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Ab initio investigation of the SCN^- chemisorption of single-walled boron nitride nanotubes

Alireza Soltani[a,*], Nasim Ahmadian[b], Yaser Kanani[c], Aliakbar Dehnokhalaji[d], Hossein Mighani[d]

[a] Young Researchers Club, Gorgan Branch, Islamic Azad University, Gorgan, Iran
[b] Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran
[c] Department of Chemistry, Gorgan Branch, Islamic Azad University, Gorgan, Iran
[d] Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran

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ABSTRACT

The thiocyanate anion (SCN^-) adsorption capacity of zigzag single-walled boron nitride nanotubes (SWBNNTs) is studied via first-principles theory. Binding energy corresponding to the most stable configuration of SCN^-/BNNT is found to be $-148.42\ kJ\ mol^{-1}$, which is typical for the chemisorptions. Our results indicate that both aluminum and gallium doping can significantly enhance the adsorption energy of SCN^-/BNNTs complexes. Our electronic results reveal that there is a significant orbital hybridization between two species in adsorption process being an evidence of strong interaction. Thus, we arrive at the prediction that the BNNTs nanocage can be implemented as suitable sensor for practical applications.

1. Introduction

The discovery of single-walled carbon nanotubes (SWCNTs) [1] has raised intensive efforts for determining the properties and applications of this fascinating novel material [2,3]. CNT is one of the best materials based on its interaction with other molecules such as H_2, Cl_2, NO, OCN, and CO regarding to a numerous capable applications like storage, chemical sensors, and electronic devices [2–6]. CNTs have extraordinary chemical, physical, geometrical properties and also a large surface area making them as promising candidate using in nanoelectronics, nanoscaling, biotechnology, and biosensors [7–11]. Adsorption of alcohols and hydrocarbons on CNTs [12–14], the detection of gas molecule [15,16], organic vapors [17], various ions, and biomolecules [18] are other empirical researches which have been made on CNTs. Considering electronic properties of CNTs, tubular diameter and chirality are two restrictions. Therefore, a wide range of investigations have performed to make nanotubes which are independent from these factors. Moreover, nanotubes containing atoms of groups III and V of the periodic table of elements are considered to be a suitable case as a replacement of CNTs [19–22]. Boron nitride nanotubes (BNNTs) for the first time at 1994 stabilized computationally [23], and afterwards synthesized [24]. Subsequently, a numerous experimental and theoretical investigations have been dedicated to consider the electronic properties and different structures of BNNTs. BNNTs are considered to be polar materials due to the slight positive charges of boron (B) atoms and the slight negative charges of nitrogen (N) atoms; while there is no polarity in CNTs. This could be a reason to apply BNNTs in electronic and mechanical devices. BNNTs are semiconductors with a constant band gap of ~5.5 eV, being almost independent of tubular diameter and helicity. Brilliant properties such as; large iconicity, high thermal conductivity, superior resistance to oxidation, and high mechanical strength [25–30], make BNNTs highly useful materials for the broad diversity of applications. For example, numerous studies both theoretically and experimentally have been allocated to examine their application in nano-electronic fields [31,23], force sensors [24,25], gas storage [26], particularly in hydrogen storage [27,28]. The need for detectors with high specificity and sensitivity has directed scientists to serve tubular structures. Electronic conductance changes in BNNTs upon exposure to gas molecules. Based on this feather, they can be served as nanotube molecular sensors [29]. On the other hand, reaction between CS_2 and NH_2-species and also reaction between CH_3SCN and e^- generate thiocyanate anion (SCN^-) [32,33], and it can be finding in interstellar ice and dust clouds [34]. Quite fadeaway or reducing SCN^- in human body [35] is of high prominence regarding to human host defense system [36,37]. It may happen via biosynthesis of hypothiocyanite by a lactoperoxidase [38–40]. Since SCN^- has attracted interests of environmental scientists, information about how different nano surfaces interact

* Corresponding author. Tel.: +98 9113702973.
E-mail address: alireza.soltani46@yahoo.com (A. Soltani).

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with SCN^- seems to be important [41]. Recently, Baei et al. [33] have investigated the adsorption properties of SCN^- on (6, 0), (7, 0), (8, 0), and Al-doped (6, 0) zigzag SWCNTs via first-principles theory based on DFT calculations. They reported that the interaction between CNTs and SCN^- radical is week, while Al doping on the CNTs can significantly enhances adsorption capability in CNTs. The aim of this study is to investigate the SCN^- adsorption capability of the *zigzag* and *armchair* BNNTs and examine the effect of Al and Ga doping on the electronic structures, potential applications as nanosensor, and adsorption capability of BNNTs through DFT calculations. In the middle of our research, we found that very recently Baei and Varasteh Moradi [42] have theoretically suggested that bonding of SCN^- to BNNTs caused to complexes with low adsorption energy based on the single point energy (SPE) calculations, while SCN^-/Ga-doped on the zigzag (6, 0) BNNT system shows the involvement of covalent interactions in the adsorption. In our opinion, their binding results do not provide substantial validity due to the lack of geometry optimization of corresponding complexes. Hope our results can provide experiments with useful information on designing sensors employing the BN nano-materials.

2. Computational methods

In this research, we considered the adsorption behavior of the SCN^- on the *zigzag* single wall (6, 0), (8, 0), (10, 0), and Al-, Ga-doped (6, 0) BNNTs in which the ends of the BN nanotubes are saturated by hydrogen atoms. All the geometry optimizations and energy calculations are performed using Gaussian 98 program package [43] at the level of density functional theory (DFT) with B3LYP/6-31G* [44–46]. The hydrogenated (6, 0), (8, 0), (10, 0), (5, 5), Al-doped (6, 0) and Ga-doped (6, 0) zigzag BNNTs have 60 ($B_{24}N_{24}H_{12}$), 80 ($B_{32}N_{32}H_{16}$), 100 ($B_{40}N_{40}H_{20}$), 70 ($B_{25}N_{25}H_{20}$), 60 ($B_{24}N_{23}H_{12}Al$) and 60 ($B_{24}N_{23}H_{12}Ga$) atoms, respectively. The binding energy of an SCN^- on the BNNT is determined through the following equation:

$$\Delta E_{ad} = E_{BNNT\text{-}SCN^-} - (E_{BNNT} + E_{SCN^-}) \quad (1)$$

$$\Delta E_{ad} = E_{Al\text{-}BNNT\text{-}SCN^-} - (E_{Al\text{-}BNNT} + E_{SCN^-}) \quad (2)$$

$$\Delta E_{ad} = E_{Ga\text{-}BNNT\text{-}SCN^-} - (E_{Ga\text{-}BNNT} + E_{SCN^-}) \quad (3)$$

where $E_{(BNNT\text{-}SCN^-)}$ is the total energy of the BNNTs interacting with the SCN^-. E_{BNNT} is total energy of the pure BNNT and E_{SCN} is the total energy of an isolated SCN^-. Natural charge analysis with full NBO calculations were performed by using DFT/B3LYP method with 6-31G* basis set for optimized structures. The electrophilicity concept was stated for the first time in 1999 by Parr et al. [47,48]. μ is defined according to the following equation:

$$\mu = -\chi = \frac{-(I + A)}{2} \quad (4)$$

χ is defined as the negative of μ, as follows: $\chi = -\mu$. Furthermore, η can be approximated using the Koopmans' theorem [49,50] $I(-E_{HOMO})$ is the ionization potential and $A(-E_{LUMO})$ the electron affinity of the molecule. $\eta = (I - A)/2$. S and ω are defined as following equations, respectively.

$$S = \frac{1}{2\eta} \quad (5)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (6)$$

The maximum amount of electronic charge, ΔN_{max}, that the electrophone system may accept is given by Eq. (7) as [51]:

$$\Delta N_{max} = \frac{-\mu}{\eta} \quad (7)$$

3. Results and discussion

3.1. The SCN^- adsorbed on the pristine BNNTs

We first examine the interaction between SCN^- and the pristine BNNTs including *zigzag* (6, 0), (8, 0), (10, 0) *zigzag* and (5, 5) *armchair* BNNTs complexes the most stable configuration. We considered one adsorption configuration of SCN^- via its expected active site (N-side) on the BNNTs surface consisting of the top sites directly above the boron (B1-approach), as depicted in Fig. 1(a–d).

The optimized pristine BNNTs and SCN^- were used for the molecule adsorption. The optimized geometries of pristine (6, 0) (8, 0), (10, 0) *zigzag* and (5, 5) *armchair* BNNTs were found to be with B—N bond lengths are about 1.449, 1.449, 1.450, and 1.446, and with the diameter of the nanotubes are about 4.808, 6.393, 7.958, and 6.835 Å, respectively. The computed C≡N and C—S equilibrium bond length are 1.180 and 1.676 Å in the pure SCN^-, respectively. We have performed full structural optimization of the most stable configurations, namely, SCN^- from N-side approaching B1 atom of the (6, 0), (8, 0), (10, 0), and (5, 5) BNNTs. Binding studies indicate that adsorption energy for thiocyanate anion (SCN^-) on the exterior surface of pristine (6, 0), (8, 0), (10, 0), and (5, 5) BNNTs for the most stable configuration (N-side) are about −148.42, −132.38, −112.98, and −105.95 kJ mol^{-1}, and the equilibrium distance between the closet atoms of four species are 1.550, 1.557, 1.569, and 1.572 Å, respectively. After the SCN anion chemisorbed on the (6, 0) (8, 0), (10, 0) *zigzag* and (5, 5) *armchair* BNNTs, the equilibrium B—N bond lengths are about 1.539, 1.538, 1.536, and 1.554 Å, respectively. In comparison with the pristine form, the B—N bond lengths are longer for the SCN^- adsorbed on the BNNTs. for SCN^- adsorbed on BNNTs, the C≡N and C—S equilibrium bond length are 1.177 and 1.627 Å, respectively. Khalaji et al. [52] reported that the bond lengths of C—S and C—N of SCN^- are 1.642 and 1.162 Å, respectively. This experimental data is in good agreement with our study. Additionally, the obtained E_{ad} for SCN^- from N-side of atom is more than that of S-side atom [41,42]. The discrepancy in adsorption energy (E_{ad}) between configurations can be due to the polarization of SCN^-. Since S atom is less electronegative than N atom thus for configuration, in which nitrogen atom orients toward the BNNTs surfaces, interaction between SCN^- and surfaces is more than that of configuration, in which S atom orients toward the surfaces. We found that in all cases, SCN^- prefers to be adsorbed directly on the top site of the B1 atom of the BNNTs via its N-side. On the other hand, the adsorption energy of the SCN^- slightly decreases at each particular site of the interaction as the BNNT diameter increases. We found that the binding energy for the favorable energetically configuration is −148.429 kJ mol^{-1}, and the equilibrium distance between the closet atoms of two species is 1.550 Å. It is obvious that after full optimization of the favorable energetically configuration, the binding energy is notably changed in comparison with SPE calculations highlighting SPE cannot accurately suggest the adsorption nature between two species [42]. Natural charge analysis shows that in this configuration 0.45 e charge transferred from SCN^- to the (6, 0) BNNT. These findings suggest the attachment of strong interaction (chemisorptions) in the adsorption.

3.2. The SCN^- adsorbed on the Al- and Ga-doped BNNTs

To examine the effect of metal doping on the adsorption behavior of SCN^- on (6, 0) BNNTs system for the most stable configuration, we substitute B1 atom of the (6, 0) BNNT by Al and Ga atoms and then consider the interaction of SCN^- approaching directly above Al and Ga atoms of Al/Ga-doped (6, 0) BNNT via its N and S sides, the perpendicular approach of SCN^- to the Al/Ga doped (6, 0) BNNT, as represented in Fig. 2.