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Sensing performance of boron nitride nanosheets to a toxic gas cyanogen chloride: computational exploring

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ABSTRACT

The adsorption of a toxic gas, cyanogen chloride (CNCl) on pristine, Al– and Si–doped BN nanosheet investigated using density functional theory (DFT). The adsorption energies of the most stable complexes of CNCl on pristine, Al– and Si–doped BN nanosheet are –19.96, –95.02 and –176.90 kj/mol, respectively. We found that the CNCl gas has a chemisorption interaction over the Al– and Si–doped BN, with significant change in the structure shape of the CNCl molecule. The value of adsorption interaction energy of Si-boron nitride is very large than that of the Al-boron nitride toward the toxic gas. As a result the Si-boron nitride nanosheet is more reactive to dissociate the gas molecule into safely small fragments. The adsorption of the CNCl molecule can significantly decrease the HOMO–LUMO energy gap of the Al–doped BN by about 14.06%. It is suggested that the Al–doped BN can be considered as a potential nanostructure for sensing the toxic CNCl.

1. Introduction

Cyanogen chloride (Cl−C≡N) is a colorless, chemically reactive, lachrymatory (tear–producing), and volatile gas. Cyanogen chloride is a chemical warfare agent due to the highly poisonous agent. Exposure to this gas may cause paralysis, vomiting, drowsiness, coughing, convulsion, throat confusion, edema, and death [1, 2]. Therefore, the design of an effective system to monitoring this toxic gas is an important effort for the environmental and biological security.

Some methods such as the electrochemical, spectrophotometric and gas chromatographic methods have been already reported in monitoring the CNCl gas [3−5]. Most of these techniques are expensive and need to the complicated instruments. High adsorption capacity, high surface/volume ratio and suitable electronic sensitivity of nanostructures led to use in the gas sensor field [6, 7].

To date, numerous nanostructured material based sensors have been experimentally and theoretically suggested for different gases [10–16]. Boron nitride ~~(BN) n~~anostructures are the important class of nanostructures with wide band gap, special electronic, optical and magnetic properties [17–20].

Many studies have been focused on the fullerene–like BN nanoclusters, nanosheets and nanotubes as gas sensors [21–25]. Herein, we study the adsorption of CNCl molecule on pristine, Al and Si–doped BN sheet to study the possible sensing character of the BN sheet to CNCl molecule.

2. Computational details

The interactions between pristine, Al– and Si–doped BN nanosheet and the CNCl molecule were done using the density functional theory (DFT). The full geometry optimizations and electronic properties calculations were performed on pristine, Al– and Si–doped sheet in the presence of CNCl using the M06–2X functional with 6–31+G(d) basis set using GAMESS program [26]. The adsorption energy calculations and density of states (DOS) analysis were performed at the same level of theory. The GaussSum program [27] was used to find the DOS results. The adsorption energy (E_{ad}) was defined as follows:

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$$E_{ad} = E_{(CNCl/sheet)} - (E_{(sheet)} + E_{(CNCl)}) + E_{(BSSE)} \quad (1)$$

in where, $E_{(CNCl/sheet)}$ corresponds to the energy of the sheet/CNCl complex, $E_{(sheet)}$ is the energy of the isolated sheet, $E_{(CNCl)}$ is the energy of a single CNCl molecule, and $E_{(BSSE)}$ is the energy of the basis set superposition error corrected for all interaction energies. The HOMO–LUMO energy gap was defined as:

$$E_g = E_{LUMO} - E_{HOMO} \quad (2)$$

where E_{LUMO} and E_{HOMO} are the energies of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO), respectively.

3. Results and discussion

3.1. Adsorption of CNCl on pristine BN sheet

The optimized structures, HOMO and LUMO levels and density of states (DOS) results of the pristine BN sheet are shown in Fig. 1, in which the B–N bond length ($\mathbf{l_{B–N}}$) is about 1.449 Å, which in consistent to the previous report [28]. The HOMO and LUMO are localized on the nitrogen and boron atoms, respectively, which indicates that the nitrogen atoms are electron–donating and boron atoms are electron–acceptor. In order to find the most stable configuration, the CNCl molecule was placed in vertical and parallel orientations over the BN sheet surface close to the B atom, from chlorine (–Cl–) or nitrogen (–N–) side. Full geometrical optimizations were performed with possible orientations of the CNCl molecule on the BN sheet surface.

One stable structure was obtained during full optimization which shown in Fig. 2a, in which the closet distance between CNCl and the BN sheet is about 3.139 Å. In this configuration (Fig. 2a), the CNCl gas attaches to the B atom of the sheet from N–head which E_{ad} value is –19.96 kj/mol indicating a weak adsorption. The small E_{ad} of CNCl on pristine BN sheet reveals the physical nature of the interaction between the BN sheet and CNCl in this direction. This is in consistent to the adsorption energy value of CNCl over BN nanotube (–21.21 kcal/mol) [29]. The calculated energy gaps of the pristine and BN/CNCl complex are about 7.91 and 7.72 eV, respectively. The HOMO and LUMO are mainly localized on the CNCl molecule and BN sheet at –8.13 and –0.41 eV, respectively (Fig. 2b)

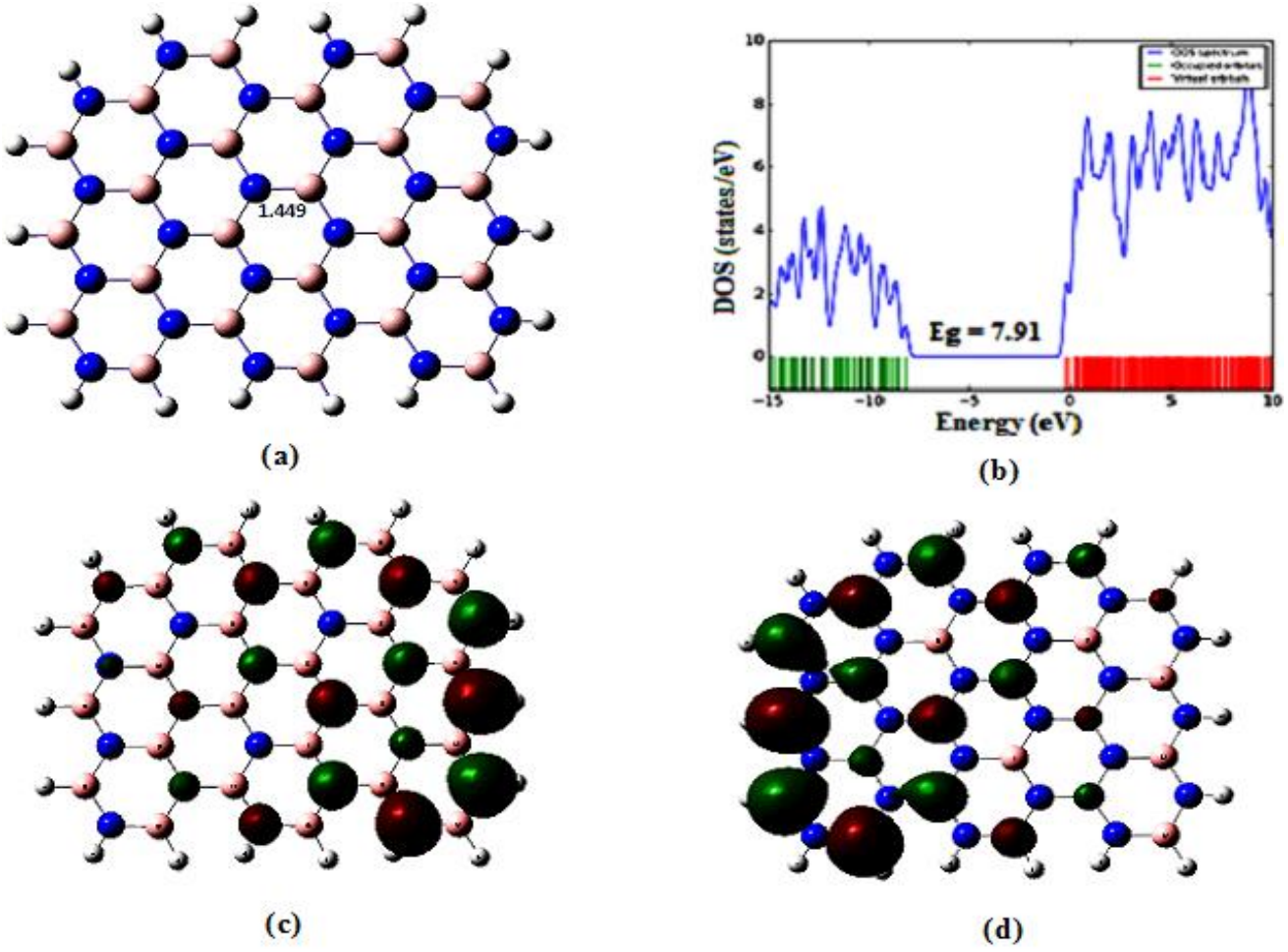

Figure 1. The optimized structure (a), density of states (DOS) plot (b) and HOMO, LUMO profiles (c, d) of the pristine BN sheet. Distance in Å. Colors for optimized structure: blue: N; pink: B; white: H.

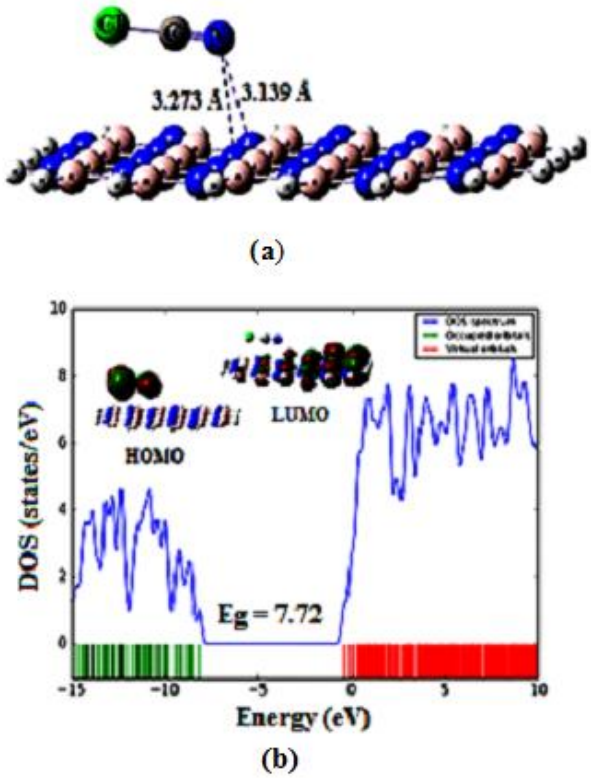

Figure 2. The optimized structure of the most stable (a), DOS plot (b) and HOMO, LUMO profiles of the BN/CNCl complex.

The DFT calculations indicate a less charge transfer of 0.04 e from the CNCl molecule to the BN sheet (Table 1).

Table 1. The adsorption energies (Ead), HOMO and LUMO energies, band gaps (Eg) and net charge transfer (qCT) of the structures.

Structures	E_{ads} (kj/mol)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)	$\%\Delta E_g$	q_{CT} (e)
BN	–	–8.14	–0.23	7.91	–	–
BN/CNCl	–19.96	–8.13	–0.41	7.72	–2.40	0.04
Al–BN	–	–8.13	–0.52	7.61	–	–
Al–BN/CNCl	–95.02	–7.73	–1.19	6.54	–14.06	0.16
Si–BN	–	–6.38	–0.24	6.14	–	–
Si–BN/CNCl	–176.90	–7.38	–0.28	7.10	–11.72	–0.62

The density of states (DOS) for the BN sheet and BN/CNCl complex were calculated. The DOS plot of BN sheet indicates that the BN sheet has an insulator property with E_g of 7.91 eV (Fig. 1b). As shown in Fig. 2b, the conduction level of BN/CNCl decreases slightly (– 0.41 eV) compared to the sheet (– 0.23 eV), while valence level remains unchanged. Therefore, the E_g value decreases from 7.91 (bare BN sheet) to 7.72 eV (BN/CNCl complex). Since the energy gap of the pristine sheet is slightly changed during the adsorption process, the pristine nanosheet will not be sensitive to CNCl molecule. Thus, the pristine sheet is not energetically and electronically suitable for detecting the toxic CNCl. Since the adsorption of CNCl on the BN sheet is energetically and electronically unfavorable which a modified system needs to overcome to solve this problem. Therefore, we suggest the Al– and Si–doped BN sheet system for possible sensing of CNCl.

3.2. Adsorption of CNCl on Al–doped BN sheet

The geometrical structure, electronic properties and adsorption behaviors of Al–doped BN sheet were investigated. The geometric structure of the Al–doped BN sheet noticeably changes when Al atom is doped instead of the B atom in the BN sheet. Due to the large size of dopant Al atom, it stretches out of the plane in order to reduce strain of the ring. The formed Al–N bond length ($\mathbf{l_{Al–N}}$) is 1.737 Å, which is much longer than the corresponding B–N bond length (Fig. 3).

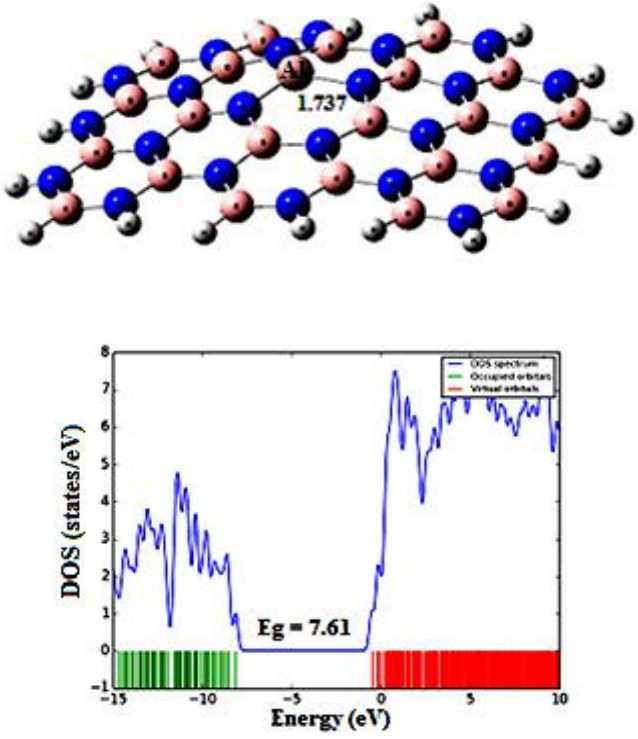

Figure 3. The optimized structure and DOS plot of the Al–BN sheet. Distance in Å.

The changes in the bond lengths adjacent to the Al atom are related to the distortion of the six-membered ring of sheet structure, which was also observed in the case of Al–doped graphene and CNT [30,31]. After optimization, the most stable configuration was obtained, in which the N-head of CNCl molecule is closer to the Al site of the Al–BN sheet. After the adsorption of CNCl molecule over the Al–BN sheet, the bond length of Al–N in Al–BN was increased from 1.737 to 1.773 Å, and the bond lengths of C–N and C–Cl in CNCl were increased from 1.157 and 1.640 Å to 1.211 and 1.727 Å, respectively indicating that the Al site is transformed from sp^2-like to more sp^3-like. Moreover, the adsorption energy of CNCl over the Al–BN sheet is – 95.02 kj/mol, which is larger than that of CNCl on the pristine BN sheet. It can be comparable

with the chemisorption value of CNCl molecule towards the Al–BN nanotube (–97.40 kj/mol) [31]. The distance between the CNCl molecule from N side and Al atom of Al–BN sheet is about 2.028 Å which is shorter than distance between CNCl molecule from N side and pristine BN sheet (Fig. 4a). Mulliken population analysis (MPA) indicates that the charge about 0.16 e was transferred from CNCl to the Al–BN sheet. The adsorption energy value, interaction distances and charge transfer exhibit that the CNCl molecule favorably adsorbed over the Al–BN sheet which can be acted as a suitable sensor of the CNCl molecule.

The calculated DOS of Al–BN sheet indicates that the energy gap value is reduced to 7.61 eV compared to the pristine BN sheet (7.91 eV). The DOS plot shows that the Al–BN sheet has still a large–gap. The DOS plot of the Al–BN/CNCl complex shows the considerable changes in HOMO and LUMO and E_g (Fig. 4b).

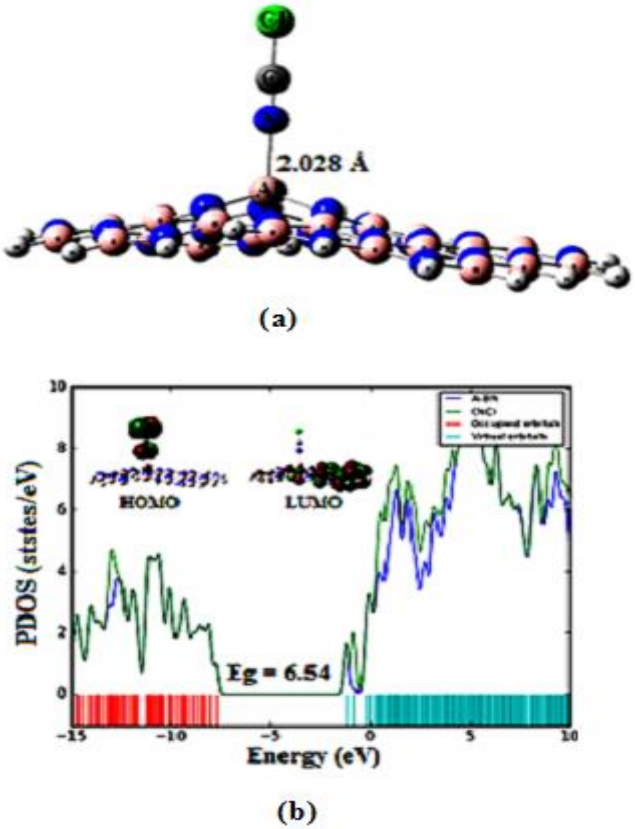

Figure 4. The optimized structure of the most stable (a), PDOS plot and HOMO, LUMO profiles (b) of the Al–BN/CNCl complex.

The HOMO, LUMO and E_g values of Al–BN–CNCl complex are –7.73, –1.19 and 6.54 eV. The conduction level shifts to a lower energies more than valence level during adsorption of CNCl over Al–BN. This indicates that the electronic properties of the Al–BN sheet are sensitive to adsorption of CNCl. The energy gap value of the Al–BN sheet decreased from 7.61 eV to 6.54 eV during adsorption of CNCl over Al–BN. The electrical conductivity of Al–BN changes because E_g changes according to Eq. (3). It is well known that the electrical conductance of compounds is exponentially related to the E_g value according to the following equation [32]:

$$\sigma \propto \exp\left(-\frac{Eg}{2kT}\right) \quad (3)$$

in where, σ is the electrical conductance and k is the Boltzmann's constant. According to the equation, smaller E_g values lead to higher conductance at a given temperature. In comparison to the pristine BN sheet, the Al–BN sheet would have a good sensing ability of CNCl. Our studies have been confirmed by Li and co–workers that they have reported the Al–doped graphene has strong chemisorption of CO molecule than the pristine graphene [30]. Thus, we believed that the Al doping process can be a suitable method for improving the sensitivity and reactivity of the BN sheet to CNCl (Table 1).

It is would be noted that very strong interaction between CNCl and doped-BN is not favorable in the CNCl detection because desorption process could be difficult and the recovery time of doped-BN sheet will be great. If E_{ad} significantly becomes more negative, enhancement of recovery time is expected based on the transition state theory [34]:

$$\tau = \nu_0^{-1} \exp\left(-E_{ad}/kT\right) \quad (4)$$

where, τ is recovery time, T is the temperature, k is Boltzmann's constant, and ν_0 is the attempt frequency. According to this equation, more negative E_{ad} values will enhance the recovery time in an exponential manner. Our calculation clarified that the adsorption energy, E_{ads}, of CNCl over Al–BN sheet is –95.02 kj/mol, and hence it has a short recovery time which this characteristic makes Al–BN sheet to be a suitable sensor.

3.3. Adsorption of CNCl on Si–doped BN sheet

To find a reliable chemical gas sensor to detect the CNCl molecule, we examined the Si–doped BN sheet. In the Si–BN sheet, the bond length of Si–N ($\mathbf{l_{Si–N}}$) is 1.723 Å (Fig. 4a), which is lower than the bond length of Al–N in the Al–BN sheet. This is due to the lesser radius of Si atom (~1.46 Å) than the Al atom (~1.82 Å). The higher bond length of Si–N respect to B–N leads to a structural deformation in the Si–BN sheet which attributed to change from sp^2 to sp^3 hybridization of Si atom. The calculated DOS for the Si–BN sheet indicates that energy gap value is decreased from 7.91 in pristine to 6.14 eV in Si–BN (Fig. 5b). The DOS plot shows that the Si–BN sheet has low band–gap and can be a semiconductor. However, the DOS plot of the Si–BN/CNCl complex indicates the slightly changes in E_g (Fig. 6b). The HOMO, LUMO and E_g values of Si–BN/CNCl complex are –7.38, –0.28 and 7.10 eV, respectively.

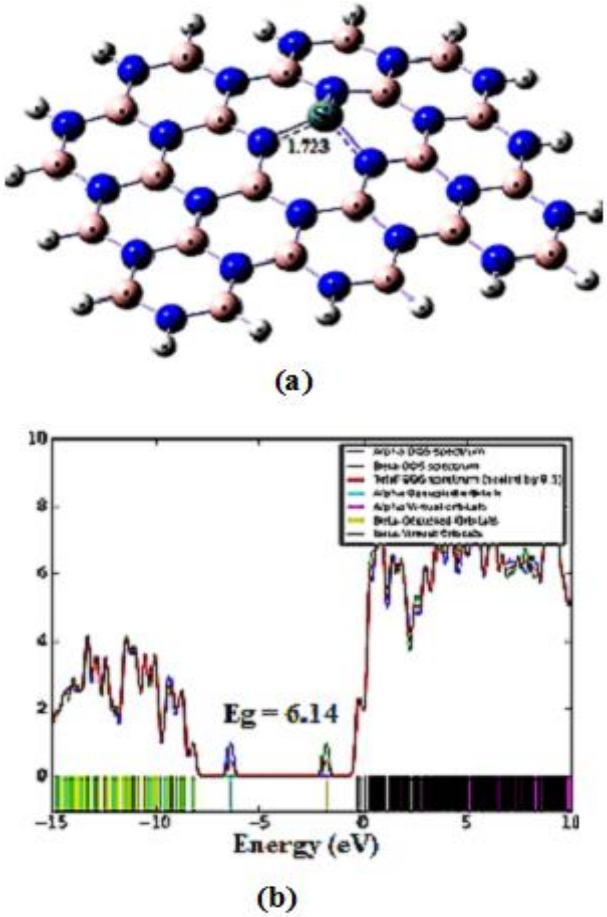

Figure 5. The optimized structure (a) and its DOS plot (b) of the Si–BN sheet.

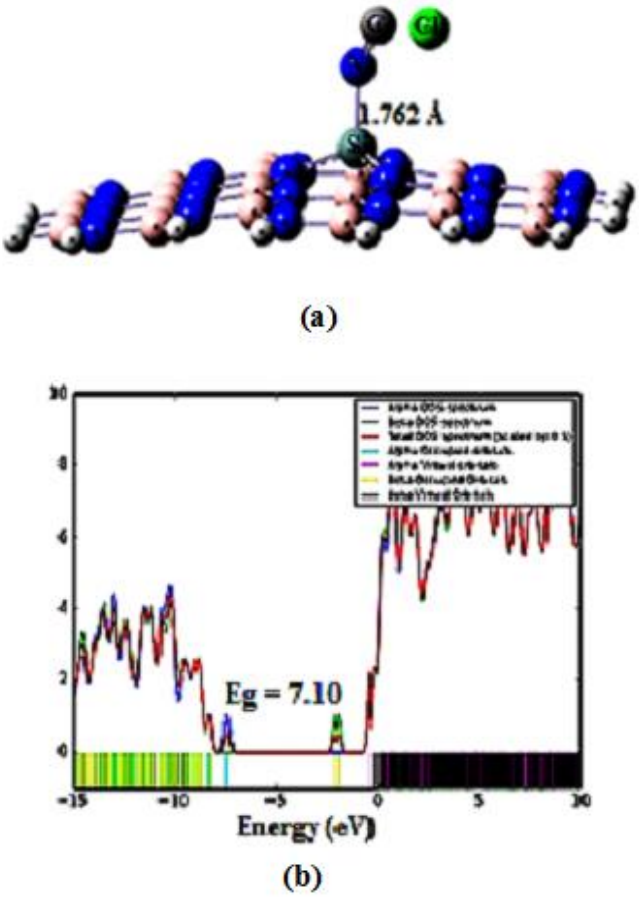

Figure 6. The optimized structure (a) and its DOS plot (b) of the Si–BN/CNCl complex.

It is revealed that the valence level shifts to a lower energy in contrast to conduction level with adsorption of CNCl over Si–BN. This indicates that the electronic properties of the Si–BN sheet are low sensitive to adsorption of CNCl compered to the Al-BN. The energy gap value, E_g, of the Si–BN sheet surprisingly increased from 6.14 eV to 7.10 eV when CNCl absorbed over Si–BN.

The MPA analysis indicates that in contrast to Al–BN, the charge of –0.62 e is unexpectedly transferred from the Si–BN sheet to CNCl. Moreover, the calculated adsorption energy of the Si–BN/CNCl complex (–176.90 kj/mol) is very high than the Al–BN complex (–95.02 kj/mol). This interaction is strong enough to dissociate the CNCl molecule over Si–BN sheet to produce the cyanide group (–CN) and the chlorine atom. A strong interaction is not favorable in the gas detection because desorption time or recovery time increases and thus the sensing ability is reduced.

Our studies clarified that the Si–BN sheet cannot act as a sensor because of high interaction energy and low sensitivity of the Si–BN sheet to CNCl molecule. The Si–BN sheet, however, can be used as a decomposition reagent for CNCl. The adsorption energy value, interaction distances and charge transfer exhibit that the CNCl molecule favorably adsorbed over Al–BN sheet This conclusion is in consistent to the Hadipour and co–workers studies [33]. which Al–BN sheet can act as a sensor of CNCl molecule. They showed that the electronic properties of Al–doped graphene have much sensitivity to the HCN molecule than Si–doped.

4. Conclusion

In this research, we examined a reliable chemical gas sensor to detect the CNCl toxic gas. To find a reliable chemical gas sensor, a pristine, Al– and Si–doped BN nanosheet were selected. The electronic sensitivity of pristine, Al– and Si–doped BN nanosheet were investigated when the CNCl gas adsorbed on the nanosheet using density functional theory. Our studies revealed that the adsorption energy of CNCl over the Al–BN sheet is –95.02 kj/mol, and hence it has a short recovery time which led to the Al–BN sheet to be a suitable sensor. Meanwhile, the Al–doped BN sheet is high sensitive to CNCl more than Si–doped BN sheet. High adsorption energy value and low change in the E_g for the Si–BN/CNCl complex caused that the Si–BN sheet does not have a suitable sensing effect. Anyway, the Si–BN sheet can be used as a decomposition agent of CNCl.

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