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Al-doped graphene-like BN nanosheet as a sensor for *para*-nitrophenol: DFT study

Ali Ahmadi Peyghan [a], Maziar Noei [b], Sirous Yourdkhani [c,*]

[a] Young Researchers and Elite Club, Central Tehran Branch, Islamic Azad University, Tehran, Iran
[b] Department of Chemistry, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran
[c] Young Researchers and Elite Club, Garmsar Branch, Islamic Azad University, Tehran, Iran

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ABSTRACT

We investigated the electronic sensitivity of pristine and Al-doped BN sheets to *para*-nitrophenol (*p*-NP) by using density functional calculations. It was found that *p*-NP adsorption on the pristine sheet is endothermic and unfavorable. By replacing adsorbing boron atom of the sheet surface by an Al atom, the sheet becomes more reactive to *p*-NP, so energy of 20.4 kcal/mol is released upon adsorption process. Upon *p*-NP adsorption on the Al-doped BN sheet, HOMO/LUMO energy gap of the sheet is dramatically decreased from 5.39 to 1.23 eV and it becomes a *p*-type semiconductor. Thus, the Al-doped BN sheet may transform the presence of *p*-NP molecule into an electrical signal, and it might be potentially used in *p*-NP sensors.

1. Introduction

Para-nitrophenol (*p*-NP) is among the most important and versatile industrial organic compounds and are widely used as raw materials or intermediates in the manufacturing of explosives, pharmaceuticals, pesticides, pigments, dye, wood preservatives, and rubber chemicals [1]. The *p*-NP is almost entirely attributed to anthropogenic sources, such as automobile exhaust gas, or as a result of the photochemical reaction of benzene with nitrogen monoxide in highly polluted air [2]. This component has toxic effects on human beings, animals, and plants. Thus, its monitoring and control of exposure, in both industrial and residential environments, are of special interest. People have been looking for good materials as gas sensors with high sensitivity for a long time.

* Corresponding author.
E-mail address: sirousyourdkhani@gmail.com (S. Yourdkhani).

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Since carbon nanotube (CNT) was discovered by Iijima [3], the properties and applications of this novel material have been investigated extensively [4–6]. CNTs have recently emerged as a promising substitute for materials of different properties and various applications in hydrogen storage, gas sensors, textiles, and many more [7,8]. Besides CNTs, graphene have attracted increasing scientific and technological interests due to their special electronic and mechanical features [9]. In graphene and similar material research, molecular interaction (e.g. of NO_2, NH_3 and so forth) with the graphene surface is a subfield of considerable interest due to potential applications such as chemical sensors, and electronic devices [10–12]. Their high surface area is beneficial to practical gas sensors. Basically, it is expected that the adsorption of gas molecules on sensors is stable and the changes of the conductivity should be observable. However, most of gases are found physisorbed on suspended intrinsic graphene. Although the physisorption can also change the conductivity of intrinsic graphene, the small binding energy and weak coupling between gases and graphene indicate the unstable configuration at room temperature and little change of electronic structure [13]. The reactivity of graphene is often adjusted by doping with other elements or topological defect [14,15]. It is important to understand and be able to quantify the modification of the surface properties by the addition of such elements.

Graphene-like boron nitrogen sheet (*h*-BN) with sp^2 bond consisting of III- and VI-group elements may be applied in electronic devices in the future. In contrast to the half-metal behavior of graphene, *h*-BN possesses polar B–N bond and a wide band gap [16–18], which promises the potential application of *h*-BN in this silicon age of semiconductors. The surface of *h*-BN nanomaterials are intrinsically inert during to the large ionicity of BN bond, making the chemical modification and practical processing of these materials difficult. For the above reasons, the *h*-BN nanomaterials have rarely been studied for sensing applications. Zhang et al. [19] have investigated adsorption mechanisms of carbon monoxide (CO) on modified *h*-BN, including Al doping, mono-vacancy and Stone–Wales defects were investigated via density functional theory (DFT). It was found that the modified graphene is more sensitive than that of perfect graphene for detecting CO molecules.

Based on our knowledge, there is no publication related to the sensing behavior of *h*-BN toward organic gas molecule, although a number of papers have been published for the small gas molecule adsorption on *h*-BN. In the present work, within the DFT framework, we are interested in the following: (1) whether there is a potential possibility of *h*-BN serving as a chemical sensor for *p*-NP; (2) if not, can we find a method for improving the sensitivity of BN sheet to *p*-NP?

2. Computational methods

A BN sheet consisted of 36 boron and 36 nitrogen atoms was selected, which its end atoms were saturated with hydrogen atoms to reduce boundary effects (Fig. 1). The full geometry optimizations and property calculations on the pristine and Al-doped sheet in the presence and absence of a *p*-NP molecule were performed using three parameter hybrid generalized gradient approximation with the B3LYP functional and the 6-31G basis set including the d-polarization function (denoted as 6-31G (d)) as implemented in the GAMESS suite of program [20]. The B3LYP density functional has been previously shown to reproduce experimental properties and has been commonly used in nanostructure studies [21–26]. It has been also demonstrated that the B3LYP provides an efficient and robust basis for calculations of III–V semiconductors by Tomić et al. [27], capable of reliably predicting both the ground state energies and the electronic structure. We have defined the adsorption energy (E_{ad}) as follows:

$$E_{ad} = E(h\text{-BN}/p\text{-NP}) - E(h\text{-BN}) - E(p\text{-NP}) + E(\text{BSSE}) \quad (1)$$

where $E(h\text{-BN}/p\text{-NP})$ is the total energy of the adsorbed *p*-NP molecule on the *h*-BN surface, and $E(h\text{-BN})$ and $E(p\text{-NP})$ are the total energies of the pristine *h*-BN, and *p*-NP molecules, respectively. $E(\text{BSSE})$ is the basis set superposition error (BSSE) corrected for all interaction energies. By the definition, negative values of E_{ad} correspond to exothermic process.