Adsorption of oxygen atom on graphene/h-BN

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INTRODUCTION

Graphene, two-dimensional monolayer sheet composed of carbon atoms, has been investigated in various fields such as new-generation electronic devices, hydrogen storage applications, and organic-related devices[1-3]. The study of supporting substrate materials for graphene and adsorption of various atoms can improve electronic properties of original graphene. The hexagonal boron nitride (h-BN), two-dimensional monolayer insulating sheet, is an attractive substrate, because it has an atomically smooth surface that is relatively free dangling bonds and charge traps. Thus, graphene on h-BN can have high quality electronic properties [4]. On the graphene/h-BN structure, we consider the oxygen adsorption that may affect electronic properties of graphene. In this study, we focus on adsorption of oxygen adatom on graphene/h-BN.

MODELS AND METHODS

To simulate the graphene/h-BN system, we consider the supercell of graphene on h-BN, as shown in Fig. 1 (a). To find stable adsorption site of oxygen adatom on graphene/h-BN, we consider top, bridge, and hollow sites on the graphene surface. For investigations, we use the LCAODFTLab in EDISON Nanophysics web site [5]. This calculation program is the SIESTA package based on density functional theory (DFT). We have performed spin polarized calculations with generalized gradient approximation (GGA) for exchange-correlation (XC) functional and a mesh of 6x6x1 k-points. The atomic positions are relaxed until the forces become smaller than 0.04 eV/Å.

RESULTS AND DISCUSSION

It is known that graphene/h-BN structure with short distance between carbon and boron atoms is most stable[6]. Thus, we investigate the stable adsorption position and energy of oxygen adatom on it.

First, we performed individually geometry optimizations of graphene and h-BN, resulting bond lengths of 1.46 Å for graphene and 1.48 Å for h-BN. The lattice mismatch of graphene is 1.5% with h-BN, so we have calculated supercells with two different lattice constants of 7.61 Å and 7.68 Å. Total energy of graphene/h-BN system with lattice constant of 7.68 Å is more lower, therefore it means energetically more stable structure than that of 7.61 Å.

Oxygen adatom is adsorbed on three different sites of graphene/h-BN, top, bridge and hollow, as shown in Fig. 1 (b-d), respectively. For oxygen adsorption on top, bridge, hollow sites, the final distances between oxygen and carbon atoms are 1.58 Å, 1.57 Å, and 1.80 Å, respectively, for the 3x3 graphene/h-BN structure with lattice parameter of 7.68 Å.

We calculated the adsorption energy from the formula

$$E_{ads} = E_{total} - E_{G/h\text{-}BN} - E_{oxygen.}$$

E_{ads} is the adsorption energy of oxygen adatom adsorbed on graphene/h-BN. E_{total} is the total energy of final structure that oxygen atom is adsorbed on graphene/h-BN. $E_{G/h\text{-}BN}$ is the total energy of graphene/h-BN, and E_{oxygen} is the total energy of an isolated oxygen atom.

Adsorption energies of oxygen adatom on graphene/h-BN are shown in Table 1. In this table, we confirm that the most stable site among top, bridge and hollow is bridge site. And for bridge sites, adsorption energy for graphene/h-BN

structure with lattice constant of 7.68 Å are more stable than that of 7.61 Å. And in some cases, oxygen adatom which initially lying on hollow site moves to bridge site. As shown in Fig. 1 (e), for the graphene/h-BN structure with lattice constant of 7.61 Å, oxygen adsorbed on top site finally moves to bridge site. The initial distance between O and C atoms is 1.0 Å, while in the final adsorption configuration oxygen atom moves to a bridge site with bond length of about 1.6 Å From these results, we found the most stable adsorption site of oxygen adatom is bridge site. This result is consistent with oxygen adsorption on pristine graphene [7].

Conclusion

In summary, we used ab initio density functional theory to investigate the most stable site of oxygen adatom on 3x3 graphene/h-BN. Our calculations show that bridge site is the most stable adsorption position for oxygen adsorption on graphene/h-BN. Our calculation will be very useful for experimental and theoretical studies for the use of atoms and molecules on graphene to make new nano devices and heterostructures.

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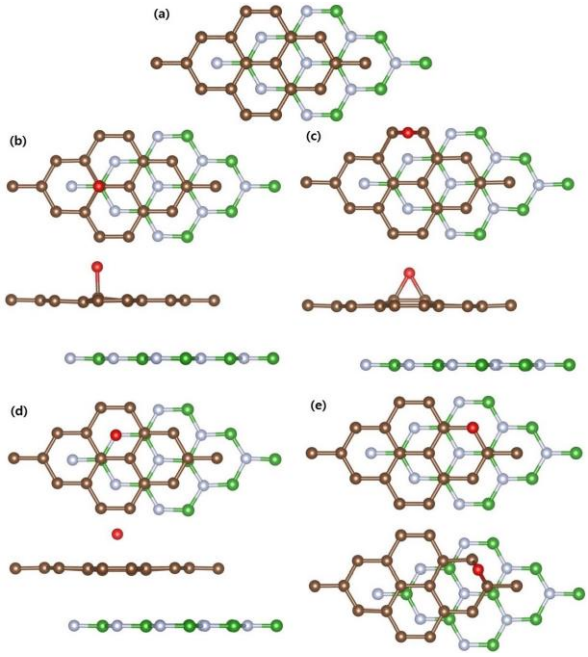

Fig. 1. (a) Structure of 3x3 graphene/h-BN. Brown, gray, green balls represent carbon, nitrogen, and boron atoms, respectively. (b-d) Final optimized structures for oxygen atom (red ball) adsorbed on graphene/h-BN depending on different adsorption sites. (e) Oxygen adsorption on top site of carbon atom of graphene with lattice parameter of 7.61 Å. The upper and lower structures are initial and final configurations, respectively.

Adsorption sites	Distance between oxygen and graphene/h-BN(Å)	Lattice constant(Å)	Adsorption energy(eV)
Top	1.0	7.61	-0.26
		7.68	-0.71
	1.6	7.61	-0.06
		7.68	0.02
Bridge	1.2	7.61	-0.42
		7.68	-0.64
	1.6	7.61	-0.70
		7.68	-0.97
Hollow	1.0	7.61	0.19
		7.68	-0.04
	1.6	7.61	0.32
		7.68	0.22

Table 1. Adsorption energy of oxygen atom on 3x3 graphene/h-BN under various conditions.