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Full Length Article

Boosting graphene reactivity with co-doping of boron and nitrogen atoms: CO oxidation by O_2 molecule

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ABSTRACT

The aim of this study is to compare the catalytic activity of BC_mN_n-doped graphene sheets (Gr-BC_mN_n; m, n = 0, 1, 2, 3 and m + n = 3) towards the oxidation of CO molecule. By performing periodic density functional theory calculations, we show how BN co-doping can boost the surface reactivity of graphene and improve its catalytic performance in the CO + O_2 reaction. Our results indicate that the positively charged B atom in Gr-BCN_2 and Gr-BN_3 sheets is beneficial to the capture of O_2 molecule and serve as the catalytic active sites for the CO oxidation reaction. Both Langmuir–Hinshelwood (LH) and Eley–Rideal (ER) mechanisms are considered for the CO oxidation reaction over Gr-BCN_2 and Gr-BN_3. It is found that the CO oxidation proceeds first via the LH mechanism CO + O_2 → OCOO → CO_2 + O∗ and then via the ER mechanism CO + O∗ → CO_2. The origin of high catalytic activity of these surfaces is attributed to the large electronegative difference between the B and N atoms.

1. Introduction

Carbon monoxide is an important air pollutant, coming mainly from incomplete burning of fossil fuels in automobiles and industrial processes. Over the past decades, much attention has been devoted to the low-temperature oxidation of CO, due to its importance in solving the increasing environmental problems [1–5]. In addition, this simple reaction is often quoted for testing the reactivity of new catalysts. Though, many efforts have been recently devoted to CO oxidation by various noble metals such as Pd, Pt, and Au [6–12]. To enhance the reactivity of these catalysts, decreasing the size of noble metal particles has been also suggested [13–17]. However, the noble metals are scare, expensive and usually need high reaction temperature for efficient operation. Hence, it is desirable to design efficient and low-cost catalysts for the low-temperature oxidation of CO.

In search of low-cost and metal-free catalysts for CO oxidation, the carbon-based nanostructures like carbon nanotubes, graphene and fullerenes have recently attracted considerable attention [18–23]. Graphene is a two-dimensional monolayer of sp^2 hybridized carbon atoms which has been the focus of intensive researches due to its excellent physical and chemical properties for various applications. In particular, the large specific surface area and high chemical stability of graphene make it as an ideal support for metal atoms and clusters to realize new carbon-metal nanocomposite catalysts [24–28]. In addition, it is proved that the existence of various vacancy defects on graphene can considerably enhance the binding and dispersion of metal atoms [29–34]. As a result, the migration barrier of the doped heteroatom on defective graphene is large enough to guarantee its stability to be utilized in catalysis applications. For example, earlier theoretical studies have demonstrated that the Al- [35,36], Si- [37], Ni [21], or Se- [38] doped graphene shows a promising catalytic activity towards CO oxidation. The origin of such enhanced catalytic activity is usually attributed to the electronegativity difference between the heteroatom and carbon atoms, which leads to a sizable charge-transfer from the heteroatom into its neighboring carbon atoms and hence the activation of the incoming O_2 molecule. Many literatures [39–41] have also reported that the introduction of electropositive boron atoms into graphene lattice can leads to a significant charge polarization of the surface and activation of the molecular oxygen in the oxygen reduction reaction.

Recent studies have demonstrated that the simultaneous introduction of two or more heteroatoms into the graphene lattice is a promising approach to further improve its catalytic activity [42–47]. For instance, Wang et al. [26] demonstrated that the B and N co-doped graphene exhibits higher catalytic activity for the reduction of O_2 than that of B- or N-singly doped graphene. This can be attributed to the synergistic effect between the B and N atoms in the BN co-doped graphene. Although the BN co-doping keeps the average electron count the same as for the pristine graphene, however, it is able considerably change the electronic structure of the carbon support due to the synergistic effect between the B and N atoms. The large electronegativity difference between the B and N atoms induces heterogeneity in the graphene surface and makes B atom as an active catalytic site to improve the ORR

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activity [45]. It should be noted that such synergy effect between the B and N atoms depends considerably on the doping configuration. Using the density functional theory (DFT) calculations, Kattel and coworkers [48] found that the adsorption of O_2 on BN_3-doped graphene is much larger than those of BN_2- or BN- ones, and predicted that the former site could easily promote the oxygen reduction reaction in the BN co-doped graphene.

Although to our knowledge, no experimental study has been published on the catalytic oxidation of CO molecule over the BN co-doped graphene, this case is actually most interesting, as it is expected to provide new strategy to fabricate metal-free catalysts based on graphene. The aim of this study is to screening the synergic effects of co-doped B and N atoms for the oxidation of CO by O_2 molecule. Considering the high catalytic activity of these co-doped graphene sheets in the oxygen reduction reaction [26,45–48], our interest here is to study how the incorporation of N atom around the B atom can modify the catalytic activity of the surface. The adsorption configurations, electronic structures, and catalytic activity of the BN co-doped graphene surface are investigated in detail. All possible reaction pathways are considered for the oxidation of CO. Our results clearly show that the BN co-doped graphene can be regarded as a potential metal-free catalyst for the CO reduction.

2. Computational details

We performed the spin-polarized DFT calculations using the $DMol^3$ [49,50] with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional [51]. A double numerical basis set with polarization function (DNP) was adopted in the calculations. To consider the van der Waals effects, the empirical correction in the Grimme's scheme was employed [52,53]. No symmetry constraint was used during the geometry optimizations. The convergence tolerance of energy of 1.0×10^{-5} Ha, maximum force of 0.001 Ha/Å and maximum displacement of 0.005 Å were employed in all the geometry optimizations. In order to achieve accurate electronic convergence, a smearing of 0.005 Ha to the orbital occupation was applied.

In the calculations, a 4 × 4 supercell of graphene (containing 32 C atoms) was used as base material. The vacuum space was set with 15 Å in the z direction to avoid the interaction between periodic images. Four different graphitic models including B-, BN-, BN_2- and BN_3- doped graphene were considered as the catalytic substrate. These are labeled as Gr-BC_3, Gr-BC_2N, Gr-BCN_2 and Gr-BN_3, respectively (Fig. 1). The 3 × 3 × 1 k points were used for calculating the Brillouin zone integration. The minimum-energy pathway (MEP) for each reaction step was obtained by linear synchronous transit (LST)/quadratic synchronous transit (QST) and nudged elastic band (NEB) methods. The nature of transition states were verified by the vibrational frequencies, which exhibit only one imaginary frequency throughout the potential energy surface. The formation energy (E_{form}) of Gr-BC_mN_n sheets was obtained by the following formula:

$$E_{form} = (E_{Gr-BCmNn} - \mu_B - n\mu_N + m\mu_C) - E_{Gr} \quad (1)$$

where $E_{Gr-BCmNn}$ is the total energy of the graphitic Gr-BC_mN_n sheet and E_{Gr} is the total energy of the pristine graphene. The μ_B, μ_C and μ_N are the chemical potentials of B, C and N atoms, respectively.

The adsorption energy (E_{ads}) of each adsorbate was computed using the following equation:

$$E_{ads} = E_{A-S} - E_S - E_A \quad (2)$$

where E_{A-S}, E_S and E_A are the total energies of the adsorbate-substrate (A–S) system, the substrate (S) and adsorbate (A), respectively. All calculated E_{ads} values were corrected by zero-point energy (ZPE) obtained from the frequency analysis. Atomic charges and charge-transfer values were obtained by the Hirshfeld charge density analysis [54]. Earlier studies [38,55,56] have frequently indicated that this method is one of the most popular approaches to obtain atomic charges in the periodic systems. Wiberg and Rablen [57] have found a good correlation between the charges calculated with the Hirshfeld and Bader approaches.

3. Results and discussion

3.1. Properties of B-doped and BN co-doped graphene sheets

In Fig. 1, we have shown the optimized structure and corresponding density of states (DOS) plot of different Gr-BC_mN_n sheets where, m, n = 0, 1, 2, 3 and m + n = 3. Table 1 summarizes the calculated atomic charge on the B atom and formation energy of each graphitic sheet. Our DFT calculations reveal that the simultaneous doping of graphene with both B and N atoms is energetically favorable, which is consistent with the previous experimental and theoretical studies [26,45,48]. The B-N and B-C bond distances in Gr-BC_2N, Gr-BCN_2 and Gr-BN_3 sheets are about 1.45 and 1.48 Å, respectively, which are slightly different than those of C-C bonds in the pristine graphene (ca. 1.42 Å). On the other hand, the Hirshfeld atomic charge on the B atom of Gr-BC_3 is only 0.04 |e|, indicating the small tendency of this site to interact with incoming O_2 or CO molecule. However, by increasing the concentration of nitrogen atoms, the positive charge on the B atom increases, a phenomenon that is beneficial for the adsorption of electron-rich molecules (Table 1). This indicates that the co-doping of B and N atoms tends to

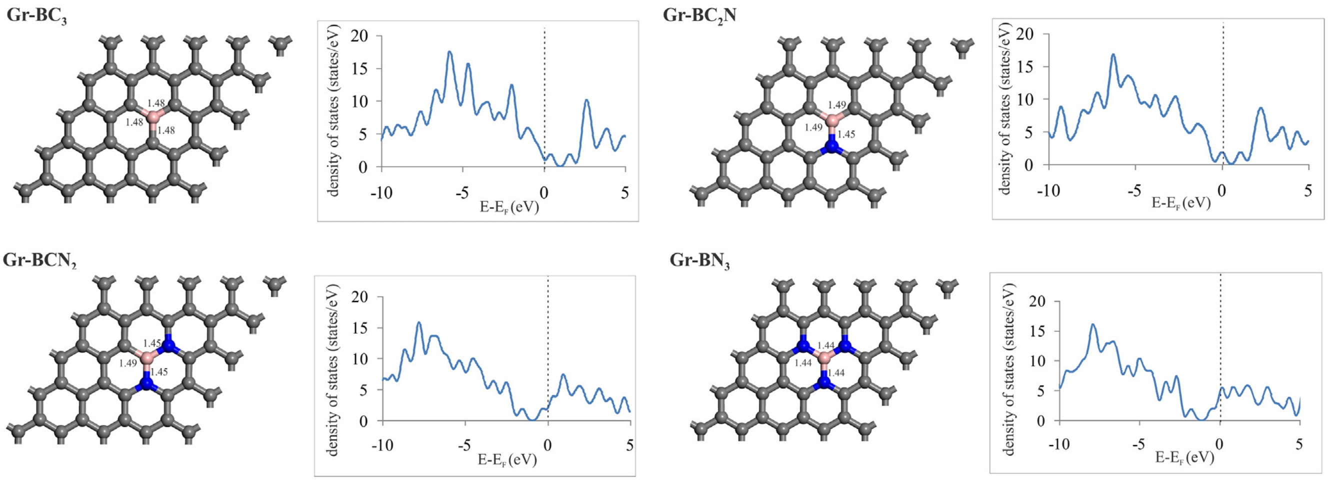

Fig. 1. The optimized structure and the corresponding DOS plots of Gr-BC_mN_n graphitic monolayers. All bond distances are in Å. In the DOS plots, the dashed line indicates the Fermi level (E_F) level, which set to be zero.