Adsorption of Phosphine on a BN Nanosurface

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ABSTRACT: *Electrical sensitivity of a boron nitride nanosheet (BNNS) to phosphine (PH_3) molecule is studied using Density Functional Theory (DFT) calculations at the B3LYP/6-31G(d) level of theory. The adsorption energy (E_{ad}) of phosphine on the surface of pristine nanosheet is about -678.96×10^{19}eV. Pristine BNNS is a suitable adsorbent for phosphine and can be used in separation processes or adsorption of phosphine toxic gas from environmental systems. Consequently, BNNS is doped by Al atom and results show that the adsorption energy range is about - 28882.18×10^{19} to -52097.61×10^{19}eV which means an increase in adsorption energy. Moreover, the HOMO/LUMO energy gap (E_g) reduces significantly. This reduction shows that the doped BNNS in the presence of phosphine is a suitable semiconductor and generates an electrical signal. Therefore it can be used potentially as phosphine toxic gas detection sensors in environmental systems.*

KEYWORDS: *Sensor; Boron nitride nanosheet; DFT; Phosphine.*

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INTRODUCTION

Phosphine is actually a colorless, combustible extremely dangerous gas which has a fishy and also garlic-like smell. Phosphine can be used as an insecticide for that fumigation of grain, animal feed, and leaf-stored tobacco. Phosphine acts on the central nervous system which leading to pulmonary swelling and symptoms like faintness, vomiting, headache [1].

BN nanomaterials include BN nanosheets (BNNSs), BN nanotubes (BNNTs) and BN nanoparticles (BNNPs).

The most important structures that can be considered as a catalyst in many cases are nanoparticles [2]

BN nanoparticles are of potential to be used in nano-dimensional electronic devices and nanofillers for composites in terms of their unique physical, mechanical and electronic properties. Also, these nanostructures have semiconductor behavior, furthermore thermal and chemical stability [3-4].

During the past decade, Boron Nitride Nanotubes (BNNTs) have attracted considerable interests owing to their unique properties such as semiconductor behavior [5]. The reason for this behavior is the total atomic number of B and N, that is an interesting issue for studying these BNNTs [6].

BN sheet has aroused extensive research interest due to its triggering properties such as high chemical stabilities, mechanical properties and high conductivity [7-8]. BNNSs are also utilized in the construction of gas sensors [9-10].

So far researchers have studied the adsorption of different molecules on the surface of nanostructures [11-14]. Although, improving the sensing performance of the pristine nanotubes and nanosheets by manipulating their structure is too expensive, finding high sensitive pristine nanotube is a highly scientific interest. Therefore, it is important to understand the advantages and disadvantages of the phosphine adsorption on the nanosheet. All the above-mentioned problems have motivated us to verify boron nitride nanosheet (BNNS) as an adsorbent, investigating their interactions with phosphine using DFT calculations.

THEORETICAL SECTION

All Computations are performed by means of GAUSSIAN 03 packing [15]. Geometry optimizations.

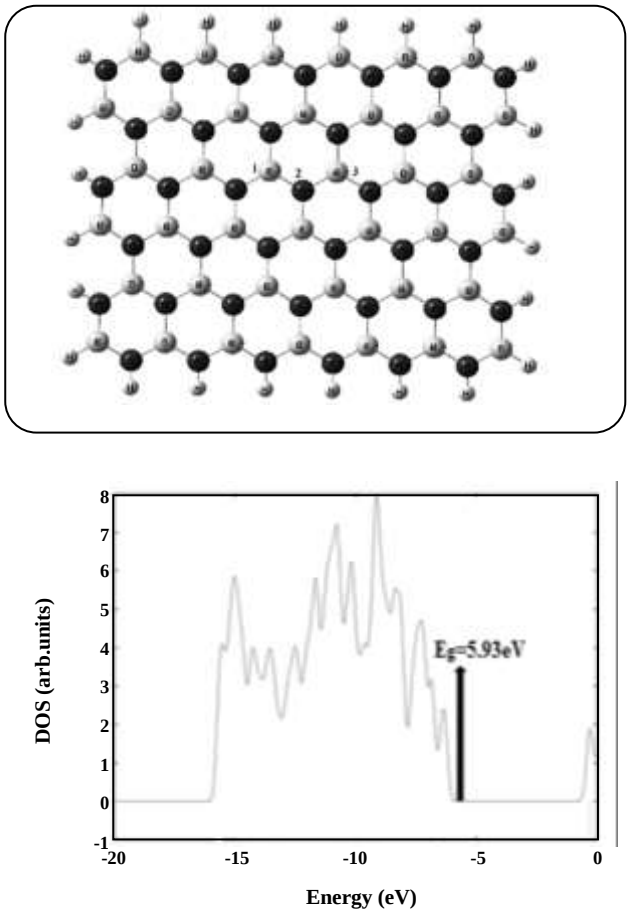

Fig. 1: Optimized structure and Density of State (DOS) diagram of the studied pristine zigzag BN nanosheet.

Density of states (DOS) analysis were performed on a (5, 0) zigzag BNNS (constructed of 39 B and 39 N atoms, saturated with Hydrogen atoms at the open ends to reduce the boundary effects) (Fig. 1), and different phosphine /BNNS complexes at B3LYP level of theory with 6-31G (d) basis set [16-21] as implemented in the GAMESS suite of program. [22]

B3LYP is a popular functional that has been commonly used for nanosheet structures [23-26]. Also, B3LYP is demonstrated to be a reliable and commonly used functional in the study of different nanostructures [27].

E_{ad} of the complex is defined as follows:

$$E_{ad} = E_{(BNNS+Phosphine)} - \left[E_{(Phosphine)} + E_{(BNNS)}\right] + \delta_{BSSE} \quad [1]$$

Where $E_{(Phosphine\ /BNNS)}$ is the total energy of the adsorbed phosphine molecule on the BNNS surface, $E_{(BNNS)}$ and $E_{(Phosphine)}$ are the total energies of the pristine BNNS and the phosphine molecule, respectively. We made phosphine molecule to be close to the nanosheet, and its adsorption has been calculated by using the Equation (1).

Distance phosphine molecule from pristine nanosheet was considered 3 A˚. In the following steps, Al atom in the nanosheet structure have been doped to examine the phosphine adsorption on the nanosheet and conductivity that is doping with Al atom. Finally, from the optimized complexes, the quantum molecular descriptors [28], including hardness (η) and electrophilicity index (ω) were calculated as follows:

$$\eta = -\left(E_{HOMO} - E_{LUMO}\right)/2 \quad (2)$$

$$\omega = \mu^2/2\eta \quad (3)$$

Note that the order of μ in Eq. (3) is chemical potential.

$$\mu = E_{HOMO} + E_{LUMO}/2$$

Where HOMO and LUMO are the highest occupied molecular orbital and the lowest un-occupied molecular orbital of the structures, respectively.

RESULTS AND DISCUSSION

Fig. 1 shows a partial structure of the optimized BNNS and its DOS plot, indicating that it is considered as a semiconductor with a HOMO/LUMO gap (E_g) of 5.93eV.

Two types of B–N bonds can be found: one with the bond length of 1.40 A˚ (B1–N2 bond, for example) in parallel with the tube axis, and another with the bond length of 1.48A˚ (N2–B3 bond, for example), but not in parallel with the tube axis.

In order to determine the most stable structures for the adsorption of phosphine on the (5,0), zigzag BNNS, the structure was allowed to relax by all atomic geometrical parameters in the optimization at the DFT level of B3LYP exchange-functional and 6-31G (d) standard basis set (Fig. 2).

The most stable configuration is shown in Fig. 2, that phosphor atom of phosphine is 4.31A˚ far from the boron atom of the nanosheet.

Adsorption energy (E_{ad}) for the mentioned configuration of phosphine and nanosheet is obtained about -678.96×10^{19}eV,

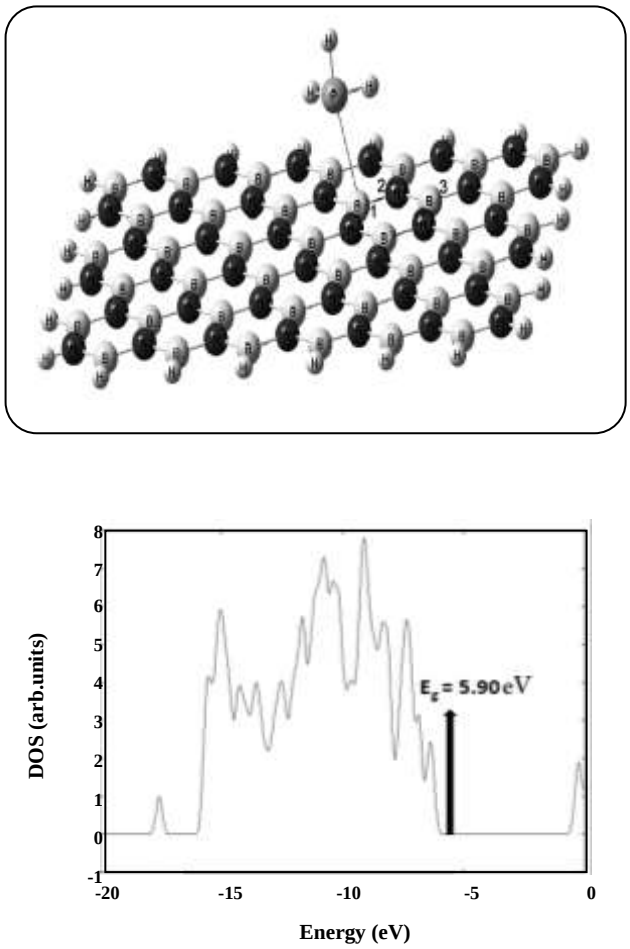

Fig. 2: Optimized structure of the Phosphine adsorbed on the BNNS and density of state diagram (DOS) of the complex. The distance is in Å

these strong interactions mean that the BNNS is not a suitable absorbent for phosphine molecule or separation of this gas from environmental systems. Then we calculated the energy gap E_g = 5.90eV using HOMO/LUMO energy for pristine nanosheet. The phosphine molecule is adsorbed on nanosheets and then the diagram which shows E_g has been obtained by using Density of State (DOS) software. After adsorption of the phosphine molecule on the surface of BNNS, the bond length of B1–N2 was 1.44 A˚ and the bond length of N2–B3 was 1.52 A˚. It is observed that bond lengths are increased compared to pristine BNNS. We know that the electronegativity of phosphorus atom in phosphine molecule is more than the electronegativity of boron atom. Consequently, Phosphorus atom draws the electronic cover of boron atom.

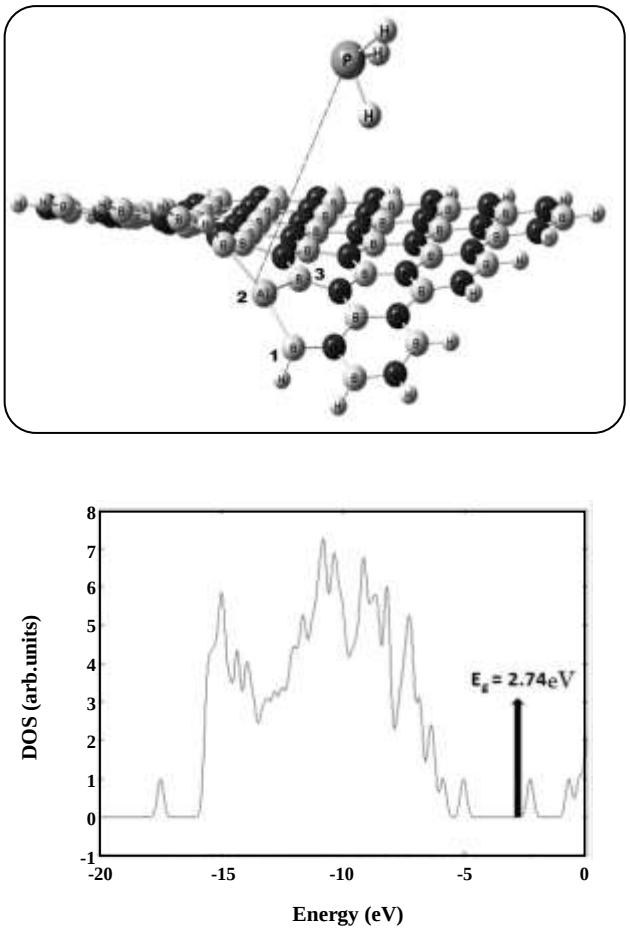

Fig. 3A: Optimized structure of the Phosphine adsorbed on the BNNS (N atom doped by Al) and density of state diagram (DOS) of the complex. The distance is in Å

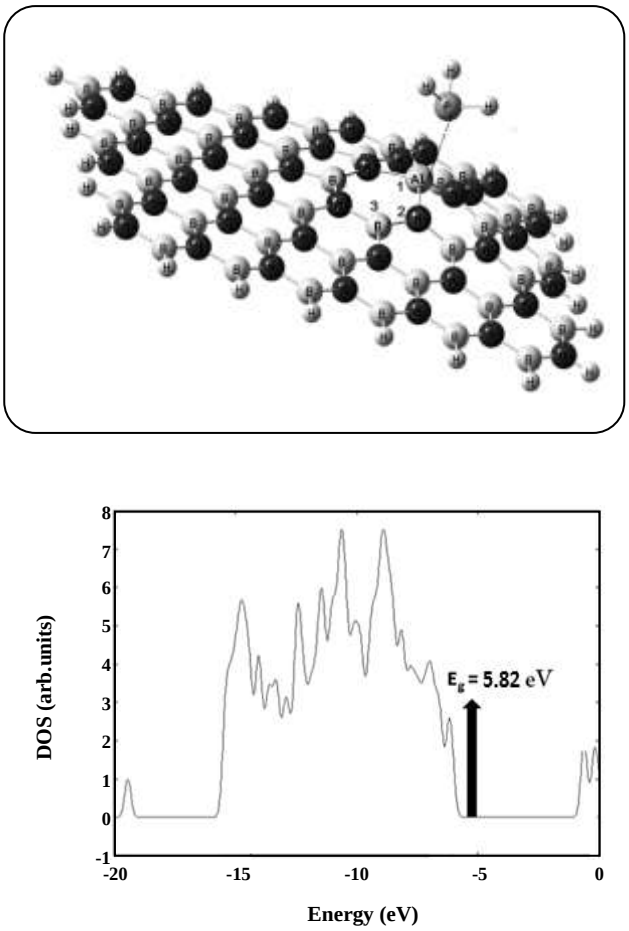

Fig. 3B: Optimized structure of the Phosphine adsorbed on the BNNS (B atom doped by Al) and density of state diagram (DOS) of the complex. The distance is in Å

Accordingly, the effective nuclear charge of boron atom impresses the nucleus of nitrogen atom more and creates a repulsion that leads to increased bond length.

In the optimized complex of BNNS (doped by Al) and molecule phosphine, the Al atom is projected out of the surface nanosheet in order to reduce stress from other atoms in nanosheet. To examine the sensitivity of the adsorption phosphine on the surface of BNNS, its examining has been done two times, once N atom doped by Al (Fig. 3A) and another time B atom has been doped by Al atom (Fig. 3B).

N atom in BNNS doped by Al (Fig. 3A) and phosphine closed on the surface of BNNS. Adsorption energy (E_{ad}) for the mentioned configuration of phosphine and nanosheet is about -28882.18×10^{19} eV. Then we obtained the HOMO/LUMO energy and calculated E_g = 2.74eV that is listed in Table 1. After adsorption the phosphine molecule on the surface of BNNS, the bond length of B1–Al2 was 2.10 A˚ and the bond length of Al2–B3 was 2.18 A˚. It is observed that the bond lengths in this complex are increased compared to pristine BNNS. The electronegativity of aluminium atom is less than the electronegativity of nitrogen atom. Therefore, electron density between aluminium atom and boron atom is less than the electron density between the nitrogen atom and a boron atom. So, repulsion of effective nuclear charge of aluminium and boron atoms is high. As a result, when phosphorus atom in phosphine molecule become close to the doped nanosheet, the bond length of boron and aluminium is more than the bond length of boron and nitrogen in pristine BNNS.

Table 1: Calculated adsorption energy (E_{ad}, kcal/mol) , HOMO and LUMO energies, HOMO-LUMO energy gap (E_g), hardness (η), and electrophilicity (ω) of systems in eV.

SYSTEM	E_{HOMO}	E_{LUMO}	E_g	E_{ad}	η	ω
BNNS	-6.28	-0.35	5.93	-	2.96	1.84
PH_3 on BNNS	-6.23	-0.33	5.90	-0.26	2.95	1.82
PH_3 on BNNS (Al/B)	-6.06	-0.24	5.82	-19.95	2.71	1.83
PH_3 on BNNS (AL/N)	-5.06	-2.32	2.74	-11.06	1.37	4.96

In Fig. 3B, B atom in BNNS doped by Al and phosphine closed on the surface of BNNS, and phosphor atom of phosphine is 2.57A˚ far from Al atom of the nanosheet. Adsorption energy (E_{ad}) for the mentioned configuration of phosphine and nanosheet is about -52097.61×10^{19} eV and E_g= 5.82eV (Table 1), the bond length of Al1–N2 is 1.77 A˚ and the bond length of N2–B3 is 1.4 3A˚.

When Al-doped in BNNS, the adsorption energy range is -52097.61×10^{19} to -28882.18×10^{19} eV and this range is higher than pristine nanosheet. So, the BNNS doped by Al is better than pristine BNNS for adsorption phosphine molecule but these types of interactions are suitable for gas detection in sensors, since, reduction of adsorption energy (E_{ad}) causes shortening of the recovery time (τ) according to Equation (4).

$$\tau = \upsilon_0^{-1} \exp\left(-E_{ad}/kT\right) \qquad [4]$$

Where *T* is the temperature, *k* is the Boltzmann's constant, and υ_0 is the attempt frequency. After adsorption of phosphine on the mentioned nanosheet that has doped by Al, the HOMO/LUMO energy gap E_g= 5.82 will be decreased to 2.74 eV, however, the energy gap of the pristine of nanosheet is E_g=5.93eV. Therefore, a substantial increase will occur in conductivity and this phenomenon is explained in Equation 5.

$$\sigma \propto \exp\left(-E_g/2kT\right) \qquad [5]$$

Where σ is conductance, *T* is temperature, *k* is Boltzmann constant. According to this equation, when E_g decreases, this leads to an increase in the conductivity. Therefore, if we want to use the BNNS for phosphine toxic gas detection in environmental systems, the Al atom is suitable for doping in BNNS .

In order to consider the influence of phosphine adsorption on electronic properties of the BNNS, the hardness (η) and electrophilicity (ω) of the complexes are analyzed. The results in Table 1 show that the phosphine adsorption on the BNNS leads to lower hardness values than pristine BNNS. Consequently, the stabilities of complexes are decreased and their reactivities are increased. The electrophilicity index is a measure of the electrophilic power of a molecule. When two molecules react with each other, one molecule behaves as a nucleophile, whereas the other one acts as an electrophile. In phosphine adsorbed BNNS the electrophilicity of the complexes are higher than that of the pristine forms. Therefore, adsorption of phosphine can increase the reactivity of nanosheets.

CONCLUSIONS

The adsorption behavior of the phosphine molecule on the external surface of (5,0), zigzag boron nitride nanosheet (BNNS) was investigated by means of DFT calculations. According to results, the pristine BNNS can detect phosphine and be a potential efficient adsorbent for adsorption of the phosphine from environmental systems. When the BNNS surface is doped with aluminium atom, the HOMO/LUMO energy gap (E_g) was lower and the adsorption energy (E_{ad}) was higher than the pristine nanosheet. Charge transfer between the adsorbed molecule and the surface of nanosheet may also happen in this case. These results clearly show that modified nanosheet can be utilized in sensors for phosphine toxic gas detection from environmental systems and also be utilized as a semiconductor. The important point that must be noted is that these results may help to discover convenient chemical correction methods in order to expand the application fields of Nano sheets.

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