Sensors and Actuators B 197 (2014) 274–279

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Influence of topological defects on the nitrogen monoxide-sensing characteristics of graphene-analogue BN

Yadollah Yamini [a], Morteza Moradi [b,*]

[a] Department of Chemistry, Faculty of Sciences, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran
[b] Materials and Energy Research Center, Department of Semiconductors, Karaj, Iran

ARTICLE INFO

Article history:
Received 14 August 2013
Received in revised form 16 February 2014
Accepted 22 February 2014
Available online 6 March 2014

Keywords:
Nitrogen monoxide
Sensor, DFT
Graphene-like boron nitride

ABSTRACT

Electronic response of pristine and topologically defected boron nitride nano-sheets (*h*-BN) toward nitrogen monoxide (NO) molecule was investigated using density functional theory calculations. It was found that NO is weakly adsorbed on the pristine sheet, releasing an energy of 4.0 kcal/mol, and the conductance and gap of the sheet are slightly changed. Although both Stone-Wales and mono-vacancy defects make the sheet more reactive toward NO, mono-vacancy defect seems to be an inappropriate strategy to manufacture NO chemical sensors due to the longer recovery time. Our calculations show that the HOMO/LUMO gap of the pristine and Stone-Wales defected *h*-BN sheet are significantly decreased about 42% and 35%, respectively, upon NO adsorption which may increase the electrical conductance of the sheet and it might be potentially used in NO sensors.

1. Introduction

Since being first discovered in experiments in 2004 [1], graphene and graphene-like materials have been under investigation theoretically and experimentally because of their novel physical and chemical properties [2–4]. Boron nitride (BN) is a wide band gap ceramic with remarkable properties. It forms nanotubes just as carbon, and the synthesis and characterization of BN nanotubes have spawned a great interest in past few years [5,6]. Recently, several groups have reported the experimental preparation of hexagonal graphitic boron nitride (*h*-BN) single layers [7,8]. *h*-BN formation is reported to be energetically favorable, and these structures are mechanically and chemically as robust as their carbon counterparts while they exhibit better thermal conductivity [9]. In passing one notes that the successful synthesis of *h*-BN consistent with theoretical predictions [10] along with other first principle calculations on similar structures [11] reveals the importance of computational chemistry in this field.

The adsorption of chemical species affects the electrical properties of graphene and graphene-like materials and is of fundamental interest and importance in development of potential electronic sensors. The charge transfer between graphene and adsorbates can increase or decrease the carrier density in semiconducting graphenes and significantly affect its electrical conductance. Based on these observations, the application of graphenes as promising gas sensors has been suggested by several research groups [12,13]. However, several pristine graphenes are not usually able to adsorb the target molecules and cannot be used for detection of several toxic gaseous molecules. Therefore, considerable experimental and theoretical works have been focused on improvement of sensing performance of the pristine graphenes towards various desired molecules through doping or defect [14,15]. Schedin et al. [14] found that graphene is highly sensitive toward NO_2, NH_3, CO, and H_2O, especially for NO_2. Unfortunately, *h*-BN sheet has remained much less explored in comparison with graphene which may be due to the fact that the well defined synthesis of BN nanostructures is a more challenging task with respect to the case of carbon counterparts. However, some theoretical studies have scrutinized the ability of *h*-BN sheet to adsorb molecules such as CO [16], formaldehyde [17], and para-nitrophenol [18], which implies that *h*-BN sheet can be used as a proper gas sensor.

Nitrogen monoxide (NO) is one of the most dangerous gases in human daily life and is extremely toxic because of being colorless and odorless. Hence, there is an increasing demand to find fast and simple NO monitoring methods which have stimulated research activities in sensor technology field [19–21]. In this work, the adsorption of NO molecule on pristine and defected *h*-BN sheets is investigated using density functional theory (DFT) calculations. There has been focused mainly on configurations corresponding to the located minima of the NO, adsorption energies, and the

* Corresponding author. Tel.: +98 912 2467683.
E-mail address: 2m.alborzi@gmail.com (M. Moradi).

http://dx.doi.org/10.1016/j.snb.2014.02.093
0925-4005/

Table 1
Calculated adsorption energy (E_{ad} in kcal/mol), HOMO energies (E_{HOMO}), LUMO energies (E_{LUMO}), HOMO–LUMO energy gap (E_g) of pristine systems in eV.

[b] ΔE_g(%)	E_g	E_{LUMO}	E_{HOMO}	[a] Q_T (e)	E_{ad}	System
–	5.93	−0.35	−6.28	–	–	*h*-BN
−42	3.44	−2.35	−5.79	0.070	−3.2	(A) NO/*h*-BN
−42	3.41	−2.37	−5.78	0.029	−4.0	(B) NO/*h*-BN

[a] Q_T is defined as the total NBO charge on the NO molecule.
[b] The change of HOMO–LUMO gap of pristine sheet after adsorption.

electronic property changes of the sheet caused by the presence of adsorbate.

2. Computational methods

A BN sheet consisting 36 B and 36 N atoms was considered, its end atoms were saturated by hydrogen atoms to avoid the boundary effects. All calculations were performed using B3LYP functional augmented with an empirical dispersion term (B3LYP-D) with 6-31G (d) basis set as implemented in the GAMESS suite of program [22]. GaussSum program [23] has been used to obtain the density of states (DOS) results. The B3LYP density functional has been previously shown to reproduce experimental proprieties and has been commonly used for nanostructures [24–27]. Also, it has been demonstrated by Tomic et al. that the B3LYP provides an efficient and robust basis for calculations of III–V semiconductors [28], capable of reliable prediction of both the ground state energies and the electronic structure. In a defected *h*-BN systems in the presence and absence of an NO molecule, the spin unrestricted calculations were performed. Vibrational frequencies were also calculated at the same level to confirm that all the stationary points correspond to true minima on the potential energy surface. All frequency calculations were performed using numerical second derivatives and verified that all structures are true minima using frequency analysis and obtained all positive Hessian eigenvalues. Gaussview program was applied to get visual animation and also the verification of the normal modes assignment. The adsorption energy (E_{ad}) of a NO molecule on the *h*-BN is obtained using the following equation:

(1)$Ead = E(h-BN/NO) - E(h-BN) - E(NO)$where E (*h*-BN/NO) is the energy of *h*-BN/NO complex and, E (NO) and E (*h*-BN) are referred to the energies of an isolated NO molecule and the *h*-BN, respectively. The negative value of E_{ad} indicates the exothermic character of the adsorption.

3. Results and discussion

3.1. NO adsorption on pristine BN sheet

The optimized structure, geometry parameters, and density of states (DOS) plot of the *h*-BN are shown in Fig. 1, in which B–N bond length is 1.45 Å, in good accordance with experimental and previous theoretical results [29,8]. The charge analysis using the natural bond orbital (NBO) analysis indicates that about 0.51 *e* charges are transferred from the B atom to its adjacent N atom within the sheet, indicating partially ionic character of the B–N bonds in the sheet. For adsorption of single NO on *h*-BN, different possible adsorption configurations are considered, including O or N atom of NO molecule close to either B or N site of BN sheet. Several other configurations with the NO molecule located parallel to the hexagonal plane and N–O bond perpendicular to the center of the ring or B–N bond were also tested. After full relax optimization, two stable (local minima) NO/*h*-BN complexes were found, as shown in Fig. 2, denoted by **A** and **B**. More detailed information including values of E_{ad}, electronic properties and the charge transfers (Q_T) are listed in Table 1. In the **A** configuration, NO molecule was located atop of B site from its oxygen head with bond length of 2.88 Å and corresponding calculated E_{ad} value is about −3.2 kcal/mol. The most stable configuration is **B**, in which N atom of NO is close to a B atom of the sheet by a distance of 2.73 Å with E_{ad} of −4.0 kcal/mol. Here, it should be noted that stretching mode of N–O bond in the adsorbed NO occurs at slight lower frequency of 1947 cm^{-1} compared to that of the free molecule (1991 cm^{-1}), confirming weakness of the interaction. These data indicate that the NO molecule undergoes physical adsorption on the pristine sheet due to weak van der Waals interaction between the *h*-BN and NO. Moreover, it is obvious from Table 1 that the calculated deformation energies are nearly zero, which indicate that *h*-BN undergoes no distortion while NO molecule approaches it.

In the following, the effect of NO adsorption on electronic properties of the sheet has been studied. As shown by the calculated DOS and the energy gaps (E_g) between the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) in Fig. 1 and Table 1, the pristine *h*-BN is found to be a semiconductor with a wide band gap of 5.93 eV. It should be noted that herein, the E_g also stands for SOMO (singly occupied molecular orbital)/LUMO energy gaps in open shell systems. According to Fig. 2, it can be seen that the NO/*h*-BN complexes attain E_g value of 3.44–3.41 eV. It is well known that the E_g (or band gap in bulk materials) is a major factor determining the electrical conductivity of a material and there is a classic relation between them as follows [30]

$$\sigma \propto \exp\left(\frac{-E_g}{2kT}\right) \quad (2)$$

where σ is the electrical conductivity and k is the Boltzmann's constant. According to the equation (2), a smaller E_g at a given temperature leads to a larger electrical conductivity. For example, in the configuration **B** (as the most stable one), the DOS almost remains constant near the conduction level and valence level has a distinct change compared to that of the pristine *h*-BN and the E_g decreases from 5.93 to 3.41 eV upon the adsorption of NO molecule. The considerable change about 42% in the E_g value demonstrates the high electronic response of the pristine *h*-BN toward the NO molecule. Therefore, the presences of the NO molecules may be monitored by calculating the conductivity change of *h*-BN before and after the adsorption process.

Recently, some theoretical researchers have focused on design of gas sensor based on the relationship of E_g and with conductivity of adsorbate. For example, Peyghan and coworkers [31] have theoretically investigated the detection of phosgene by BN nanotubes. They have shown that band gap of pristine BNNT is insensitive toward phosgene, but band gap of nanotube was dramatically affected by phosgene molecule when a scandium atom was doped on nanotube. In another work, Bahrami et al. [32] have shown that E_g of Ga- Al- and F- doped B_{80} fullerene were changed in the presence of NH_3 molecule. As a result, Eq. (2) is a promising index for prediction of sensing behavior of nanostructured system toward specific gas molecules.

3.2. NO adsorption on SW-defected BN sheet

The typical topological defect in the nanostructures is SW defect which consists of two pairs of five-membered and seven-membered rings. Qin et al. conducted DFT investigations of formaldehyde adsorption on graphene with SW defects. It was found that the graphene with SW defect is more sensitive than that of perfect grapheme toward detecting formaldehyde molecules. The SW defect is created by rotating a B–N bond 90° and the relaxed geometry of *h*-BN with SW defect (SW-*h*-BN) as shown in Fig. 1. A main change in the atomic structure is that the B–N bonds belonged to the defect are compressed and stretched. Especially, the rotated