Theoretical Investigations into Defected Graphene for Electrochemical Reduction of CO₂

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Supporting Information

ABSTRACT: Despite numerous experimental efforts that have been dedicated to studying carbon-based materials for electrochemical reduction of CO₂, a rationalization of the associated trends in the intrinsic activity of different active motifs has so far been elusive. In the present work, we employ density functional theory calculations to examine a variety of different active sites in N-doped graphene to give a comprehensive outline of the trends in activity. We find that adsorption energies of COOH* and CO* do not follow the linear scaling relationships observed for the pure transition metals, and this unique scaling is rationalized through differences in electronic structure between transition metals and defected graphene. This finding rationalizes most of the experimental observations on the carbon-based materials which present promising catalysts for the two-electron reduction of CO₂ to CO. With this simple thermodynamic analysis, we identify several active sites that are expected to exhibit a comparable or even better activity to the state-of-the-art gold catalyst, and several configurations are suggested to be selective for CO₂RR over HER.

KEYWORDS: Density functional theory (DFT), Calculated limiting potential, Hydrogen evolution reaction (HER), Scaling relation, Free energy diagram

INTRODUCTION

Global average carbon dioxide (CO₂) concentration at the surface—the main driver of recent climate change—has reached 400 ppm for the first time in recorded history. In recent years, several strategies have been proposed to mitigate atmospheric CO₂ concentration, including CO₂ capture, storage, and conversion into valuable products. Among these, electrochemical conversion and reduction of CO₂ coupled with a renewable energy source (such as wind or solar) has attracted much attention as an approach to generate carbon-neutral fuels or industrial chemicals.29–33 Many potential electrocatalysts have been suggested, including transition metals (e.g., Cu,1–4 Au, and Ag), transition metal oxides (e.g., RuO₂, oxide-derived copper),5–11 transition metal dichalcogenides (e.g., MoS₂, MoSe₂),12,13 metal-functionalized porphyrin like structure,14–17 and metal–organic frameworks.18,19

Carbon-based materials are particularly interesting potential catalysts for the CO₂ reduction reaction (CO₂RR) due to their low cost and ability to form a wide range of nanostructures.20–24 They are chemically inactive at negative potential ranges and present high overpotentials for the hydrogen evolution reaction compared to metal surfaces.25 Pristine graphene does not exhibit any activity. However, introducing dopants26,27 and defects28 during the synthesis tailors the electronic structure and catalytic properties of nanostructured carbon materials.28 N-doping has been shown to significantly enhance the CO₂ reduction activity.30,31 Different types of naturally occurring defects can also modulate the catalytic activity.26,34,35 It is interesting to note that there is an interplay between N-doping and the number of generated defects.36 N-doping is energetically more favorable near the defects especially around the pentagons and represents the important role of defect-induced strain in the stability of the N-dopant.36

Figure 1 displays the performance of several carbon-based materials that have been tested and reported for the electrochemical reduction of CO₂.29,30,37–41 The reported overpotentials and Faradaic efficiencies in Figure 1a correspond to the maximum collected CO in each report. The partial current
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The potential of U = −0.12 V vs the reversible hydrogen electrode (RHE) is obtained by shifting the chemical potential of the electrons at the equilibrium maximum potential allowed by thermodynamics. The potential at which the electrochemical reaction takes place is called the limiting potential, which can be obtained by the difference between the equilibrium potential and overpotential. At the limiting potential, all the reaction steps are downhill in free energy.

RESULTS AND DISCUSSION

Taking into account the two-dimensional graphene sheets as a model system, we introduce different types of defects as depicted in Figure 1a, including mono vacancies (MV) as well as several double vacancies (DV), such as 555-777, 55-6-777, and Stone Wales 55-77. We also consider two different line defects including 558 and 555-777. Here, 5, 6, 7, and 8 refer to the pentagon, hexagon, heptagon, and octagon, respectively, in the defect configuration. Further details on the relative stability of different modeled defect configurations are provided in Table S2 in the Supporting Information. Our calculations indicate that MV is too reactive to contribute to the CO₂ reduction catalysis, while some of the DVs can catalyze CO₂RR.

Using DFT calculations and the computational hydrogen electrode approach (SI), the CO₂ reduction reaction mechanism has been explored and reported on transition metal surfaces.45 A simple thermochemical analysis shows the pathway for CO₂ reduction to CO through COOH* and CO* intermediates

\[
\text{CO}_2 + * + (\text{H}^+ + e^-) \rightarrow \text{COOH}^* \\
\text{COOH}^* + (\text{H}^+ + e^-) \rightarrow \text{CO}^* + \text{H}_2\text{O} \\
\text{CO}^* \rightarrow \text{CO} + * \\
\text{Total: } \text{CO}_2 + 2(\text{H}^+ + e^-) \rightarrow \text{CO} + \text{H}_2\text{O} \\
E^0 = -0.12 \text{ V}
\]

If the surface adsorbs CO weakly, the CO molecule readily desorbs from the surface, and the major product will be CO gas. Au and Ag, for example, bind CO weakly and are selective for the two-electron reduction of CO₂ to CO.46 On the other hand, for the transition metal surfaces that bind CO, further reduced products past CO may be produced, where the activity has been suggested to be limited by the reduction of CO* to CHO*.1

Figure 2b displays the calculated chemisorption energies of COOH* vs CO* on the studied active motifs as well as transition metals (111) surfaces. As can be seen, there is a linear scaling relation between COOH* and CO* adsorption energies in the case of transition metals.45 The orange dashed line shows the chemical potential of CO in the gas phase, separating the region that CO can be bound to the surface and therefore gets further reduced from no adsorption regime. Copper is in the border and weakly binds CO, while gold and silver are in the no adsorption regime. We note that most of the examined active sites do not fall on the known scaling line for the transition metals because they do not bind CO. This is the reason that carbon-based materials represent especially interesting alternatives for the two-electron reduction of CO₂ to CO.

For the examined active sites in Figure 2a with positive CO* binding energy, the activity toward CO production can be determined exclusively by the COOH* binding strength. An optimal COOH* binding strength, not too weak and not too strong, is desirable in line with the Sabatier principle (Figure 2c). The equilibrium potential for two-electron reduction of CO₂ to CO (eq 4) is −0.12 V vs RHE. Using thermodynamic

### Table 1

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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Aqueous Electrolyte</th>
<th>References</th>
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<td>0.1 M KClO₄</td>
<td>[4]</td>
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<td>N-doped carbon nanotubes</td>
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<tr>
<td>4</td>
<td>N-doped reduced graphene oxide</td>
<td>0.1 M KClO₄</td>
<td>[4]</td>
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<td>This work</td>
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<td>6</td>
<td>~20-40nm Au nanoparticles</td>
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<td>8</td>
<td>~8 nm Au nanoparticle</td>
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Figure 1. Performance map for CO₂RR over reported N-doped carbon-based materials as well as N-doped reduced graphene oxide (N-rGO) studied in this work (experimental details are in the Supporting Information). Au and Ag are reported for comparison. Representative CO (a) Faradaic efficiencies, (b) current density, and their corresponding overpotentials are plotted for each reported catalyst. Data for the plots are listed in the Supporting Information, Table S1.
Figure 2. (a) Optimized structures of different examined carbon structures with and without N-doped, where LD stands for line defect. Here, 5, 6, 7, and 8 refer to the pentagon, hexagon, heptagon, and octagon in the defect configuration. Color code: C, gray; N, blue. (b) Calculated chemisorption energies of COOH* vs CO* intermediates for examined carbon-based materials. Numbers refer to the structures shown in panel (a). Transition metals (111) are depicted in black, adapted from ref 45 for comparison. Energies for CO* are relative to gas-phase CO and H₂ and for COOH* are relative to gas-phase CO₂ and H₂. The vertical dashed line corresponds to the chemical potential of CO in the gas phase. (c) Activity volcano for two-electron reduction of CO₂ to CO. (d) Free energy diagram of CO₂ to CO conversion on different examined active sites displayed in panel (a) at equilibrium potential of −0.12 V vs RHE. (e) The p-projected density of states for pure graphene and N-doped defective carbon labeled as number (5) in panel (a) as an example.
considerations alone, the ideal catalyst should have a COOH* binding energy of 0.12 eV at zero applied potential.

The horizontal red line in Figure 2b displays the adsorption energy of the ideal catalyst that effectively catalyzes the two-electron reduction of CO₂ to CO. The vertical distance between this line and each point in the graph can be used as a metric for activity. Interestingly, many of the examined active sites show higher activity than Au for the two-electron reduction of CO₂ to CO. This information can be translated into a thermodynamic activity volcano (Figure 2c) with COOH binding energy as descriptor and a free energy diagram at the equilibrium potential of −0.12 V vs RHE (Figure 2d). These plots suggest that the COOH* formation is rather difficult and is the bottleneck step for CO production on pyrrolic-N (Figure 2a (15)) and N-doped at pristine graphene (Figure 2a (1)). Therefore, the overall CO₂ reduction activity is severely limited by formation of COOH*. Pyridinic-N (14), on the other hand, has a surmountable *COOH formation energy at relatively low overpotentials, and CO desorption is facile. This has been previously reported by Wu et al., who assigned the CO₂ reduction activity on N-doped carbon nanotube to the pyridinic-N based on a similar thermodynamic analysis. Figure 2b and c show that several defects with and without N-doped are as active as pyridinic-N for the CO₂RR. For example, the S58-line defect (Figure2a (12)) and N-doped in the S55-6-777 (Figure2a (7)) defective structure show comparable activity to pyridinic-N. Moreover, there are a number of other sites, such as N-doped S5-77 (Figure2a (5)), S55-6-777 (Figure2a (6)), N-doped S58-line defect (Figure2a (13)), and S55-777 defect (Figure2a (2)), that exhibit lower activity than pyridinic-N but represent activities close to or higher than Au and Ag.

The difference in scaling behavior between transition metals and defective graphene can be rationalized through their differences in electronic structure. CO binds to transition metals through the interplay between attractive π* and repulsive σ interactions with the metal d-states.46 Pristine graphene is a semiconductor with no states at the Fermi level (Figure 2e), which does not provide attractive interactions with CO. Intense electron localization, however, is present around N-dopants and defects in graphene (Figure 2e). Such sites introduce the possibility for covalent bonds to COOH, which is a radical, but not CO, which has a closed shell configuration. This bonding picture is similar to that suggested for transition metal dichalcogenide edges  and p-block dopants in metals, both of which show similar deviations from transition metal scaling relations.

**HER Analysis.** In general, the carbon-based materials represent high overpotentials for a hydrogen evolution reaction (HER) compared to metal surfaces.25 Herein, we analyze the competition between HER and CO₂RR using the thermodynamic limiting potentials Uₐ. It was shown that the difference between the thermodynamic limiting potentials for CO₂RR and HER, Uᵢ(CO₂) − Uᵢ(H₂), follows trends in selectivity on transition metals, and the magnitude of this difference for the metals is less than 0.5 V on the metals that reduce CO₂ with significant Faradaic efficiency (FE).45 For metals binding CO* weaker than Cu, Uᵢ(CO₂) is determined by the COOH* formation from CO₂. For Cu and metals binding CO* stronger than Cu, protonation of CO* to CHO* determines the limiting potential.

Assuming that the corresponding electrochemical barriers scale similarly in both carbon-based and transition metal catalysts, we can apply the same analysis in the present work to obtain an estimate of the selectivity. This analysis does not apply for the catalysts with strong CO* binding energy, where the CO desorption process is slow and the Faradaic efficiency is negligible.

Figure 3a and b display the Uᵢ(CO₂), Uᵢ(H₂), and (Uᵢ(CO₂) − Uᵢ(H₂)) for the configurations shown in the free energy

![Figure 3a](image)

![Figure 3b](image)

**Figure 3.** (a) Calculated limiting potentials for HER and CO₂RR. (b) Calculated Uᵢ(CO₂) − Uᵢ(H₂) on the active sites studied in Figure 2d compared to Au(111).

**CONCLUSION**

In summary, we have studied a diverse range of possible active sites in N-doped carbon-based materials and showed that the calculated adsorption energies do not follow the scaling relations established for transition metal surfaces. This difference in scaling is rationalized by the presence of electron localization in the defective sites of graphene which binds COOH but not CO. This unique scaling rationalizes the numerous experimental reports of low overpotentials for CO₂ reduction to CO on carbon-based materials. We used the calculated COOH* adsorption energy as an activity metric to map out the trends in activity of different active site motifs. COOH* adsorption energies vary significantly depending on the type of active site,
allowing for a wide range of possible activities. Based on this simple thermodynamic picture, several configurations are suggested to be selective for CO₂RR over HER, and pyridinic-N is suggested to be the most selective site for the CO₂RR over HER. Future work will investigate activation energies and kinetics in order to fully evaluate the efficiency and selectivity of candidate active site motifs.

**COMPUTATIONAL DETAILS**

Density functional theory calculations for the carbon-based materials were performed using the QUANTUM ESPRESSO program package and the Atomic Simulation Environment (ASE). The electronic wave functions were expanded in plane waves up to a cutoff energy of 500 eV, while the electron density was represented on a grid with an energy cutoff of 5000 eV. Core electrons are approximated with ultrasoft pseudopotentials. We use the BEEF-vdW exchange-correlation functional, which has been shown to accurately describe chemisorption as well as physisorption properties on graphene. For adsorption studies, a supercell of lateral size of (4 × 4) for nondefective and (8 × 8) for defective structures are used, and a vacuum region of at least 18 Å is used to decouple the periodic images. The functional, which has been shown to accurately describe chemisorption as well as physisorption properties on graphene, was allowed to relax until the maximum force on each atom was below 0.05 eV/Å for each calculation.

**ASSOCIATED CONTENT**

Supporting Information
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Information as mentioned in the text. (PDF)

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**Notes**

The authors declare no competing financial interest.

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**REFERENCES**