Achieving Selective and Efficient Electrocatalytic Activity for CO2 Reduction on N-Doped Graphene

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The CO2 electrochemical reduction reaction (CO2RR) has been a promising conversion method for CO2 utilization. Currently, the lack of electrocatalysts with favorable stability and high efficiency hindered the development of CO2RR. Nitrogen-doped graphene nanocarbons have great promise in replacing metal catalysts for catalyzing CO2RR. By using the density functional theory (DFT) method, the catalytic mechanism and activity of CO2RR on 11 types of nitrogen-doped graphene have been explored. The free energy analysis reveals that the zigzag pyridinic N- and zigzag graphitic N-doped graphene possess outstanding catalytic activity and selectivity for HCOOH production with an energy barrier of 0.38 and 0.39 eV, respectively. CO is a competitive product since its free energy lies only about 0.20 eV above HCOOH. The minor product is CH3OH and CH4 for the zigzag pyridinic N-doped graphene and HCHO for zigzag graphitic N-doped graphene, respectively. However, for Z-pyN, CO2RR is passivated by too strong HER. Meanwhile, by modifying the pH value of the electrolyte, Z-GN could be selected as a promising nonmetal electrocatalyst for CO2RR in generating HCOOH.

Keywords: density functional theory, N-doped graphene, CO2 reduction reaction, catalytic activity, Gibbs free energy

INTRODUCTION

As one of the greenhouse gases, the continual accumulation of CO2 causes global warming, which significantly hinders the sustainable development of human society (Thomas et al., 2004; Lewis et al., 2006; Cook et al., 2010). The unbalanced CO2 emission and consumption is becoming a pressing issue (Kondratenko et al., 2013; Appel et al., 2013). In this aspect, CO2 electrochemical reduction reaction (CO2RR) by using the renewable energy sources (Yi et al., 2019; Wang et al., 2020; Lu et al., 2021) offers a promising way to produce fuels and value-added chemicals. Up to now, the major obstacle for CO2RR is the lack of electrocatalysts with high stability and efficiency. Particularly, the cathode electrocatalyst materials play a key role in the complicated product distribution of CO2RR (Lim et al., 2014; Zhu et al., 2016). Therefore, searching for suitable electrocatalysts for CO2RR is one of the hot topics in recent years. Till now, a lot of electrocatalysts for CO2RR have been studied, including noble metals (Zhu et al., 2013; Kang et al., 2014; Gao et al., 2015; Kim et al., 2015), base metals (Hori et al., 1985; Hori et al., 1986; Nie et al., 2013; Zhang et al., 2014a), alloys (Kim et al., 2014; Bai et al., 2017), and metal oxides (Lee et al., 2015; Ren et al., 2015). It is well known that Ag and Au are prone to produce CO via the two-electron reaction pathway (Zhu et al., 2013; Kim et al., 2015). In addition, Cu is recognized as a state-of-the-art CO2RR catalyst for generating multi-electron products, such as CO, HCOOH, CH3OH, and CH4 (Hori et al., 1985; Hori et al., 1986; Nie...
et al., 2013). However, the high cost, low efficiency due to the competitive hydrogen evolution reaction (HER), and high overpotential restrict their practical implementation and industrial-scale development in CO₂RR (Lim et al., 2014).

To solve the above issues, metal-free electrocatalysts based on carbon materials have been studied, owing to their low cost, high stability, outstanding mechanical flexibility, and superior structural durability. The introduction of heteroatoms (such as N, B, and S) could not only modify the electronic structure of carbon materials but also contribute to take advantage of the existing defects appropriately (Wang X. et al., 2014). For N-doped carbon nanofibers (NCNFs), it shows negligible overpotential (0.17 V) and 13 times higher current density than bulk Ag catalyst for CO₂RR (Kumar et al., 2013). In addition, N-doped carbon nanotubes (NCNTs) (Sharma et al., 2015), N-doped nanoporous carbon–carbon nanotube composite membrane (HNCM/CNT) (Wang et al., 2017), and polypyrrolimine functionalized NCNTs have been proven to be highly active and stable electrocatalysts for CO₂RR (Zhang et al., 2014b). Remarkably, N-doped graphene possesses excellent durability in the CO₂RR process, achieving a maximum faradaic efficiency (FE) of 73% for formate with overpotential of 0.84 V (Wang et al., 2016). N-doped graphene quantum dots (NGQDs) could catalyze carbon dioxide into multicarbon hydrocarbons and oxygenates at high FE (up to 90%), with excellent selectivity (45% for ethylene and ethanol conversions) (Wu et al., 2016).

With respect to the active sites of nitrogen-doped carbon materials for CO₂RR, it is a controversial issue among the pyridinic N, pyrrolic N, graphitic N, and the C adjacent to N. Generally, these potential active sites coexist in the carbon materials, which adds to the difficulty in identifying the active site. A theoretical study indicates that for CO₂ electroreduction to CO on NCNTs, the optimal active site is pyridinic N, followed by pyrrolic N and graphitic N (Wu et al., 2015). Another study about CO₂RR on NCNTs emphasizes that the presence of graphitic and pyridinic N defects remarkably increases the selectivity toward CO formation and decreases the absolute overpotential (Sharma et al., 2015). For N-doped graphene-like material/carbon paper electrodes (NGM/CP), the FE is as high as 93.5% in producing CH₄, which is ascribed to the reactive pyridinic and pyrrolic N sites (Sun et al., 2016). A theoretical study suggested that COOH production on pyrrolic N3 is downhill by −0.21 eV, while it is uphill for pyridinic and graphitic N (Liu et al., 2016). Overall, both the experimental and theoretical studies indicate that N-doped carbon materials show significant catalytic performance of CO₂RR.

Inspired by these studies, we studied CO₂RR on N-doped graphene from the perspective of theoretical calculation in this work. To make a systematic comparison, N was doped into graphene at in-plane, zigzag edge, armchair edge, and pyrrolic edge sites, respectively. It would contribute to identifying the most dominant structure and providing a valuable design strategy for further activity enhancement in the experiment. In this study, the first-principle calculation has been performed to uncover the CO₂RR reaction pathways and electrocatalytic activity on different edges of N-doped (zigzag edge, armchair edge, and pyrrolic edge) graphene structures within a unified thermodynamic reaction scheme.

### COMPUTATIONAL METHODS AND MODELS

#### Methods

The geometry optimization and energy calculations were performed within the density functional theory (DFT) framework (Kohn and Sham, 1965) by using the Vienna ab initio simulation package (VASP) (Kresse and Furthmüller, 1996a). The ion–electron interaction was described by the projector-augmented wave (PAW) potentials (Blochl, 1994). The generalized gradient approximation parameterized by Perdew, Burke, and Ernzerhof was utilized as the exchange-correlation functional (Perdew et al., 1996). The kinetic energy cutoff of 400 eV was adopted for the plane-wave expansion. The armchair-edged ribbon, zigzag-edged ribbon, and periodic graphene slab were sampled with 4 × 1 × 1, 1 × 4 × 1, and 4 × 4 × 1 Monkhorst–Pack k-point grids (Delley, 2000), respectively. During the geometry optimization, all atoms were relaxed until the total energy was converged to 1.0 × 10⁻⁵ eV/atom, and the force was converged to 0.01 eV/Å. In addition, we considered the van der Waals (vdW) interactions by employing the semiempirical DFT-D2 forcefield approach (Grimme, 2006).

#### Models

The lattice parameters of 8.52 Å × 24.6 Å and 25.6 Å × 9.84 Å were set to model the armchair-edged graphene nanoribbon (including pyrrolic edge) and zigzag-edged graphene nanoribbon, respectively. The lattice parameters of 9.84 Å × 9.84 Å were adopted to model the periodic graphene slab. Perpendicular to all graphene structures, a vacuum layer of 15 Å was set, which was sufficiently large to minimize the image interactions.

The adsorption energy (ΔEads) of adsorbates was defined as follows:

\[
ΔE_{ads} = E_{substrate+adsorbate} - (E_{substrate} + E_{adsorbate},)
\]

where \( E_{substrate+adsorbate} \) is the total energy of the substrate with adsorbed molecules. \( E_{substrate} \) and \( E_{adsorbate} \) are the energy of the isolated substrate and free molecule, respectively.

#### Reaction Free Energy

The computational hydrogen electrode (CHE) model (Norskov et al., 2004) was adopted to evaluate the free energy change during the CO₂RR process. In the CHE model, the hydrogen atom is in equilibrium with the proton/electron pair at 298.15 K and 1 atm of pressure. In other words, the half chemical potential of gas-phase H₂ is equal to that of a proton/electron pair at 0 V in an aqueous solution.

The Gibbs free energy change (ΔG) for each elementary CO₂RR step involving proton/electron pair transfer was calculated by the expression (Norskov et al., 2004; Zuluaga and Stolbov, 2011):
\[ \Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH}, \]  

(2)

where \( \Delta E \) is the change of reaction energy based on DFT calculations. \( \Delta ZPE \) and \( \Delta S \) are the change of zero-point energy and entropy, respectively. \( T \) refers to the temperature (298.15 K). The zero-point energy (ZPE) of adsorbates has been calculated from the vibrational frequencies. For the free molecules (CO\(_2\), CO, HCOOH, CH\(_4\), CH\(_3\)OH, etc.) the vibrational frequencies and entropies are obtained from the NIST database (http://webbook.nist.gov/chemistry/). \( \Delta G_U = -neU \), where \( n \) is the number of transferred electrons, \( e \) is the elementary charge of an electron, and \( U \) is the electrode potential vs. RHE. \( \Delta G_{pH} = 2.303 k_B T \times \text{pH} \), \( k_B \) is the Boltzmann constant. In this work, the value of pH was set as 0 for the acid medium (Faccio et al., 2010; Shang et al., 2010). Approximate solvation corrections with a dielectric constant of \( \varepsilon = 80 \) are applied for the simulation of an aqueous environment (Mathew et al., 2019).

RESULT AND DISCUSSION

Adsorption of the Key Intermediates

In previous reports, the N-doped graphene materials have been widely studied as ORR electrocatalysts, which showed better stability and tolerance to methanol crossover effect than commercial Pt/C catalyst (Geng et al., 2011; Lin et al., 2013; Gong et al., 2009; Qu et al., 2010). Under different temperatures, the synthesizability of each type of the N-doped graphene materials is different. It is relatively easy to synthesize different types of N-doped graphene by controlling the temperature (Lin et al., 2013). The studied structures include five N-doped armchair graphene types, four N-doped zigzag graphene types, in-plane graphitic N (GN), and pyrrolic edge N (PyrroN)-doped graphene. For N-doped armchair graphene, it includes graphitic N (A-GN), pyridinic N (A-pyN), hydrogenated pyridinic N (A-pyN-H), oxidized pyridinic N (A-pyN-O), and pyridinic N hydroxide (A-pyN-OH), as shown in Figure 1. For N-doped zigzag graphene, four structures are considered, i.e., graphitic N (Z-GN), pyridinic N (Z-pyN), hydrogenated pyridinic N (Z-pyN-H), and oxidized pyridinic N (Z-pyN-O). These doped structures could be generated at high temperatures in the pyrolysis process of N-containing compounds (Wu et al., 2011; Li et al., 2012; Wang Q. et al., 2014; Holby et al., 2014).

During the CO\(_2\)RR process on the studied compounds, the intermediates mainly include CO\(_2\), COOH, HCOO, HCOOH, CO + H\(_2\)O, COOH, H\(_2\)COO, and COH + H\(_2\)O. By exploring different adsorption sites (N and its adjacent carbon atoms),
the most favorable adsorption configurations and sites are obtained (Supplementary Figures 1–8). Since the two main reactions on various N-doped graphene are HCOOH and CO generation pathways, we focus on the adsorption energies of CO2, COOH, HCOO, HCOOH, and CO as listed in Table 1, together with the bond distance between the adsorbed intermediates and catalyst surface. It is seen that the adsorption of CO2 molecule is weak all the time (-0.06 eV < -0.13 eV), and linear structure is maintained above the surface. To achieve high selectivity for HCOOH or CO, COOH (or HCOO) should be adsorbed strongly, but HCOO or CO should be adsorbed weakly for desorption. Therefore, strong COOH (HCOO) binding but weak HCOO (CO) adsorption is essential for the formation of HCOOH or (CO) (Sharma et al., 2015; Wu et al., 2015).

As shown in Supplementary Figures 2, 3, COOH could not be absorbed on GN and PyrroN, and is weakly adsorbed on A-pyN-H (-0.20 eV), Z-pyN-H (-0.43 eV), and Z-pyN-O (-0.59 eV) (Table 1). For the remaining structures, the adsorption of COOH is relatively strong, with the adsorption energy ranging from -0.95 to -2.48 eV. However, HCOO exists only on four N-doped graphene structures, that is, A-pyN, A-pyN-O, A-pyN-OH, and Z-GN. The adsorption energies for the four structures are in the range of -1.87 eV ~ -0.84 eV (Table 1).

For HCOOH, the adsorption energies for the studied compounds are in the range of -0.43 ~ -0.06 eV, which are relatively weak and facilitate its desorption from the catalyst surface. Similar to the HCOOH molecule, the adsorption energies of CO are in the range of -0.26 ~ -0.03 eV (Table 1).

**Reaction Mechanism**

The possible reaction pathways for the studied compounds are summarized in Figure 2. Based on the computational hydrogen electrode (CHE) model (Norskov et al., 2004), the limiting potential is obtained by $U_L = \Delta G_{\text{MAX}}^e$, where $\Delta G_{\text{MAX}}^e$ denotes the maximum free energy difference between the two successive reaction steps. The reduction step corresponding to the limiting potential is defined as the potential determining step (PDS). The calculated adsorption energies (Eads, eV) and the shortest distances (d, Å) between the intermediate and N-doped graphene.

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**N-Doped Armchair Graphene Nanoribbons**

As shown in Figures 2A–E, the energy of CO2 increases by 0.25–0.37 eV from the free molecule to the adsorbed state. After CO2 is adsorbed on the catalyst surface, it would be hydrogenated by (H+ + e-) pair. The formation of an O-H bond would produce COOH, while the formation of the C-H bond would generate the HCOO intermediate.

The reaction of CO2+H++e-→*COOH on A-GN, A-pyN, A-pyN-H, A-pyN-O, and A-pyN-OH is uphill by 1.16, 0.84, 2.14, 1.38, and 1.41 eV, respectively. For CO2+H++e-→*HCOO, the energy increases by 1.73, 1.38, and 1.81 eV for A-pyN, A-pyN-O, and A-pyN-OH, respectively.

The hydrogenation of COOH would generate COOH, HCOOH, and CO + H2O. Due to the large energy increase for producing COOH, that is, 1.55, 0.96, and 1.26 eV for A-GN, A-pyN, and A-pyN-OH, respectively, further discussion is not omitted. In COOH, if the OH moiety binds (H+ + e-), it would produce CO + H2O. If the carbon atom in COOH binds (H+ + e-), it would produce HCOOH. The production of HCOOH and CO is all thermodynamically downhill.

Similarly, the hydrogenation of HCOOH may produce H2COO and HCOOH. As *HCOO→H2COO step is endothermic with a large free energy increase (0.88 eV for A-pyN, 0.93 eV for A-pyN-O, and 1.86 eV for A-pyN-OH), further discussion is not provided. Thus, the final product from HCOOH is HCOOH.

As illustrated in Figures 2A–E, the COOH intermediate has better performance in producing HCOOH than HCOO. For CO2→*CO2→*COOH→*HCOOH→*CO, the PDS is *CO2→*COOH (Table 2), which is in agreement with the previous study (Wu et al., 2015). According to the free energy barrier (Figures 2A–E), A-pyN exhibits the highest catalytic activity toward HCOOH with a free energy barrier of 0.84 eV (Figure 2B). The order of catalytic activity for COOH to HCOOH/CO is A-pyN > A-GN > A-pyN-O > A-pyN-OH > A-pyN-H. In addition, CO2→*CO2→*COOH→*CO→H2O is the secondary pathway with slightly larger endothermic energy than CO2→*CO2→*COOH→*HCOOH.

**N-Doped Zigzag Graphene Nanoribbons**

The reaction pathways on N-doped zigzag graphene nanoribbons (Figures 2F–I) are similar to those on N-doped armchair...
FIGURE 2 | The free energy change for reaction pathways of CO₂RR on various N-doped graphenes. (A) A-GN, (B) A-pyN, (C) A-pyN-H, (D) A-pyN-O, (E) A-pyN-OH, (F) Z-GN, (G) Z-pyN, (H) Z-pyN-H, (I) Z-pyN-O, (J) GN.
graphene nanoribbons. The HCOO intermediate could only stably exist on Z-GN among these N-doped zigzag graphene nanoribbons. To produce HCOOH, the \( \text{CO}_2 \rightarrow \text{HCOO} \rightarrow \text{HCOOH} \) pathway is more favorable than the \( \text{CO}_2 \rightarrow \text{CO} \rightarrow \text{HCOOH} \) pathway (Figure 2F). In particular, on Z-GN, the hydrogenation of HCOO generates not only HCOOH but also O + HCHO with an energy barrier of 0.40 eV (Figure 2F). As illustrated in Figure 3, after the formation of O + HCOO, the remaining O atom could be easily hydrogenated into water due to the downhill process. The PDS for producing HCHO is the HCOO formation step with \( U_L = -0.81 \) V.

For the \( \text{CO}_2 \rightarrow \text{COOH} \) step, it occurred on Z-GN and Z-pyN most easily, in which the energy is uphill by 0.39 eV for Z-GN and downhill by -0.11 eV for Z-pyN, respectively (Figures 2F,G). While for the other two structures, large uphill energy barriers are required, that is, 1.88 eV for Z-pyN-H and 1.72 eV for Z-pyN-O, respectively. After the formation of COOH, its hydrogenation may generate HCOOH, CO + H₂O, or COOH, in which the formation of HCOOH is the most favorable, followed by CO + H₂O and COOH. Our calculations indicated that the COOH intermediate on Z-pyN needs an energy barrier of 0.83 eV to form COHOH (Figure 4). After the formation of COHOH, an energy increase of 0.41 eV is required to produce CO + H₂O. The further hydrogenation of COH is relatively easy due to the downhill energy process to release the two competitive final products, that is, \( \text{CH}_3\text{OH} \) and \( \text{CH}_4 \). A previous study indicated that the formation of \( \text{CH}_4 \) and \( \text{CH}_3\text{OH} \) is through CO intermediate (Hori et al., 2008), which is different from our results.

### GN and PyrroN-Doped Graphene

As mentioned above, the pyrrolic N-doped structure has no catalytic activity for CO₂RR. For GN, the free energy increase is the largest among all the N-doped graphene structures (2.55 eV). Thus, the catalytic activity of GN is omitted.

In a word, for the studied structures, the most favorable product is HCOOH, followed by CO and COHOH. In particular, the formation of HCOOH and CO is competitive since the free energy of CO is more thermodynamically favorable by only about 0.20 eV than that of HCOOH. This energy difference is similar to the value of 0.28 eV reported earlier (Liu et al., 2016). In a word, Z-pyN and Z-GN possess the highest catalytic activity toward HCOOH due to the smallest limiting potential of \(-0.38\) and \(-0.39\) V, respectively (Table 2), which is lower than \(-0.44\) for PyrroN3 (Liu et al., 2016).

### Hydrogen Evolution Reactions

Hydrogen evolution reaction (HER) is the competitive reaction for CO₂RR since the evolution of H would consume the proton–electron pair (\( \text{H}^+ + e^- \)) and passivate the catalytic activity of CO₂RR. For the studied structures, the results showed that Z-pyN-O and Z-pyN have large energetic downhill for the adsorption of H*, indicating the enhanced HER in thermodynamic (Figure 5). For Z-GN and A-pyN, they have a negligible free energy barrier (0.03 and 0.04 eV) of H*. For the remaining structures, HER is hindered by large free energy barriers. Therefore, for the most favorable Z-pyN and

| PDS | \( U_L \) | \( U_0 \) | \( \eta \) | Product |
|------|--------|--------|--------|---------|
| Z-GN | \( \text{CO}_2^* + \text{H}^* + e^- \rightarrow \text{COOH} \) | -0.39 | -0.25 | 0.14 | HCOOH |
| Z-GN | \( \text{CO}_2^* + \text{H}^* + e^- \rightarrow \text{COOH} \) | -0.39 | -0.11 | 0.28 | CO |
| Z-GN | \( \text{CO}_2^* + \text{H}^* + e^- \rightarrow \text{HCOO} \) | -0.81 | -0.07 | 0.74 | HCHO |
| Z-pyN | \( \text{CO}_2^* + \text{H}^* + e^- \rightarrow \text{COOH} \) | -0.38 | -0.25 | 0.13 | HCOOH |
| Z-pyN | \( \text{CO}_2^* + \text{H}^* + e^- \rightarrow \text{HCOO} \) | -0.38 | -0.11 | 0.27 | CO |
| Z-pyN | \( \text{COOH}^* + \text{H}^* + e^- \rightarrow \text{HCOOH} \) | -0.83 | 0.02 | 0.81 | HCHO |
| Z-pyN | \( \text{COOH}^* + \text{H}^* + e^- \rightarrow \text{HCOOH} \) | -0.83 | 0.17 | 0.66 | CH₄ |
| PyrroN3 | \( \text{COOH}^* + \text{H}^* + e^- \rightarrow \text{HCOOH} \) | -0.44 | — | — | HCOOH |
| Edge-2gN | \( \text{CO}_2^* + \text{H}^* + e^- \rightarrow \text{COOH} \) | -0.52 | — | — | CO |

The "*" denotes the adsorption state of the species.

**FIGURE 3 |** The free energy change for the reaction of \( \text{CO}_2 + 4\text{H}^* + 4e^- \rightarrow \text{HCHO} + \text{H}_2\text{O} \) on Z-GN.
Z-GN, CO₂RR would be suppressed by HER. However, by choosing a suitable electrolyte, the activation energy of HER would be increased. For instance, according to the expression \[ \Delta G_{pH} = 2.303 k_B T \ln(pH) \], in which pH = 0 is selected in the above study, \( \Delta G_{pH} = 0.42 \text{ eV} \) is obtained for pH = 7.0. Thus, the activation energy of HER on Z-GN would be increased from \(-0.03\) to \(0.39\) eV, comparable to the free energy barrier of \(0.38\) eV in the CO₂RR process. Thus, the HER could be suppressed by increasing the pH value for Z-GN. While for Z-pyN, CO₂RR is passivated by too strong HER. In a word, Z-GN could be selected as a promising nonmetal electrocatalyst for CO₂RR in generating HCOOH.

### CONCLUSION

We have performed the DFT method to elucidate the reaction mechanism and activity of CO₂RR on 11 types of N-doped graphene catalysts. It indicates that for all the studied structures, the formation of HCOOH is the most favorable, followed by CO.
Among these structures, Z-pyN- and Z-GN-doped graphene exhibit the best catalytic activity for producing HCOOH with free energy barriers of 0.38 and 0.39 eV, respectively. The potential determining step (PDS) is CO$_2$→*CO for Z-pyN and *CO$_2$→*COOH for Z-GN, respectively. Meanwhile, CO is the competitive product which lies 0.20 eV above HCOOH. For the zigzag graphitic N-doped graphene, it could also produce CH$_3$OH and CH$_4$ as the minor products which need to overcome an energy barrier of 0.83 eV. The minor product for the zigzag graphitic N-doped graphene is HCHO, with an energy barrier of 0.81 eV. However, for Z-pyN, CO$_2$RR is passivated by too strong HER. Meanwhile, by modifying the pH value of electrolyte, Z-GN could be selected as a promising nonmetal electrocatalyst for CO$_2$RR in generating HCOOH.

**AUTHOR CONTRIBUTIONS**

The author confirms being the sole contributor to this work and has approved it for publication.

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**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2021.734460/full#supplementary-material

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