



Divacancy-nitrogen/boron-codoped graphene as a metal-free catalyst for high-efficient CO oxidation

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HIGHLIGHTS

- The formation of B-doped GN4 sheet can be stable enough at high temperature.
- Strong adsorption and high activation of CO and O₂ molecules adsorb on B-GN4 sheet.
- The catalytic reactions of CO oxidation on B-GN4 sheet are comparably investigated.
- Dissociative adsorption of O₂ molecule is an energetically more favorable process.

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ABSTRACT

Metal-free catalysts have attracted wide attention due to their potentially catalytic applications. We performed density functional theory (DFT) calculations to investigate the different reaction mechanisms for CO catalytic oxidation on single-atom B incorporated into divacancy-nitrogen-doped graphene sheet (B-GN4). The calculated results show that the B atom can be strongly trapped at the active center of GN4 sheet and the formed B-GN4 configuration can be stable enough at high temperature. Based on the strong adsorption and significant activation of the reactants (CO and O₂), the possible catalytic reactions of CO oxidation on the B-GN4 sheet are comparably studied through the Eley–Rideal (ER) and Langmuir–Hinshelwood (LH) mechanisms. In the sequential reactions, the dissociative adsorption of an O₂ molecule as a starting step and following by the ER reactions (2O + 2CO → 2CO₂) have much smaller energy barriers than the traditional ER and LH mechanisms. Besides, the dissociative reaction of CO molecule on the B-GN4 sheet, the formation process and surface activity of B-C codoped GN4 sheet (BC-GN4) are analyzed. This result indicates that the B-GN4 sheet as an anode material can promote the CO oxidation reaction, which provides a comprehensive understanding of graphene-based metal-free catalyst.

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1. Introduction

As a carbon allotrope, graphene nanomaterials have attracted more and more attention due to their excellent performance [1], such as high thermal, conductivity and mechanism properties [2–5]. Especially, the huge surface-volume ratio of graphene can be used as a promising substrate to deposit the metal catalysts [6–9]. Generally, platinum (Pt) and its alloy have been used as electro-catalyst for fuel cells [10]. Recent results demonstrated that small Pt clusters on graphene systems exhibit high stability and catalytic activity for CO oxidation [11–14]. Downsizing the nanoparticles catalyst is one of the ways to reduce the Pt loading and the cost of

catalyst. Some works investigated that the single-atom Pt anchored on graphene [15–17] and other metal oxide (SnO₂ [18] and FeO_x [19]) presented the high catalytic activity. However, the Pt-based catalysts suffer from very limited reserves, high cost and susceptibility to time-dependent drift. Therefore, it is necessary to identify non-precious metals or even metal-free catalysts to reduce or replace the Pt-based catalysts in fuel-cell technologies.

Graphene can be considered either as a metal with vanishing Fermi surface or a semiconductor with zero bandgap, yet these properties weakens the catalytic activity and limits the broader applications of pristine graphene (pristine-graphene) in such as electrocatalysis, nanoelectronics and energy storage [8,20–25]. Fortunately, the chemical doping has been proposed to regulate its electronic and electrochemical properties by changing the electronic density of graphene system [26]. The introductions of metal impurities have been demonstrated both experimentally and theoretically as a successful method to tune the electronic, magnetic property and surface activity of graphene [27–30]. Recently, Chambers et al. demonstrated that metastable induced electron spectroscopy (MIES) can be used to measure directly the structural and electronic characteristics of graphene samples [31]. The metal-decorated graphene exhibit the high gas sensitivity for the adsorbed molecules (H₂O, H₂, NH₃, NO₂ and CO) through the charge transfer at their interfaces [32–35]. Compared with noble metal catalysts (Au, Pd and Pt) [36–38], some results confirmed that the non-noble metal atoms (Co, Fe, Ni and Al) doped graphene configurations were quite stable and can effectively enhance the catalytic activity of graphene sheet [39–42]. For example, theoretical studies found that the single-atom Ni– [43], Fe– [44–46], Al– [47] and Co [48] embedded graphene systems presented the high catalyzing for CO oxidation. Although the above results illustrated that the single-atom metal catalyst can increase the active sites and enhance the chemical activity significantly of graphene sheets, however, with reducing the consumption of metal catalysts, it is important to exploit efficient metal-free catalysts for the CO oxidation, in order to satisfy the further needs for practical application.

Functionalization of modified graphene as metal-free catalysts (nitrogen, boron, sulfur, silicon and phosphorus) for enhancing oxygen reduction reaction (ORR) have been investigated through experimental and theoretical studies [49–58]. Some computational results investigated the silicon-decorated graphene sheets can be used as a sensor for detecting gas molecules [59] and acts as a metal-free catalyst N₂O reduction [60,61] and CO oxidation [62]. Dai et al., investigated that the B-, S- and P-doped graphene could be a good sensor for the adsorbed NO₂, SO₂ and O₂ [63,64]. Compared with other non-metal atoms, the N-doped graphene is the most intensively studied doping model due to the N element is next to C and its electronegativity is larger than that of C atom. The N heteroatom could be introduced directly during the graphene grown by chemical vapor deposition method [65] and then improve the surface activity of graphene by turning the electronic structure and local curvature. The incorporation of N atoms into the graphene matrix can lead different doping configurations [66] and are recognized as a high electrocatalytic activity toward ORR [67] or NO reduction [68]. Recently, many studies proposed that the active sites would consist of metal atoms coordinated by four pyridinic N within graphitic sheets (GN4) [69,70]. The formation of GN4 sheet is energetically stable in the actual operated environments and could be one better candidate for improving the dispersion and the reactivity of supported catalysts [71,72]. These studies have evaluated ORR catalysis based on heteroatom-doped graphene sheets, however, more in-depth studies on the catalytic performance of GN4 configuration are still lacking. It is expected to explore the novel metal-free catalyst and stimulate widely applications in more

reactions.

The catalytic oxidation of carbon monoxide (CO) is often regarded as a vital prototype reaction in heterogeneous catalytic processes [73,74] and also be useful to evaluate the reactivity of some new catalysts. Recently, the calculated results shown that a single Co atom incorporated with pyridinic nitrogen graphene [75] and a Fe stabilized by divacancy-nitrogen-doped graphene [76] exhibit highly catalytic efficient for CO oxidation. Meanwhile, the ORR activity of metallic heteroatoms into GN4 systems is comparable to or even higher than that of Pt-based catalyst [77,78]. Compared with metal atoms, there is a lack of systematical study on the geometric, electronic and catalytic properties of non-metal (NM) atom coordinate GN4 sheet, since the formation of NM covalent bonds are stronger than that of NM-metal or metal bonds. This issue is unresolved that whether the NM coordinated GN4 (NM-GN4) exhibits highly catalytic reactivity, and largely the lack of knowledge on the exact active site and the catalytic mechanism toward CO oxidation. Herein, we choose the B atom due to it is one electron deficient and is less electronegative than that of carbon atom. Moreover, the B atom as electron acceptors and N atom as electron donors could lower the valence band and elevate the conduction band that results in electron relocalization and activation of graphene sheet, and the formation of B and N structure showed an excellent ORR performance in alkaline solutions [79,80]. Thus, it is natural to ask whether the B atom coordinated GN4 (B-GN4) configuration can be used to achieve new functionalities.

In this work, the adsorption stability and electronic structures of reactive gases (CO and O₂) on the B-GN4 sheet are investigated using the first-principle based on density functional theory (DFT). The sequential CO oxidation reactions on the B-GN4 sheet are systematically analyzed through considering both the Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) mechanisms. It is found that the CO oxidation reactions are more likely to proceed rapidly (~ 0.5 eV) on the B-GN4 sheet. Compared with other initial reactions, the dissociation of O₂ molecule is an energetically more preferable process and then the generated O atoms reacting with two CO molecules by the ER reaction. To the best of our knowledge, few reports provide much systemic information about the catalytic activity of NM-GN4 sheet for CO oxidation. These results suggest that the configuration of GN4 sheet could provide a valuable reference for designing the novel metal-free catalyst.

2. Computational model and methods

Spin-polarized DFT calculations are carried out by the Vienna *ab initio* simulation package (VASP) [81,82] with the projector augmented wave (PAW) pseudo-potentials [83]. Exchange-correlation functions is described with the generalized gradient approximation (GGA) in the form of Perdew, Burke, and Ernzerhof (PBE) functional [84]. Previous studies in our group have demonstrated that the PBE functional used in the DFT calculations is an appropriate level of theory for an accurate description of the structural and electronic properties of graphene-based materials [85–87]. The kinetic energy cutoff for the plane-wave basis set is chosen to be 450 eV. The B 2s²2p¹, C 2s²2p², N 2s²2p³ and O 2s²2p⁴ states are treated as valence electrons. An armchair edge of graphene ribbon with a 4 × 7 supercell is adopted and the vacuum layer is set to 20 Å to avoid the interaction among mirror images. The calculated lattice constant of graphene sheet is 2.47 Å, which quite approximates to the experimental value of 2.46 Å [88]. In order to improve convergence of states near the Fermi level (E_F), the Brillouin zone (BZ) integration is sampled using a 3 × 1 × 1 *Γ*-centered Monkhorst-Pack (MP) grid and a *Γ*-centered MP grid of 15 × 1 × 1 is used for the final density of states (DOS) calculations.

Bader charge analysis [89] was used to evaluate the atomic

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