55 eV for Fe@N$_2$C$_{18}$-I, -0.50/-0.48 eV for Fe@N$_2$C$_{18}$-II, -0.59/-0.52 eV for Fe@N$_2$C$_{18}$-III, -0.54/-0.52 eV for Fe@N$_1$C$_{18}$, and -0.20/-0.32 eV for Fe@N$_4$C$_{16}$, respectively. The N$_2$ adsorption structures are shown in Figure 4A and B, and Supplementary Figure 7. In the proceeding section, the PDSS for the considered routes on Fe@C$_{20}$ are the first hydrogenation step of N$_2$ (*N$_2$ → *NNH). Then, we evaluate the $\Delta G$ values of the first hydrogenation step of N$_2$ on the Fe$_2$ site of 2D Fe@N$_x$C$_{20-x}$ (x ≤ 4) [Supplementary Table 5]. The free energy changes on these N-substituted materials range from 0.45 to 1.23 eV. The $\Delta G$ values of the Fe@N$_1$C$_{19}$ (0.74 eV), Fe@N$_2$C$_{18}$-I (0.61 eV), Fe@N$_2$C$_{18}$-II (0.73 eV), Fe@N$_2$C$_{18}$-II (0.65 V), and Fe@N$_4$C$_{16}$ (0.67 V) are much smaller than those of the FeCN$_2$ (0.94 eV) and FeCN$_3$ (0.92 eV) [59], suggesting the more pronounced effect of the DAC environment than the SAC environment on the NRR performance. Unfortunately, all of them have free energy change values higher than 0.59 eV of Fe@N$_{20}$ [Figure 4C], and

![Figure 3](https://example.com/fig3.png)

**Figure 3.** Different eNRR mechanisms on Fe@C$_{20}$ (A and B) and the free energy diagrams (C and D). Data denote the $\Delta G$ of each elementary step. eNRR: Electrochemical nitrogen reduction reaction.
therefore, these subsequent pathways will not be considered. In contrast, the free energy change for the first hydrogenation of side-on adsorption on Fe₃@N₄C₁₆ (0.45 eV) is smaller than that of Fe₃@C₂₀. It is worth noticing that after the first hydrogenation of end-on adsorbed N₂, the *NNH configuration is automatically transformed to the side-on adsorbed *NNH configuration after structural optimization. Therefore, we only concentrated on the enzymatic and consecutive eNRR paths over Fe₃@N₄C₁₆.

On the Fe₃@N₄C₁₆, the free energy change for each elementary step along the enzymatic mechanism was 0.21, 0.45, -0.07, 0.01, 0.09, -2.12, 0.19, and 0.40 eV, and along the consecutive mechanism, it was 0.21, 0.45, 1.08, -1.43, -0.36, -1.38, 0.19 and 0.40 eV, respectively [Figure 4D]. Notably, although the ΔG of nitrogen adsorption is a positive value (0.21 eV), the adsorption energy before correction is negative (-0.20 eV), and the elongation of the N–N bond (1.17 Å) further suggests that the nitrogen was activated. However, in terms of the overall reaction, this small positive value is smaller than the free energy change in the first step of hydrogenation, i.e., *NN → *NNH (0.45 eV). As for the eNRR on the Fe₂ site of Fe₃@N₄C₁₆, the step *NN → *NNH becomes the PDS in the enzymatic mechanism, possessing a free energy change value of 0.45 eV, which is smaller than the values on FeMo@C₆N₆ (0.53 eV) [60] and Fe/Mo-N-C (0.63 eV) [61]. Furthermore, the free energy change of releasing the second NH₃(g) (0.40 eV) is also smaller than ΔG of the PDS (0.45 eV), indicating the feasibility of recovering the clean catalyst. In addition, we used the Poisson-Boltzmann implicit solvation model to simulate an aqueous solvent environment (with a dielectric constant of ε = 80) [62] to further explore the solvation effect on the eNRR performance of Fe₃@N₄C₁₆, and the results are shown in Supplementary Figure 8. The value of ΔG_{max} in the consecutive/ enzymatic pathway on Fe₃@N₄C₁₆ with the solvent effect is reduced from 1.08/0.45 eV to 1.04/0.34 eV, which is consistent with the path selectivity of our calculations without solvent effect and demonstrates the selectivity of Fe₃@N₄C₁₆ to be
an excellent NRR catalyst.

In addition, since the 2D Fe\textsubscript{16}C\textsubscript{20-x} \((x \leq 4)\) includes both Fe\textsubscript{1} and Fe\textsubscript{2} sites, to make sure that the Fe\textsubscript{1} site is the active site for eNRR to proceed, we also calculated the adsorption energy of N\textsubscript{2} at the Fe\textsubscript{2} site for comparison [Supplementary Table 4]. The adsorption energies of N\textsubscript{2} for the side-on/end-on adsorption configuration at the Fe\textsubscript{1} site are -0.11/-0.43 eV for Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x}, -0.06/-0.39 eV for Fe\textsubscript{16}N\textsubscript{2}C\textsubscript{20-x}I, -0.08/-0.47 eV for Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x}II, and -0.17/-0.43 eV for Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x}III. For \(x = 1, 2\), it indicates that N\textsubscript{2} prefers to adsorb at Fe\textsubscript{1} sites, while N\textsubscript{2} may prefer to adsorb on the Fe\textsubscript{2} site of Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x} (-0.08/-0.58 eV) and Fe\textsubscript{16}N\textsubscript{2}C\textsubscript{20-x} (0.15/-0.44 eV). Therefore, we further tested for further hydrogenation of N\textsubscript{2} (*NN → *NNH) on the Fe\textsubscript{1} site for \(x = 3, 4\). However, the free energy changes for the first step of hydrogenation of N\textsubscript{2} end-on adsorbed on the Fe\textsubscript{1} site are 0.95 (Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x}) and 1.24 eV (Fe\textsubscript{16}N\textsubscript{2}C\textsubscript{20-x}), respectively. Such large free energy change is also unfavorable for eNRR, and for the reaction on Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x}, even though nitrogen tends to adopt end-on adsorption on the Fe\textsubscript{1} site, it is difficult to proceed the next step of the hydrogenation after this active site is occupied by nitrogen, and thus, the preferred N\textsubscript{2} adsorption on Fe\textsubscript{1} site will not affect the reaction on the Fe\textsubscript{1} site. Besides, to guarantee the selectivity towards eNRR instead of HER, the adsorption of *H at the Fe\textsubscript{2} site for \(x = 1~4\). The adsorption strength of N\textsubscript{2} at Fe\textsubscript{2} sites prevails that of *H at Fe\textsubscript{2} (Fe\textsubscript{1}) site: -0.62/-0.55 vs. -0.28 (0.24) eV for Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x}, -0.59/-0.55 vs. -0.48 (0.25) eV for Fe\textsubscript{16}N\textsubscript{2}C\textsubscript{20-x}I, -0.50/-0.48 vs. -0.30 (0.65) eV for Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x}II, -0.59/-0.52 vs. -0.24 (0.09) eV for Fe\textsubscript{16}N\textsubscript{2}C\textsubscript{20-x}III, -0.59/-0.52 vs. -0.39 (0.23 eV) for Fe\textsubscript{16}N\textsubscript{2}C\textsubscript{20-x}, and -0.20/-0.32 vs. 0.02 (0.45) eV for Fe\textsubscript{16}N\textsubscript{2}C\textsubscript{20-x}.

All the above calculations show that the Fe\textsubscript{2} site remains the active center with N-doping varying from 1 to 4, and N-doping will not change the selectivity toward eNRR to HER. Most importantly, with the lowest \(\Delta G_{\text{min}}\) and the preferential adsorption of N\textsubscript{2} against *H, Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x} distinguishes itself as the most promising candidate for eNRR.

The origin of different eNRR performance of Fe\textsubscript{16}N\textsubscript{2}C\textsubscript{20-x} \((x = 0~4)\)

As an eNRR catalyst, the free energy change results show that the limiting potential of Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x} (0.45 eV) is smaller than that of Fe\textsubscript{16}C\textsubscript{20} (0.59 eV) and is even better than the reported \(U_{\text{g}}\) values FeN\textsubscript{4}/G (FeN, moiety embedded in graphene, 1.30 eV)\textsuperscript{[63]} and FeN\textsubscript{4}/FeMoPPc (FeN, moiety embedded with polyphthalocyanine, 0.66 eV)\textsuperscript{[64]}. To figure out the origin of the significantly improved eNRR activity of Fe\textsubscript{16}N\textsubscript{1}C\textsubscript{20-x}, we analyzed the geometric and electronic structures of Fe\textsubscript{1} sites in Fe\textsubscript{16}N\textsubscript{2}C\textsubscript{20-x} \((x = 0~4)\). As illustrated in Supplementary Table 6, the Fe–Fe bond length of the Fe\textsubscript{1} site shows slight variation for \(x = 0~3\) \((d_{\text{Fe–Fe}} = 2.22~2.24\ \text{Å})\) and an obvious drop to 2.16 Å for \(x = 4\), and the Fe\textsubscript{1}-d orbitals exhibit a better hybridization with the adsorbed N\textsubscript{2}–p orbitals.
orbitals [Supplementary Figure 9], which further leads to more efficient activation of N–N as demonstrated by the lower \( \Delta G \) of the first hydrogenating step. Besides, both the \( d \)-band center and the \( p \)-band center of \( \text{Fe}_2 \)-bonded C/N in \( \text{Fe}_2@\text{N}_x\text{C}_{20-x} \) have moderate values among \( \text{Fe}_x@\text{N}_x\text{C}_{20-x} \ (x = 0\sim4) \), showing an inverse volcano relationship [Figure 5 and Supplementary Table 6].

CONCLUSIONS

In summary, we theoretically investigated the eNRR performance of \( \text{Mo}_3@\text{C}_{20} \) and \( \text{Fe}_3@\text{C}_{20} \) monolayers based on the experimentally synthesized 2D \( \text{Ag}_3@\text{C}_{20} \) structure. Our calculations revealed that \( \text{Fe}_3@\text{C}_{20} \) exhibits good activity and selectivity for eNRR with a predicted limiting potential of \(-0.59\) V. By further investigation of the synergy between the active \( \text{Fe}_2 \) site and its coordination, we found that the N-containing environment would tune the electronic properties and, thus, enhance the catalytic efficiency, where 2D \( \text{Fe}_x@\text{N}_x\text{C}_{20-x} \) is demonstrated as the superior electrocatalyst with a limiting potential of \(-0.45\) V. Moreover, the \( \text{Fe}_x \) sites in our designed \( \text{Fe}_x@\text{N}_x\text{C}_{20-x} \) materials have much smaller \( \Delta G_{\text{max}} \) than those of Fe-based SACs such as \( \text{FeN}_4/G \) (1.30 eV)\(^{[63]} \), \( \text{FeCN}_2 \) (0.94 eV) and \( \text{FeCN}_3 \) (0.92 eV)\(^{[59]} \), and the best candidate \( \text{Fe}_x@\text{N}_x\text{C}_{20-x} \) also has smaller \( \Delta G_{\text{max}} \) than that of the Fe-based triple-atom catalyst \( \text{Fe}_3@\text{C}_2\text{N} \) (0.57 eV)\(^{[65]} \). These findings provide new ideas for the development of new eNRR catalysts following experimental fabrication to theoretical prediction to experimental guidelines and highlight the important role of the metal-coordination environment.

DECLARATIONS

Authors’ contributions

Performed the computations and drafted the manuscript: Han B
Provided guidance and revised the manuscript: Li F

Availability of data and materials

Supplementary materials are available from the Journal of Materials Informatics or from the authors.

Financial support and sponsorship

This work was supported by the National Natural Science Foundation of China (11964024), the “Grassland Talents” project of the Inner Mongolia autonomous region (12000-12102613), and the young science and technology talents cultivation project of Inner Mongolia University (21200-5223708). We thank the computational support from Beijing PARATERA.

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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