

Article

Curvature-Influenced Electrocatalytic NRR Reactivity by Heme-like FeN₄-Site on Carbon Materials

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Abstract: Two-dimensional carbon materials and their derivatives are widely applied as promising electrocatalysts and supports of single-atom sites. Theoretical investigations of 2D carbon materials are usually based on planar models, yet ignore local curvature brought on by possible surface distortion, which can be significant to the exact catalytic performance as has been realized in latest research. In this work, the curvature-influenced electrocatalytic nitrogen reduction reaction (NRR) reactivity of heme-like FeN₄ single-atom site was predicted by a first-principle study, with FeN₄-CNT(*m,m*) (*m* = 5–10) models adopted as local curvature models. The results showed that a larger local curvature is favored for NRR, with a lower limiting potential and higher N₂ adsorption affinity, while a smaller local curvature shows lower NH₃ desorption energy and is beneficial for catalyst recovery. Using electronic structures and logarithm fitting, we also found that FeN₄-CNT(5,5) shows an intermediate-spin state, which is different from the high-spin state exhibited by other FeN₄-CNT(*m,m*) (*m* = 6–10) models with a smaller local curvature.

Keywords: electrocatalytic NRR; carbon nanotube; single-atom catalyst; ammonia synthesis; surface distortion



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1. Introduction

Two-dimensional carbon materials, including but not limited to graphene [1], graphdiyne [2,3], and their derivatives [4], are well developed as promising electrocatalysts and supports of single-atom sites [5–7]. Considering their flexibility, synthesized 2D carbon materials do not maintain ideally planar structures and form locally distorted surfaces, affecting their catalytic performance in electrochemistry [8,9]. In most cases, planar structures are used in theoretical investigations for the sake of simplification [10–13], while possible influence brought about by a local curvature originated from distortion is rarely discussed compared with planar models. Recent works have gradually started to investigate curvature-influenced electrocatalytic processes like the oxygen reduction reaction (ORR) [14,15], hydrogen evolution reaction (HER) [16], CO₂ reduction reaction (CO₂RR) [17,18], and peroxymonosulfate (PMS) activation [19]. Previous research results have shown that the curvature of surface structures makes a notable difference to catalytic

performance, and by adjusting the local curvature, a higher catalytic efficiency and new reaction behavior can be achieved, as have been well summarized in review articles [20–23].

The electrocatalytic nitrogen reduction reaction (NRR) is an environmentally friendly and sustainable method for synthesizing ammonia (NH_3) and has gained increasing attention in recent years, and more and more efficient electrocatalysts that activate N_2 molecules have been discovered and designed for NH_3 production [24–26]. Experimentally, Ziming Zhao et al. synthesized a high-efficiency NRR electrocatalyst, 2D $\text{C}_3\text{N}_4\text{-NV}$, and its abundant N vacancy facilitates N_2 adsorption and activation [27]. Compared with Bi nanoparticles, Bi quantum dots (Bi QDs) show a high NH_3 yield, and the size of Bi particles obviously affects their NRR catalytic performance [28]. In addition, plenty of research has been conducted on the theoretical investigation of the electrocatalytic NRR based on planar models [29–32], yet how and to what extent curvature influences NRR performance is rarely discussed. In this work, by constructing heme-like FeN_4 single-atom sites on carbon nanotubes (CNTs) with different chiral indices (m,m), where $m = 5\sim 10$ (Figure 1), the curvature-influenced electrocatalytic NRR reactivity was investigated via first-principle calculations. The larger chiral index m corresponds to the gradual increase in the nanotube diameter and decrease in the local curvature. Our results showed that a larger curvature is favored for N_2 adsorption and exhibits lower limiting potential, while a smaller curvature is beneficial for NH_3 desorption so as to help catalyst recovery. Moreover, as a model for large curvature, $\text{FeN}_4\text{-CNT}(5,5)$ shows a different electronic structure compared with other models.

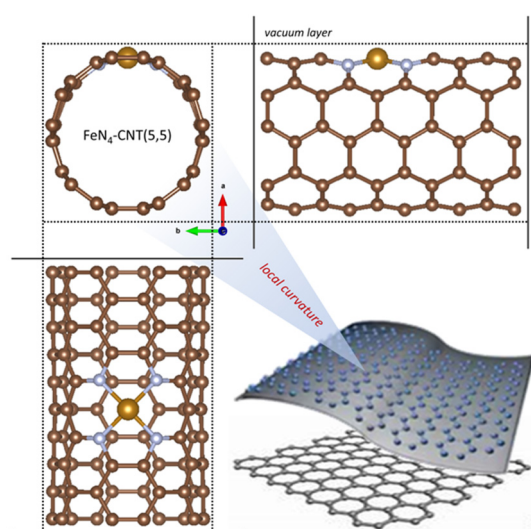
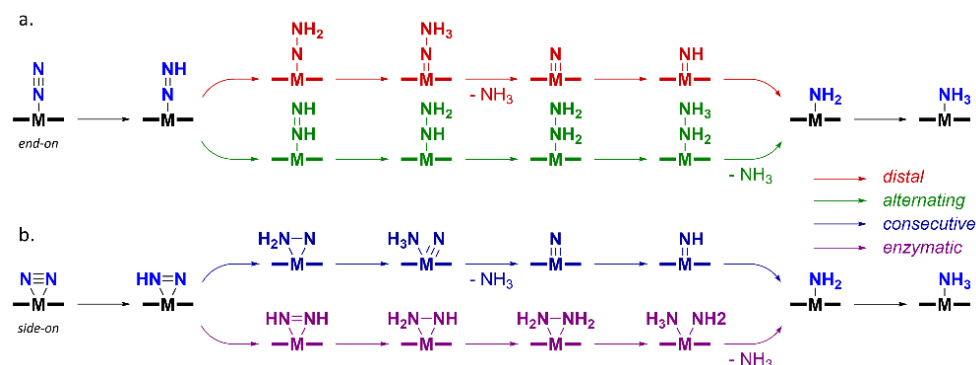


Figure 1. Top and side view of $\text{FeN}_4\text{-CNT}(5,5)$ as an example. Fe, C, and N are displayed in gold, brown, and blue, respectively.

2. Results and Discussion

The electrocatalytic NRR involves six hydrogenation steps, which is generally considered to have distal and alternating pathways on single-atom sites with end-on N_2 adsorption configuration, as depicted in Scheme 1a. Since we are applying an FeN_4 -site as metallic center, which has almost planar heme-like coordination form and side-on N_2 adsorption configuration is generally considered to be unfavored, we therefore excluded consecutive and enzymatic pathways (Scheme 1b) started with the side-on configuration in the following discussion.



Scheme 1. Common N_2 adsorption configurations and reaction pathways of electrocatalytic NRR on heme-like single-atom site (M: metal). (a) Distal and alternating pathways; (b) consecutive and enzymatic pathways.

We first look into the influence on the electronic structure of a metallic center brought about by a local curvature. Many studies have confirmed that the Fe center is the active site of FeN_4 -doped carbon materials [33,34]. As shown in Figure 2a and Figure S1, the projected density of states (PDOS) of Fe 3d orbitals in FeN_4 -CNTs, as well as 2s and 2p orbitals of free and absorbed N_2 , were calculated to reveal the electronic structure of FeN_4 -CNTs and related catalytic intermediates. The PDOS of Fe 3d orbitals in FeN_4 -CNTs is mainly distributed near the Fermi level with a notable spin asymmetry of different spin states, indicating a high-spin metallic center, regardless the local curvature of carbon materials.

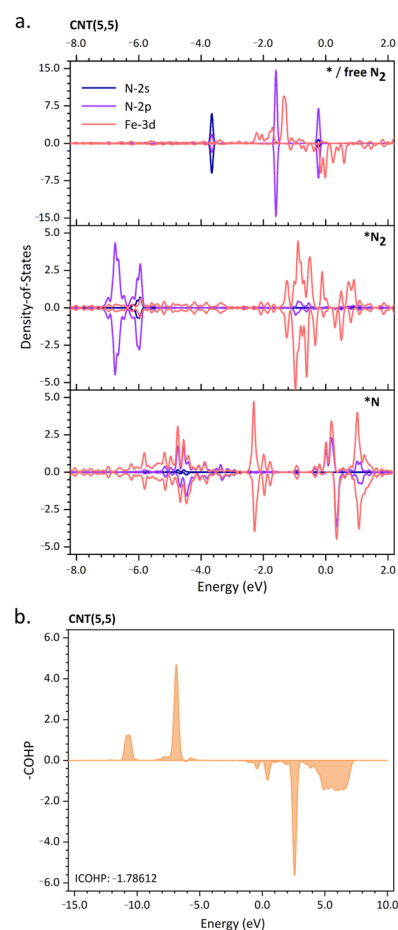


Figure 2. (a) Projected density-of-states (PDOS) results of free N_2 , FeN_4 -CNT(5,5), $N_2@$, and $N@FeN_4$ -CNT(5,5) as examples; (b) COHP results of $N_2@FeN_4$ -CNT(5,5) as an example.

As is displayed in Figure 2a and Figure S1, the adsorbed N_2 retained its spin-symmetry in *N_2 intermediate, while the PDOS of the Fe 3d orbitals becomes more spin-symmetric and less magnetic, giving evidence to a low-spin metallic center, where N_2 shows a feature of π -acid strong-field ligand. Therefore, FeN_4 -CNTs are considered to have strong affinity to N_2 adsorption, which is essential to N_2 activation and following N_2 reduction steps. A similar low spin state is observed for all *N intermediates, with stable Fe-N covalent bond formed to stabilize the highly active single nitrogen atom, enabling N-N bond cleavage in the distal pathway. Comparing the DOS of free and adsorbed N_2 , it can be found that the valence orbitals of N_2 exhibit a significant decrease and move down after adsorption. In free N_2 , the N-N σ^* orbital is located near the Fermi level, while this signal shows a significant decrease in *N_2 , suggesting that the N-N σ bond is weakened after N_2 adsorption, promoting the activation of N-N bond. In addition, the overlap of Fe 3d orbitals and 2p orbitals of N_2 at -6.0 to -8.0 eV indicates the d- π orbital interaction. Similar results on N_2 adsorption electronic structure are observed by the crystal orbital Hamiltonian population (COHP) calculation. As shown in Figure 2b and Figure S2, overlaps in the range of -12.0 ~ -5.0 eV show two positive -COHP regions, corresponding to the stable bonding structure revealed by a change in the PDOS. The integral crystal orbital Hamilton population (ICOHP) value reflects the Fe-N bond strength between FeN_4 -CNTs and N_2 , where the larger -ICOHP value represents a stronger interaction between the catalyst and N_2 [35,36]. In FeN_4 -CNT(5,5) to (10,10), the -ICOHP value gradually increases, which means that the binding of N_2 to the catalyst gradually increases.

Based on the designed adsorption models, both the distal and alternating pathways were calculated for FeN_4 -CNTs to investigate how the NRR performance can be affected by the local curvature of carbon materials, the Gibbs free energy profiles of which are displayed in Figure 3. It can be seen that regardless of the local curvature, both the distal and alternating pathways share the same rate-determining step, which is the first hydrogenation step ($^*N_2 \rightarrow ^*NNH$), requiring an increasing limiting potential of 1.07 to 1.14 eV from FeN_4 -CNT(5,5) to (10,10). This points out that the electrocatalytic capacity of the FeN_4 -site on distorted carbon materials gradually decreases with a lower local curvature. Considering that the smaller local curvature gives a more similar electronic structure and catalytic properties compared with ideally planar graphene-based single-atom site, as shown in Figure 4a, a logarithm relationship was found between the first hydrogenation energy and the local curvature of carbon materials (evaluated by nanotube size, m). Including or excluding FeN_4 -CNT(5,5) in the logarithm fitting does not brought much difference to the R^2 value, showing that the FeN_4 -CNT(5,5) model with a large local curvature is still within a reasonable range of catalytic performance, and therefore, it is acceptable for modulating the influence on the electrocatalytic NRR brought on by the local curvature.

The desorption energy of NH_3 is crucial to the recovery of catalyst, as shown in Figure 3, and as the local curvature gets smaller from FeN_4 -CNT(5,5) to (10,10) models, the desorption energy of NH_3 decreases from 0.92 to 0.33 eV, showing that a smaller local curvature is favored by NH_3 desorption and the catalyst recovery process. We can still find a logarithmic relationship between the NH_3 desorption energy and local curvature, as displayed in Figure 4b; including the FeN_4 -CNT(5,5) model in the fitting candidates gives an R^2 value of 0.8706, while excluding the FeN_4 -CNT(5,5) model gives an R^2 value of 0.9916. This indicates that a different adsorption electronic structure is formed in the $NH_3@FeN_4$ -CNT(5,5) intermediate, compared with other FeN_4 -CNT models. By analyzing the PDOS results (Figure 2a and Figure S1), we may find that the PDOS diagrams of *N_2 and *N intermediates are almost identical to each other, while the PDOS of Fe 3d orbitals in FeN_4 -CNT(5,5) has a slight difference compared with other FeN_4 -CNT models. The spin-up

contribution of $\text{FeN}_4\text{-CNT}(5,5)$ is smaller than that in $\text{FeN}_4\text{-CNT}(m,m)$ ($m = 6\sim 10$) models; therefore, compared with the high-spin metallic center in $m = 6\sim 10$ models, $\text{FeN}_4\text{-CNT}(5,5)$ shows an intermediate-spin state. Considering that the Fe atom of the FeN_4 -site on carbon materials should have a formal oxidation state of +3 [37], the high-spin state has its all 3d orbitals singularly occupied, therefore forming an adsorption structure determined by the interaction when coordinated by the weak ligand NH_3 . Meanwhile, the intermediate-spin state of $\text{FeN}_4\text{-CNT}(5,5)$ has an empty 3d orbital, and can form effective adsorption towards NH_3 , resulting in significantly higher NH_3 desorption energy in $\text{FeN}_4\text{-CNT}(5,5)$.

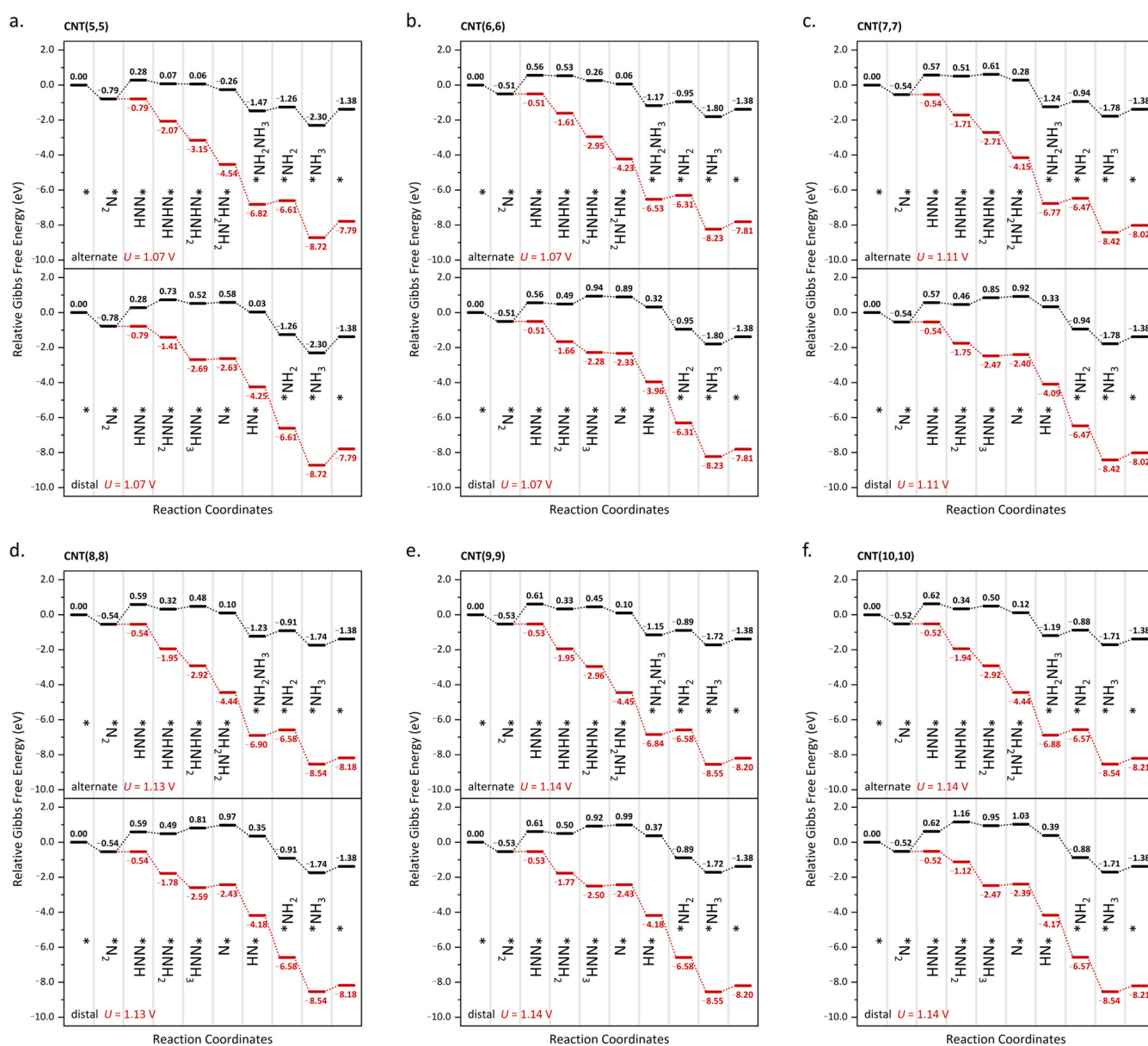


Figure 3. Gibbs free energy diagrams of alternating and distal NRR pathways on $\text{FeN}_4\text{-CNT}$ s with different sizes.

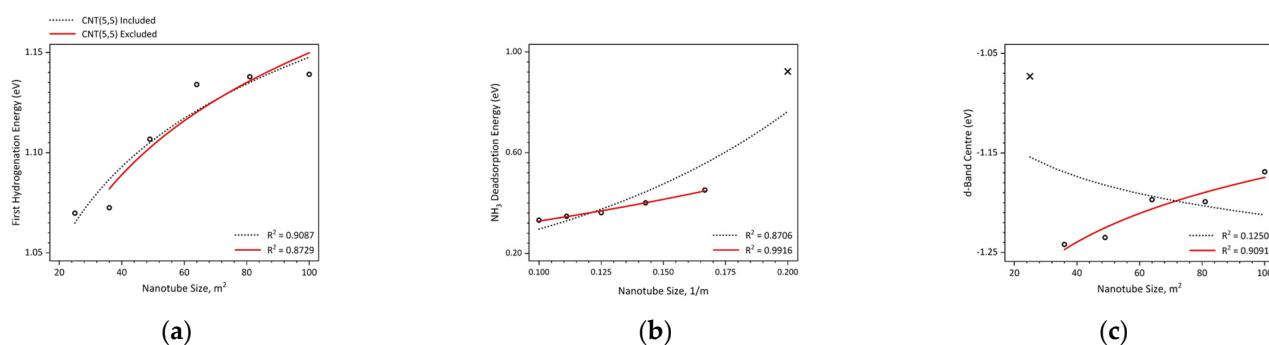


Figure 4. Logarithm relationships between (a) the first hydrogenation energy (ΔG_1 , eV) and local curvature revealed by nanotube size (m^2); (b) NH_3 desorption energy and $1/m$; (c) d-band center of Fe and m^2 .

Correspondingly, the d-band center calculation of FeN_4 -CNT models reveals a similar conclusion. As shown in Figure 4c, the logarithm fitting of the d-band center with local curvature (evaluated by m^2) shows that excluding FeN_4 -CNT(5,5) from fitting candidates gives a well-fitted relationship with an R^2 value of 0.9091. Meanwhile, including the FeN_4 -CNT(5,5) results in the R^2 value of 0.1250 therefore shows that the electronic structure of FeN_4 -CNT(5,5) is highly different from other FeN_4 -CNT models. This is in consistent with the PDOS results.

Adjusting the curvature of carbon materials can change the adsorption energy and energy barriers of the electrocatalytic process, which is an effective method to optimize the electrocatalytic performance of the catalysts [22]. Our work investigates the regulation of the curvature-influenced NRR catalytic reactivity of carbon materials at the atomic scale and analyzes the internal reasons for the curvature influence: a larger local curvature is favored for NRR, and a smaller local curvature shows lower NH_3 desorption energy, an electronic structure analysis shows that the metal centers of FeN_4 -CNT(m,m) ($m = 5\sim 10$) models are in intermediate- and high-spin states. These results are complementary to the electrocatalytic performance of FeN_4 -CNTs and provide reliable theoretical guidance for the optimization and modification of the electrocatalytic performance of carbon materials.

Moreover, we should also point out that, in some studies, a linear relationship was used to reveal the relationship between the curvature and catalytic performance [38], while we suggest that any catalytic performance cannot keep increasing/decreasing with the curvature. This is because the limitation has already been established by the graphene-based single-atom catalytic site (with no curvature). Therefore, any catalytic performance will finally converge to that in a graphene-based site, pointing out that a function type with a converging behavior should be applied instead of a linear relationship. That is the reason we used logarithm fitting in Figure 4.

3. Computational Methods

All the calculations in this work were performed using the spin-polarized density functional theory (DFT) method of the Vienna Ab initio Simulation Package (VASP) [39]. The Perdew–Burke–Ernzerh (PBE) functional of generalized gradient approximation (GGA) was utilized to describe the electron exchange–correlation interaction [40]. The projector-augmented wave (PAW) method was applied to describe the ion–electron interaction and a plane-wave cutoff energy of 450 eV was employed in all calculations. Grimme’s DFT-D3 dispersion correction was adopted to consider van der Waals interactions [41]. The Brillouin zone integration was performed with a $1 \times 1 \times 5$ grid centered at the gamma (Γ) point [42]. The convergence threshold for energy and force was 10^{-5} eV and $0.02 \text{ eV} \cdot \text{\AA}^{-1}$, respectively. The space in a - and b -axes was set to $30.0 \text{ \AA}$ to prevent the interaction introduced by the

periodic boundary condition. The crystal orbital Hamilton population (COHP) was used to measure the bonding between atoms by using the concept of the LOBSTER code [43].

The Gibbs free energy of the intermediates was calculated using the computational hydrogen electrode (CHE) model proposed by Nørskov et al. [44]. Based on the model, the reaction Gibbs free energy (ΔG) of each elementary step can be defined by Equation (1):

$$\Delta G = \Delta E - T\Delta S + \Delta ZPE + \Delta G_U + \Delta G_{pH} \quad (1)$$

where ΔE is the electronic energy difference for reactions directly obtained from DFT calculations. ΔZPE and ΔS are the differences between the adsorbed species and the gas phase molecules in zero-point energy and entropy, respectively. $\Delta G_U = -eU$ is the free energy contribution related to applied potential U , which is determined by $U = -\Delta G_{PDS}/e$, where ΔG_{PDS} is the free energy change in potential-determining step (PDSs). ΔG_{pH} refers to the correction of free energy caused by pH ($\Delta G_{pH} = 2.303 k_B \cdot \text{pH}$), and the pH value is set to zero in this work [45].

The d band center (ε_d) is a well-defined electronic descriptor for metal-contained catalysts and is given by Equation (2) [46,47]:

$$\varepsilon_d = \frac{\int n_d(\varepsilon)\varepsilon d\varepsilon}{\int n_d(\varepsilon) d\varepsilon} \quad (2)$$

where ε , $d\varepsilon$, $n_d(\varepsilon)$ represent the energy level, differential of energy, and density of states (DOS) corresponding to energy levels, respectively.

4. Conclusions

The catalytic performance influenced by the local curvature of 2D carbon materials and their derivatives has been noticed in recent research, urging theoretical research to focus on curvature models beyond ideal planar models. In this work, the electrocatalytic NRR reactivity curvature-influenced by the heme-like FeN₄ single-atom site was investigated by a first-principle study, with FeN₄-CNT(*m,m*) (*m* = 5~10) models as theoretical models for possible surface distortion. Our results show that a larger local curvature gives a lower limiting potential and higher N₂ adsorption affinity, which is favored by the high-efficiency electrocatalytic NRR. Meanwhile, a smaller local curvature also has a minor advantage over NH₃ desorption, which contributes to catalyst recovery. These curvature performance trends were well fitted in the logarithm relationships. Moreover, an electronic structure analysis also found that the higher curvature in FeN₄-CNT(5,5) leads to an intermediate-spin state, which is different from other curvature models with a high-spin state, and influences the binding mode taken by key catalytic intermediates. Our findings pointed out that curvature influence should be well considered in future theoretical and also experimental studies to discover new electrocatalysts or to make modifications based on known ones.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules30081670/s1>, Figures S1 and S2: PDOS and COHP results; Table S1: Optimized cell parameters of FeN₄-CNT; Tables S2–S13: Thermochemical data of catalytic intermediates of FeN₄-CNT(*m,m*) (*m* = 5~10) models.

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Conflicts of Interest: The authors declare no conflicts of interest.

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