LETTERS TO THE EDITOR

Effect of boron on graphite oxidation - a theoretical study

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Oxidation is a serious problem for C/C composites above 400°C, which limits their application at high temperatures. It is experimentally shown that boron (B), when substituting for C atoms in the graphite structure, may significantly improve the oxidation behavior of a C/C composite [1-4]. However, there is very little known about the role of boron in reducing the oxidation rate of graphite although several oxidation-inhibition mechanisms has been proposed [3,5]. One of the proposed mechanisms involves the alteration of reactivity at active sites on the edges of graphene layers by boron atoms. The main objective of this paper is to examine the possibility and validity of this particular mechanism by investigating the effect of boron atoms on the electronic properties of graphite using the semi-empirical Molecular Orbital Package (MOPAC). One main advantage of MOPAC is that one can easily obtain accurate geometric optimization and electronic structural parameters of atom clusters.

Because of the weak interlayer interactions in graphite, we consider graphene monolayer with edges; a schematic representation of the atomic arrangement of which is shown in Fig. 1. It is generally believed that the edge sites are terminated with hydrogen atoms. However, since we are mainly interested in the electronic density distribution along the edge of graphene layer during oxidation, we assumed that the hydrogen atoms which were bonded to the carbon atoms were oxidized and removed from the edges, prior to the oxidation of
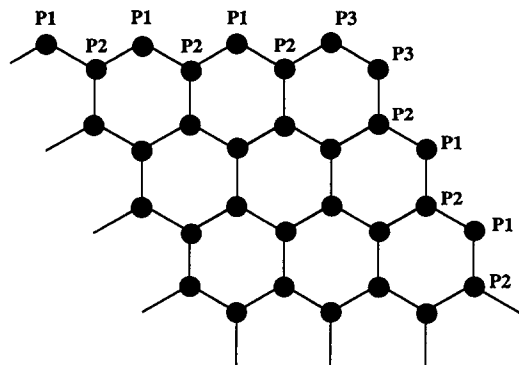

Fig. 1. The schematic representation of the atomic arrangement close to the edges of a graphene layer.

carbon atoms. Therefore, we considered bare carbon clusters without hydrogen termination. For the particular edge orientations shown in Fig. 1, there exist only two distinguishable positions at the edges, P1 and P2, plus the corner positions where two edges meet, P3. For the sake of our discussion, let us first distinguish between atom clusters and a graphene layer with edges: a cluster is a small collection of atoms, none of which behaves the same as those in the corresponding bulk, whereas a graphene layer with edges is a large cluster in which, away from the edges, atoms behave the same as those in the bulk. Therefore, the question is then how many atoms is necessary for a cluster to be considered a graphene layer with edges. In this work, using the MOPAC with AM1 parameters, we determine the proper size of a cluster being a graphene layer by comparing the charge distribution and bond-lengths in a cluster with the corresponding values in bulk graphite. Two clusters with 32 and 54 carbon atoms were considered. The structures of those clusters were labeled with M1 and M2 and shown in Fig. 2a and 2b, respectively. Comparing with Fig. 1, the edge positions, E and E1 in M1 and E, E1, ... , E5 in M2, correspond to the P1 sites; F, F1, F2, and F3 in M1, and F, F1, ... , F11 in M2, correspond to P2 sites; and G, ..., G7 in M1, and G, ..., G11 in M2, correspond to P3 sites. The structures of these two clusters were optimized by minimizing their total energies. For the atoms at α, β, γ and λ sites inside the two clusters, the corresponding bond-lengths and charge distributions were determined and listed in Table 1. It can be seen that the bond lengths and charge distributions around sites α, β, γ and λ in M2 is very uniform and quite close to the values (i.e., 0.00 and 1.42Å [9]) in the corresponding bulk graphite while those in M1 show significant inhomogeneity. This implies that a cluster with 54 carbon atoms is large enough to be considered as a graphene layer with edges. Therefore, it is reasonable to assume that the electronic properties calculated for atoms at positions Ej, Fj and Gj (where, j can be 1, 2, ...) in M2 are representative of those at the edges (position P1, P2 and P3) of a large graphite sheet (Fig. 1).

Since oxidation is an electrophilic reaction in which oxygen atoms draw electrons from the atoms that it reacts with, the ability of the atoms to donate electrons can be considered as their oxidation reactivity. In bulk graphite only the electrons occupied on the states around
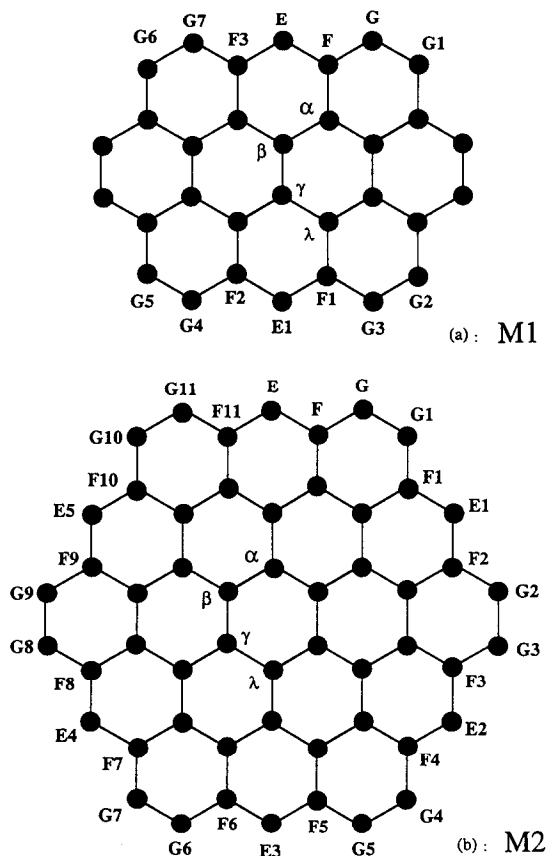
Fig. 2. The 2-D clusters: (a) M1 and (b) M2.

Fig. 3. The distributions of high energy molecular orbitals in M2 and M3.

the Fermi surface would contribute to the oxidation reaction [5]. In a graphene layer with edges, the electrons on those orbitals close to the highest occupied molecular orbital (HOMO) are believed to make the main contribution to the oxidation reaction. Therefore, the oxidation reactivity of the atoms depends on the occupation of their electrons on the occupied orbitals close to HOMO. In MOPAC, this reactivity (R) can be characterized through the coefficient C_j^i [10],

$$R = \sum_j 2 \sum_i (C_j^i)^2 \qquad (1)$$

where C_j^i is the electronic occupation coefficient on orbital j and i labels the atomic orbital S, Px, Py and Pz, respectively. The summation runs over the high occupied molecular orbitals including the highest occupied one. For a cluster of different size, the number, j, is different.

For the cluster M2, the distribution of high occupied molecular orbitals is shown in Fig. 3. The eight orbitals close to HOMO are so close to each other that all the electrons on these orbitals are believed to be involved in the oxidation reaction. Based on the eight orbitals, the
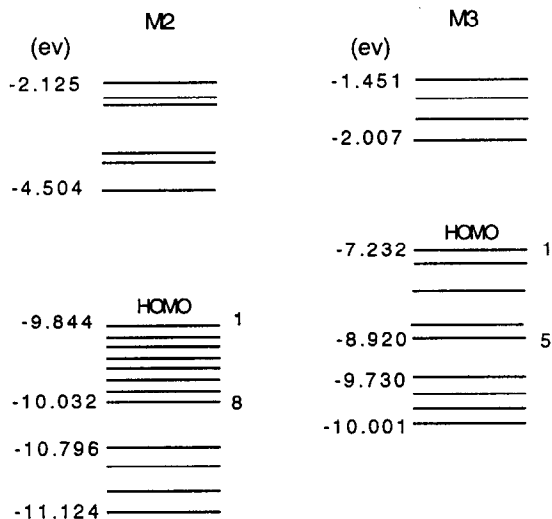
reactivities at positions E, F, G, and α were calculated (Table 2). The reactivity of carbon at position E is 1.4912, which is more than ten times greater than those on the other three positions F, G and α. The corresponding electronic density distribution on these orbitals is shown in Fig. 4a, where light and dark colors represent high and low values for the electron densities. It is shown that the electronic densities on E, E1, E2, E3, E4, and E5 are identical and are much higher than those at other sites. Therefore, all the positions represented by E's are active sites at edges of a graphene layer and it is expected that the oxidation will start from those positions. It may be speculated that the oxidation product, C-O, will be gasified, resulting in new active sites, and consequently the oxidation will continue.

If the carbon atoms on active sites or any edge positions were replaced by boron atoms, the reactivity of atoms on edge sites with oxygen would be different. In order to understand how boron-doping changes the electronic properties of atoms on the edge sites of a graphene layer, a cluster M3 was designed, in which the carbon atoms on the six E positions were replaced by boron atoms. The distribution of high occupied molecular orbitals for M3 is shown in Fig. 3. It can be seen that the difference in the energy levels between successive orbitals around HOMO is larger in M3 compared to those in M2. Since there are six electrons less in M3 than in M2, we include only five high occupied orbitals (each orbital has two electrons) in the calculation of the reactivity and the results were presented in Table 2. It is clearly shown that the oxidation reactivities on positions E, F, G and α were changed. The reactivity of boron on the E positions was decreased significantly, from 1.4912 to 0.4144, which is more than three times less than that of carbon on the E

Table 1. The bond-lengths and charge distributions around α, β, γ, λ sites in M1 and M2.

	M1			M2	
Charge(Electrons)		Bond-Length (Å)	Charge(Electrons)		Bond-Length(Å)
α	0.01	α-β 1.45	α	-0.01	α-β 1.44
β	-0.02	β-γ 1.40	β	-0.01	β-γ 1.44
γ	-0.02	γ-λ 1.45	γ	-0.01	γ-λ 1.44
λ	0.01		λ	-0.01	

Table 2. The oxidation reactivities of atoms on
E, F, G and α in M2 and M3.

	M2		
E	F	G	α
1.4912	0.1304	0.0916	0.1104
	M3		
E	F	G	α
0.4144	0.1826	0.1313	0.1704

position in M2. At the same time, the reactivities on F, G, and α sites were slightly increased. The electronic density distribution on these five orbitals for M3 is shown in Fig. 4b. By comparing to the electronic density distribution for M2 (Fig. 4a), it can be concluded that the electronic density distribution is more spatially uniformly distributed in M3 than in M2. Although the reactivities on the E positions (the active sites) in M3 were considerably reduced by boron substitution, they are still more active than F, G, and α. Therefore, the oxidation-inhibition of graphite by boron-doping was accomplished through the reduction of reactivitiy at the boron-substituted site. Furthermore, since the boron atoms on the edges of a graphene layer are relatively more active than the carbon atoms on other sites, they may first react with oxygen, resulting in the formation of boron-oxide[11] on the edges, which may further inhibit the oxidation.

Based on the results obtained in this study, it can be concluded that (1) there are sites on the edges of a graphene layer which are much more reactive with oxygen than the others, e.g., the P1 sites in Fig. 1; and (2) the reactivity of graphite is significantly reduced by replacing the carbon atoms on these active sites by boron atoms.
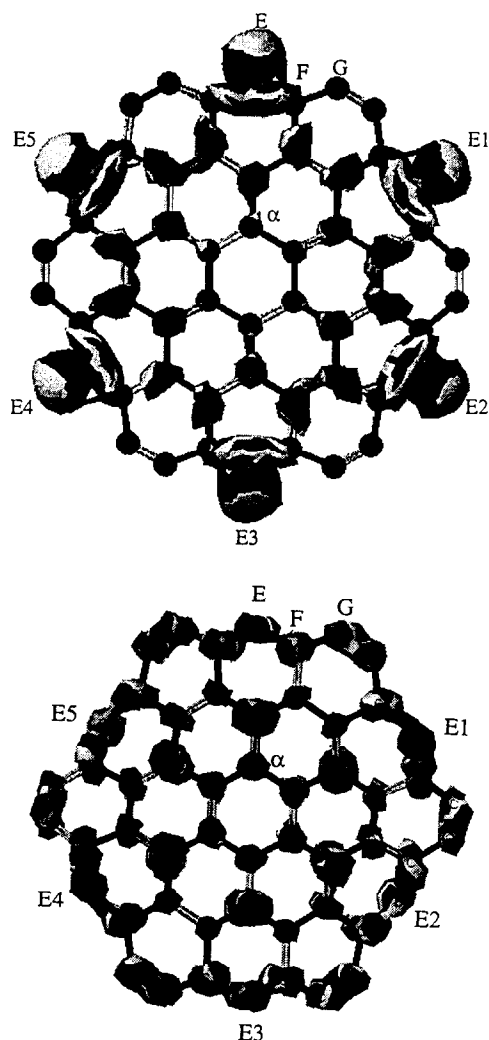
Fig. 4. The electron density distributions on high occupied molecular orbitals in (a) M2 and (b) M3.

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