Applied Surface Science 434 (2018) 604–612

Contents lists available at ScienceDirect

Applied Surface Science

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

Full Length Article

Adsorption modes of molecular iodine on defected boron nitrides: A DFT study

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ARTICLE INFO

Article history:
Received 21 August 2017
Received in revised form 30 October 2017
Accepted 31 October 2017

Keywords:
Iodine
Boron nitride
Adsorption
DFT
Vacancy
Magnetic properties

ABSTRACT

The interaction of molecular iodine with pristine and monovacant boron-nitride quantum dots (QDs) have been investigated using density functional theory. It was found that removing one B or N single atom significantly decreased the calculated E_g values at various exchange functional. In B-defected BN system, the localized spin densities canceled each other and overall polarization of system was found to be equal to unity. For N-defected system there was smaller spin densities localized on each closest B atoms. Both B- and N-vacancies caused appearance of new states in gap region. Our calculation revealed that spin density and polarization of defected system are localized on vacancy region and other atoms did not take part in this polarization. The results of electron localization function for N-DBN showed there was high density region at the position of removed nitrogen atom. The calculated adsorption energies implied that there was no significant chemical interaction between iodine molecule and pristine BN sheet. We suggested that when a deficiency was imposed to the BN sheet, the reactivity of the modified system toward iodine molecule significantly could increase. We found strong interaction between iodine and nitrogen atoms of B-DBN system. In the case of I_2/N-DBN system the neighbor atoms had no contribution in spin polarization of the system and it seemed that all spin density of system transferred to the iodine molecule after adsorption. Strong correlation between molecular iodine orientation and BN-QDs via their interactions type has been clarified in this work. These findings may provide a deeper insight into halogen molecules interactions with low dimensional defected boron nitrides.

1. Introduction

Because of its essential role in various features of medicine, industry and atmospheric chemistry, iodine has been the subject of several investigations [1–4]. For example some of the gaseous iodine isotopes (^{131}I) have important rule in nuclear facilities and often are known as hazardous radioactive compounds [5,6].Iodine is also used successfully in dealing with simple goiter disease [7].

To control of releasing this gas to the environment, especially in nuclear power plants, a variety of technologies have been suggested to remove or capture gaseous iodine from atmosphere. It's well-known that capturing or sensing gas molecules by typical sorbent is directly connected to the nature of interaction formed between sorbent and adsorbent structures. In this regard, theoretical investigations may provide useful information for understanding the fundamental basis of gas/sorbent interactions [8–10]. Among various quantum mechanical methods used in computational chemistry, density functional theory (DFT) has been shown to be useful approach to modeling molecular interactions [11–13]. The adsorption of diatomic halogens including iodine on graphene and graphite have been investigated by Rudenko et al. based on Van der Waals corrected density functional theory [14]. They found that Vander Waals interactions significantly affect the probable bond formed in graphene/halogen supersystems.

In particular, the interaction of molecular iodine with a variety of chemical systems has been the subject of several investigations. Tkatchenko et al. showed that DFT approach could be successfully apply to investigate the adsorption of molecular iodine on the Pt(111) surface [15]. Benes's group used spectrophotometric method to investigate the interaction of iodine with aromatic hydrocarbons [16]. Their findings strongly confirmed the presence of acid/base interaction between iodine and studied hydrocarbons. The adsorption of iodine on Ni (111) surface was studied by Komarov et al. [17]. They suggested that nucleation and the growth of nickel iodide islands take place when chemisorbed iodine is saturated. The high-temperature superconducting cuprates (such as $Bi_2Sr_2CaCu_2O_8$) is one of the materials which were used for surface investigations. DFT calculations showed that in the adsorption of iodine on $Bi_2Sr_2CaCu_2O_8$ system, high-symmetry sites and the

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https://doi.org/10.1016/j.apsusc.2017.10.232
0169-4332/

potential above the Bi centers were altered by iodine molecules [18].Yuan et al. investigated iodine adsorption in zeoliticimidazolate frameworks (ZLFs) in a multi-component system based on DFT methods [19]. The results of their studies confirmed that ZIFs could be efficient candidate for iodine adsorption. Recently, Hassani et al. suggested that sulphur-doped fullerene could be an appropriate candidate for iodine sensor devices [20].

On the other hand, boron nitride (BN) which is known as two dimensional nano-structures has attracted a great deal of attention over the recent decades owing to its motivating properties and applications. A short survey in the literature reveals numerous publications in which the hexagonal BN has been used as proper gas adsorbent system [21–26]. It has been also suggested that modifying BN structures via atom doping, decorating or deficiency could increase the reactivity of the system toward the gas molecules. For instance, Matarin et al. showed that in the case of small polar gas adsorbed on defected boron nitride nanotubes (BNNTs),large charge transfer from the gas molecules to the BNNT is seen [27]. These results confirmed that adsorption potential of BNNTs is significantly in connection with structural defects in BN systems.

Moreover, these low dimensional systems showed significant magnetic properties through vacancy formation in their geometrical structure. Xue et al., reported direct relation between system dimension and spin polarization on the defect neighbor atoms of BN sheets and nano-ribbons (BN-NR) [28].

In this study we have used density functional theory to model the interaction of molecular iodine with pristine and defected BN quantum dots (BN-QDs). To explore the role of probable dispersion forces in I_2/BN systems, three density functionals namely, B3LYP, CAM-B3LYP and B97D were applied to calculate structural and energetic properties [29–32]. Two types of defects for BN QDs were considered by removing boron or nitrogen atoms from the pristine BN. These mono-vacancies can distort charge and spin distribution over the BN atoms, which in turn may affect the interaction character in I_2/BN systems.

We applied different initial orientations for iodine molecule to interact with pristine and monovacant BN-QDs in order to find the global minimum energy configurations on the I_2/BNs potential energy surfaces.

These interactions may have covalent or non-covalent nature, where the covalent nature is frequently confirmed via strong charge localization between bonding atoms. The characterization of non-covalent interactions is not feasible with typical charge and energy difference analysis and one should look for alternative approaches to evaluate such weak interactions.

Recently, Johson et al. introduced a new method based on first and second charge spatial derivatives to find critical points and categorize weak interactions [33]. We utilized this method in our case to find deeper aspects of iodine and BN-QD interactions.

This paper has been organized in following sections: initially the details of computational tools employed are presented, secondly the electronic structure of pristine and defected BN-QDs are discussed based on several descriptors such as geometrical parameters, energetics, frontier orbitals distribution and their composition, spin densities and electron localization function (ELF). Finally, we will focus on the interaction of molecular iodine and pristine and monovacant BN-QDs. It is believed that the results of current study would provide precious insight to the interaction nature of iodine and BN-QDs.

2. Computational details

Due to different arrangement of boron and nitrogen atoms in boron nitride systems, several structural forms with individual properties may be existed. It is well-known that hexagonal boron nitride (h-BN) wherein B and N atoms are connected via covalent bonds is the most stable structure suggested for boron nitride nano-sheets. Modeling the sorbent structure was carried out via utilizing a rectangular edge-passivated cluster including totally 66 nitrogen and boron atoms with a diameter of 18.3 Å. The applied model is regularly employed by theoretical research groups for modeling the BN surfaces [34]. The defects are introduced via removing a single atom from the pristine sheet. Separately removing B and N atoms leads to formation of defected boron nitride structures (DBN) denoted as B-DBN and N-DBN, respectively (see Fig. 1).Hereto model molecular iodine adsorption on the BN surfaces only the interaction of a single iodine molecule with sorbent has been considered and all possible collective effects are neglected. The B97D/6–31 + G* level of theory without any symmetry constrain were utilized for geometry. We also compared the results of calculated geometrical parameter, gap of energies (E_g) and the adsorption energies (E_{ad}) for iodine on pristine/defected BN structures using gradient-corrected correlation functional of Perdew, Burke and Ernzerhof (PBE) and B3LYP functional which the latter is consist of hybrid Becke–Hartree–Fock exchange and a Lee–Yang–Parr correlation functional with nonlocal corrections [29–32]. To calculate adsorption energies for each system, the following general equation was applied:

$$E_{ad} = E(I_2/BN) - [E(I_2) + E(BN)] + E(BSSE)$$

where $E(I_2/BN)$ is the total energy of the adsorbed I_2 moleculeon the BN surface, and E(BN) and $E(I_2)$ are the total energies of the BN, and I_2molecule, respectively. E (BSSE) is the basis set superposition error (BSSE) which has been corrected for all interaction energies. Similar procedure was considered for adsorption of iodine on B-DBN and N-DBN systems.

Considering possible orientations of iodine and existence of vacancies on the BN-QDs, the interaction between iodine and BN-QD could have both covalent and non-covalent characters. While covalent interactions are too straightforward to study from charge distribution between molecules, recognition and categorizing the non-covalent ones are complicated. The strength of the non-covalent interaction (e.g. halogen bonding) depends mostly on the electrophilicity of the Lewis acid (the "halogen donor") and the nucleophilicity of the Lewis base (the "halogen acceptor"). An elegant way to assess the characteristics of such interactions is accessible by analyzing the sign of λ, the second derivative of the electronic density in the perpendicular direction of the bond ($\partial^2\rho/\partial y^2$), in a critical point where the following reduced gradient equals to zero [33]:

$$s = \frac{1}{2(3\pi^2)^{1/3}} \frac{\nabla\rho}{\rho^{4/3}}$$

A negative λ is a sign of attractive interaction (with an accumulation of density perpendicular to the bond), while a positive value implies steric repulsion (density depletion). In this formalism Van der Waals interactions are described by low electron density ρ at the critical points, and thus $\sin(\lambda_2) < 0$. This method, known as Non-covalent interactions (NCI) analysis and it is implemented in Multiwfn and Jmol code packages [35,36]

All electronic structure calculations were performed using GAMESS suite of program [37]. Multiwfn package has been utilized to provide the results of orbital composition analysis and calculation of density of states for alpha and beta spins [36].

3. Results and discussions

3.1. BN, B-DBN and N-DBN quantum dots

Fig. 1 shows schematic representation of optimized geometry of BN, B-DBN and N-DBN with selected geometrical parameters at