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Cyclosarin nerve agent interaction with the pristine, Stone Wales defected, and Si-doped BN nanosheets: Theoretical study

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ABSTRACT

Never agent identification and disposal is vital for both civilian and military defense resources. Herein, using density functional theory calculations, the reactivity and electronic sensitivity of pristine, Stone Wales (SW) defected, and Si-doped BN (Si-BN) nanosheets toward cyclosarin nerve agent were investigated. It was found that the interaction of cyclosarin with the pristine BN sheet is very weak and also that is not energetically favorable with SW defected one. Unlike the SW defect, replacing a B atom by Si atom significantly makes the cyclosarin adsorption energetically favorable. Calculations show that the carbonyl and etheric oxygen atoms of cyclosarin attack the Si atom of Si-BN with the adsorption energies of −73.5 and −136.9 kJ/mol, respectively. The cyclosarin nerve agent can be decomposed by the Si-BN sheet which is thermodynamically highly favorable. Upon this process, the HOMO and LUMO levels are significantly unstabilized and the HOMO-LUMO gap significantly changed by about 24.2%. The cyclosarin presence and its decomposition by Si-BN sheet can be recognized because of the electrical conductivity change of the sheet.

1. Introduction

Decomposition of nerve agents is an important chemical process for hazardous chemical wastes disposal [1]. Also, their identification is vital for both civilian and military defense resources [2]. To date, many methods have been introduced for nerve agent detection and decomposition [3–5]. By advent of nanotechnology, nanostructures have attracted an extensive attention as gas sensors, and surfaces for gas adsorption and decomposition because of their surface/volume ratio [6–17]. Single-walled carbon nanotubes have been used to recognize nerve agents with reproducible resistance change [18]. However, practically, working with carbon nanotubes is a hard task due to their electronic dependency on the chirality [19]. Recently, a great attention has been devoted to the inorganic BN nanostructures whose electronic properties are less depended on the chirality which makes them more suitable for electronic devices [20–23].

An important isostructural arrangement of graphene is hexagonal BN nanosheet 'white graphene' which has been synthesized using various methods [24]. Many researchers investigated the gas adsorption and sensing properties of the withe graphene [25–29]. Also, doping, creating defects, and functionalization approaches have been investigated as strategies to tailor the reactivity and sensitivity of nanomaterials [30–39]. It has been indicated that BN nanosheet can be employed in the pristine form for detection of NO_2 gas and in the Al-doped form for sensing the nitrophenol [30]. Computational methods significantly help the experimentalist to understand the adsorption and sensing behavior of different surfaces to chemicals. In this letter, we explore the adsorption behavior and sensitivity the pristine, Stone-Wales detected (SW-BN) and Si-doped BN (Si-BN) nanosheets to cyclosarin nerve agent by means of density functional theory (DFT) calculations.

Experimentally, several works have been published on the synthesis of different Si-BN nanomaterials [40–42]. Fan et al. have reported the growth of silicon-doped BN nanotubes via catalyst-assisted pyrolysis of a boron-containing polymeric precursor, characterizing their morphologies and structures using electron microscopy and Raman spectroscopy [40]. Also, Si-doped BN films with various Si concentrations were obtained by in situ cosputtering during ion beam assisted deposition by Ying et al. [41]. Si-doped multiwalled BN nanotubes were synthesized via thermal chemical vapor deposition by Cho et al. [42]. Electron energy-loss spectroscopy showed that 5% of Si atoms were homogeneously doped into the nanotubes. X-ray absorption and photoelectron spectroscopy measurements indicated that the Si–B and Si–N bonding structures are produced.

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2. Computational methods

The all calculations were performed using the B3LYP functional augmented with an empirical dispersion term (B3LYP-D) and the 6–31G* basis set as implemented in the GAMESS code [43]. B3LYP delivers an efficient and robust basis for III–V semiconductor calculation and has been frequently used for nanomaterials [44–51]. We used a model of BN nanosheet which is consisted from 36 B and 36 N atoms that its dangling bonds is saturated with hydrogen atoms to reduce the boundary effects. Previously, this model has been frequently used for different purposes and it has been indicated that it is a good representative for larger BN nanosheets [25–27,29,30]. GaussSum code was hired to attain DOS results [52]. The adsorption energy (E_{ad}) is predicted as follows:

$$E_{ad} = E\,(\text{cyclosarin/adsorbent}) - E\,(\text{adsorbent}) - E\,(\text{cyclosarin}) + E\,(\text{BSSE}) \quad (1)$$

where E(adsorbent) is the total energy of a pristine, SW-BN or Si-BN sheet. E (cyclosarin/ adsorbent) is the total energy of the complex of the adsorbed cyclosarin molecule on the adsorbent. E (BSSE) is the basis set superposition error (BSSE) corrected for all adsorption energies. To predict the electronic sensitivity Eq. (2) was used which relates the HOMO-LUMO gap (E_g) to the electrical conductivity of a semiconductor as follows:

$$\sigma = A\,T^{3/2}\exp(-E_g/2kT) \quad (2)$$

where k is the Boltzmann's constant and A (electrons/m^3 $K^{3/2}$) is a constant.

3. Results and discussion

3.1. The cyclosarin on the pristine BN sheet

We have shown the structure of BN nanosheet in Fig. 1, revealing that the B-N bond lengths are about 1.44–1.47 Å in agreement with previous reports [25]. The HOMO and LUMO of the sheet are lied at −6.30 and −0.42 eV, respectively, representing an E_g of about 5.88 eV which is approximately in accordance with the experimental bad gap (~5.50 eV) [53]. To obtain the stable cyclosarin/BN complexes, several initial structures entailing single atom (F, O, and H), two, three, and more atoms near the surface of the BN were explored. It was predicted that the molecule tends to escape from the surface of BN sheet upon the relax optimization and a weak interaction is predicted. Finally, in the most stable form, the cyclosarin located on the surface of the BN as shown in Fig. 1 with adsorption energy of about −1.32 kJ/mol. Because of this weak interaction, the electronic properties of the BN sheet are not significantly affected by the adsorption process.

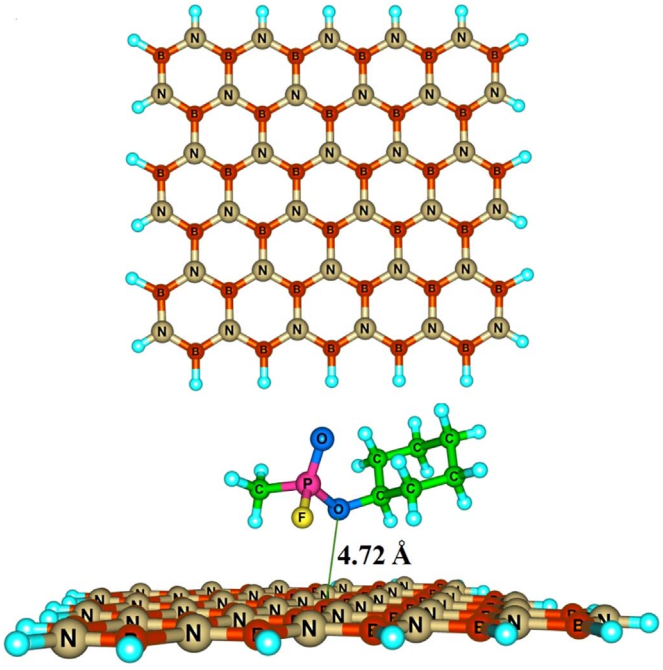

Fig. 1. Optimized structure of BN nanosheet and its complex with cyclosarin nerve agent.

3.2. The adsorption of cyclosarin on the SW-BN sheet

The optimized structure of SW-BN sheet is shown in Fig. 2. As it was schematically indicated (Fig. 2), for creating SW defect, four adjacent hexagonal rings at the center of BN sheet are changed into two pentagonal and two heptagonal rings when the bond uniting two of the adjacent rings rotates. Length of the rotated bond is change from 1.44 to 1.39 Å due to a structural distortion. Upon the SW-defect formation an N-N and a B-B bond are formed with length of about 1.48 and 1.67 Å, respectively. The energy is needed for SW defect formation is calculated to be about −133.6 kcal/mol. In the other words, the pristine BN sheet is more stable than the SW-BN by about 133.6 kcal/mol. The HOMO is unstabilized by about 0.48 eV by shifting from −6.30 eV in the pristine BN sheet to −5.82 eV in the SW-BN sheet. While the LUMO is stabilized by changing from −0.42 to −0.81 eV. Also, their shapes are significantly changed by localizing on the newly formed B-B (LUMO) and N-N (HOMO) bonds as shown in Fig. 2. Finally, the E_g is somewhat decreased from 5.88 to 5.01 eV, indicating that existence of SW defects decreases the electrical resistance of the BN sheet. As it was mentioned before the calculated E_g of the pristine BN is larger than that of the experimental value which may be due to the naturally existence of defects in the real BN sheet.

It is expected that the high electron heads (O-head and F-head) of cyclosarin molecule attack the electron deficient B-B site of the SW defect. Our calculations indicate that when the molecule is located from its F head on the B-B site, it reoriented and tends to attach from its carbonyl O-head to a B atom of B-B bond as shown in Fig. 3. The length of newly formed O-B is about 1.75 Å and a local deformation is occurred in the adsorption site. The adsorbing B atom is projected out of plan and the lengths of its surrounding bonds are perturbed. These findings show that the interaction between the cyclosarin molecule and SW-BN sheet is much stronger than that with the pristine BN sheet. But the calculated adsorption energy is positive for this interaction (Table 1) because of the large structural deformation that compensates the released energy. To show the strength of the adsorption we used the following equation to find the binding energy:

$$E_{bin} = E\,(\text{cyclosarin/SW-BN}) - E_{sp}\,(\text{SW-BN}) - E_{sp}(\text{cyclosarin}) + E\,(\text{BSSE}) \quad (3)$$

where E (cyclosarin/SW-BN) is total energy of cyclosarin/SW-BN complex, and E_{sp} (SW-BN) is single point energy of the SW-BN after removing the cyclosarin from the complex and also E_{sp} (cyclosarin) is the single point energy of cyclosarin after removing the SW-BN from the complex. Finally the predicted binding energy is predicted to be about −63.2 kJ/mol, indicating a strong interaction. The HOMO and LUMO levels are unstabilized upon the cyclosarin adsorption process. But Table 1 shows that the E_g of the SW-BN is not sensibly affected. Thus, the electrical conductivity of the SW-BN will not vary meaningfully based on the Eq. (2). It can be decided that although the SW defect considerably increases the reactivity of the BN sheet, its effect on the electrical sensitivity is negligible.

3.3. The cyclosarin adsorption on the Si-BN sheet

Herein, we will explore the effect of Si-doping on the reaction of the