Interaction of boron with graphite: A van der Waals density functional study

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ABSTRACT

Boron doping has been widely investigated to improve oxidation resistance of graphite. In this work the interaction of boron with graphite is investigated by a van der Waals density-functional approach (vdW-DF). The traditional density-functional theory (DFT) is well accounted for the binding in boron-substituted graphite. However, to investigate the boron atom on graphite surface and the interstitial impurities require use of a description of graphite interlayer binding. Traditional DFT cannot describe the vdW physics, for instance, GGA calculations show no relevant binding between graphite sheets. LDA shows some binding, but they fail to provide an accurate account of vdW forces. In this paper, we compare the calculation results of graphite lattice constant and cohesive energy by several functionals, it shows that vdW-DF such as two optimized functionals optB88-vdW and optB86b-vdW give much improved results than traditional DFT. The vdW-DF approach is then applied to study the interaction of boron with graphite. Boron adsorption, substitution, and intercalation are discussed in terms of structural parameters and electronic structures. When adsorbing on graphite surface, boron behaves as π electron acceptor. The π electron approaches boron atom because of more electropositive of boron than carbon. For substitution situation, the hole introduced by boron mainly concentrates on boron and the nearest three carbon atoms. The B-doped graphite system with the hole has less ability to offer electrons to oxygen, ultimately resulted in the inhibition of carbon oxidation. For interstitial doping, vdW-DFs show more accurate formation energy than LDA. PBE functional cannot describe the interstitial boron in graphite reasonably because of the ignoring binding of graphite sheets. The investigation of electron structures of boron doped graphite will play an important role in understanding the oxidation mechanism in further study.

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1. Introduction

Graphite is an effective nuclear moderator for use in high temperature gas cooled reactors. However, graphite is easily oxidized under air at temperatures greater than $450\,^\circ$C. Because oxidation degrades the mechanical properties and thermal properties of graphite, its oxidation behavior has always aroused keen interest. Boron doping has been widely investigated to improve oxidation resistance of graphite. It has been found that the oxidation rate of graphite is decreased by a factor of 3–6 due to the boron substitution [1,2]. Radovic and co-workers have manifested the inhibiting effect was the result of three possible mechanisms: (1) Enhance-

ment of graphitization by boron substitution, (2) Substitutional boron is oxidized to B_2O_3 acting as physical blockage [3], even though no sufficient evidence has proved this mechanism [4]. (3) Redistribution of π electrons in the basal plane, according to the study on boron doped graphite by Semi-empirical molecular orbital approaches [5]. Theoretic studies show that the replacement of atom by doping can alter the band structure of graphene, and many investigations have performed on the studies of electronic and optical properties of boron doped graphene or carbon nanotubes [6–9].

Boron-containing graphite materials have been synthesized using a variety of methods. The maximum solubility of boron in graphite is 2.35 at.% at $2350\,^\circ$C by solid-state diffusion process between B_4C and graphite sheets [10]. While by chemical vapor deposition (CVD), boron concentrations are mainly in the range of 15–19 at.% [11–13]. Different boron-containing concentrations will result in different catalytic or inhibiting effects upon carbon

oxidation. Radovic and co-workers have reported that boron presenting as substituted atoms in the carbon lattice acts as a catalyst at low loadings and as an inhibitor at higher loadings [1]. Wu has also confirmed both catalytic and inhibiting effects of substitutional boron in carbon oxidation by *ab initio* molecular orbital calculation [14]. However, the reason of both catalytic and inhibiting effects of boron in graphite is still not clear. The investigation of electron structures of boron doped graphite will play an important role in understanding the oxidation mechanism in further study.

Graphite is a semimetallic solid with strong interplanar bonds and weakly coupled layers. The relatively weak van der Waals (vdW) forces between the sheets are always ignored in the traditional DFT method. For electron exchange correlation functionals, standard DFT approaches are based on local density approximation (LDA) and generalized gradient approximation (GGA) [15,16]. GGA calculations show no relevant binding between graphite sheets [17]. LDA show some binding, but they fail to provide an accurate account of vdW forces. Neither of these traditional functionals can describe the vdW physics, and the lack of a physics basis is fundamental limitation of traditional DFT, which makes it impossible to use them to obtain meaningful properties of the graphitic materials with weak interlayer binding. In contrast, the vdW-DF method has such a physics basis that can provide the demanding binding in graphitic materials [18,19]. In vdW-DF functional the exchange-correlation energy includes the nonlocal energy term which accounts approximately for the nonlocal electron correlation effects. The nonlocal term obtained using a relatively simple double space integration represents an improvement compared to local or semilocal functionals.

Here, we provide detailed analysis and comparisons of lattice constants and cohesive energies of graphite by different correlation functionals. The doping process of boron in graphite includes the adsorption of boron on top of a graphite surface and boron substituting a carbon atom in the lattice position, and the interstitial position of boron atom between graphite sheets. We use the vdW-DF method to investigate these three interactions of boron with graphite, and compare the effects of vdW-DFs with GGA and LDA functionals, especially for the adsorption and interstitial cases.

2. Methods and details of calculation

2.1. Van der Waals density function calculations

Graphite layers are bound with van der Waals force. In our calculation, we introduce the vdW interactions in graphite system. Be different from traditional functionals, vdW-DF is a non-local correlation functional that approximately accounts for dispersion interactions. The correlation energy functional is divided into two parts, a local and a nonlocal part:

$$E_c \approx E_c^{LDA} + E_c^{nl} \tag{1}$$

where the local part E_c^{LDA} is approximated in the LDA and nonlocal part E_c^{nl} is calculated from the GGA-based n(r) and its gradients by using information about the many-body response of the weakly inhomogeneous electron gas [18]:

$$E_c^{nl} = \frac{1}{2} \int_{V_0} dr \int_V dr' n(r) \phi(r, r') n(r') \tag{2}$$

where $\phi(r, r')$ is the nonlocal kernel expressing the density of many-electron system. The analytic expression for the kernel can be found in Ref. [19].

In the Vienna ab initio simulation package (VASP), vdW-DF method is implemented using the algorithm of Román-Pérez [20]. To reduce the computational effort, the double real space integral is transformed to reciprocal space. There are several versions of

the method, the original vdw-DF by using revPBE, three "opt" functionals (optPBE-vdW, optB88-vdW and optB86b-vdW) where the exchange functionals are optimized for the correlation part [21], and the vdW-DF2 of Langreth groups by using rPW86 exchange functional [22].

2.2. Computational details

First principles DFT calculations are carried out to study the interaction of boron with graphite surface. VASP code is performed for the system structure and energy calculations [23]. The projected augmented wave (PAW) method is applied [24]. The vdW-DFs are used to describe van der Waals interaction. LDA as well as GGA parametrized by PBE is used to describe the potential. The valence electrons are described by plane wave basis sets with energy cutoff of 900 eV to a more accurate calculation [17,25]. The core electrons are represented by PAW pseudopotentials [26]. The conjugate gradient method is applied to minimize Hellmann-Feynman forces in the ionic relaxations. The energy convergence is set to 10^{-3} eV. During electronic relaxation, the blocked Davidson iteration scheme and the residual minimization method with direct inversion in the iterative subspace (RMMDIIS) are used with an energy convergence of 10^{-4} eV. Spin-polarization is applied in the calculation because some unpaired electrons of our systems are taken into consideration. Gaussian smearing method is used for the partial occupancies for each orbital, and the width of the smearing is set 0.1 eV.

Two graphite layers containing 64 atoms (before interacting with boron atom) are set using periodic boundary conditions in two spatial directions $(4 \times 2 \times 1)$. The two-layer model is used in all calculations, including calculating the lattice constants and cohesive energies of graphite. Two graphene sheets are enough to describe the interaction of boron with graphite surface because we get almost the same results after calculating the interaction between boron and a six-layer graphite model. The box size is set according to the optimized lattice constants for different correlation functionals. For example, the LDA-optimized lattice constant (a = 2.447 Å, c = 6.631 Å) is used to construct the supercell in a box of $9.788 \times 8.476 \times 20$ Å^3, and the graphene sheets are separated by a 16 Å-thick vacuum. Previous study has shown that a 11 Å vacuum layer is large enough to reduce the periodic neighbor interaction [27–29]. The graphite unit cell dimensions are given below (see Fig. 1). The k-point generated by Monkhorst-Pack scheme [30] is set to $5 \times 5 \times 1$ for the structure optimization, and increases to $12 \times 12 \times 1$ for CDD and DOS calculation. The adsorption energy of boron on graphite surface is defined as:

$$E_0 = E_{gra+B} - E_{gra} - E_B \tag{3}$$

where E_{gra+B} is total energy of the system after adsorption, E_{gra} is the energy of graphite matrix and E_B is the energy of boron atom.

While the formation energy of a substitutional impurity is defined as:

$$E_f = E_{gra+B} - (E_{gra} - \mu_C + \mu_B) \tag{4}$$

where E_{gra+B} is total energy of graphite with substitutional boron. E_{gra} is the energy of graphite matrix, μ_C and μ_B are the corresponding chemical potentials of carbon and α-boron crystal, respectively. The chemical potentials, μ_C and μ_B are approximated to an upper bound, $\mu_C = \mu_{C[bulk]}$, $\mu_B = \mu_{B[bulk]}$.

The formation energy of interstitial boron is calculated as:

$$E_f = E_{gra+B} - E_{gra} - \mu_B \tag{5}$$

where E_{gra+B} is total energy of graphite with interstitial boron. E_{gra} is the energy of graphite matrix, μ_B is the chemical potentials of boron, $\mu_B = \mu_{B[bulk]}$.