



Theoretical studies of urea adsorption on single wall boron-nitride nanotubes



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ABSTRACT

Surface modification of a boron nitride nanotube (BNNT) with urea molecule was investigated in terms of its energetic, geometric, and electronic properties using B3LYP and PW91 density functionals. In this investigation, various armchair (n,n) nanotubes, where $n = 5, 6, 7$ have been used. Two different interaction modes, including interaction with outer layer and inner layer of tube were studied. The results indicated that the adsorption of single urea molecule in all of its configurations is observed to be exothermic and physical in nature. Interestingly, the adsorption energy for the most stable configuration of urea was observed when the molecule located inside of the nanotube. Besides, the adsorption of urea on BNNTs changes the conductivity of nanotube.

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1. Introduction

Boron nitride (BN) nanotubes have attracted much attention in recent years due to its structural similarity to CNTs. The BNNTs were first theoretically predicted in 1994 and then experimentally synthesized in 1995 as being mainly semiconductor materials with wide band gaps [1,2]. Because of their excellent properties such as their mechanical properties and chemical and thermal stabilities, the BNNTs have been encouraged potential applications such as molecular sensing [3–5], field emission displayers [6–8], hydrogen storage [9–11], catalysis [12,13], nanofillers in composite materials [14,15] and switching behaviors [16]. In recent years, various theoretical investigations have been carried out to study adsorption of different gas molecules such as H_2O_2 [17], H_2 [18], O_2 [19], HCOH [20], N_2O [21], NO [22], Noble gases [23], CO_2 [24], CO [25], NH_3 [26], CH_4 [27], and aromatic molecules [28].

The biocompatibility and bioapplications of inorganic nanomaterials have become hot topics in recent years. For a nanomaterial, biocompatibility should be considered prior to any practical applications. The first biocompatibility tests on BNNTs were reported by Ciofani et al. In their experiments, PEI-coated BNNTs were used for in vitro tests on a human neuroblastoma cell line [29]. In addition, Chen et al. [30] reported that the surface of functionalized BNNTs may have glycol dendrimers capable of interacting with proteins

and cells. Urea is a metabolic end product, and the removal of its excess has been a major problem for patients' misery from chronic renal failure. It has properties such as high solubility in water [31], protein denaturant ability [32] and inhibitor for the micellar formation [33]. Urea is a good H-bond donor and an excellent receptor for highly electronegative atoms like O and N, through the formation of two or more H-bonds [34].

In the present study, our aim is to study the adsorption of urea on the inner and outer surfaces of boron nitride nanotubes with finite size and different chiralities. The structural characteristics of adsorbed urea molecule on BNNTs are investigated and the corresponding adsorption energies are computed. In order to find the preferred adsorption site, different positions and orientations were investigated. The energy gap, HOMO, LUMO, and HOMO–LUMO energies are reported. It has been shown that the interaction may change the electrical and conducting properties of the materials.

2. Computational details

All calculations were performed using density functional theory (DFT) based on Dmol3 module in Materials Studio molecular modeling software package (Accelrys) [35]. The generalized gradient approximation (GGA) with the Perdew–Wang functional (PW91) [36] and the double numerical basis set including p-polarization function (denoted as DNP) was used for exchange correlation potential since it gives reasonable binding energies [37]. Symmetry boundary condition was used in our calculations as implemented in Dmol3. Effective core potentials with double numerical

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polarization (DNP) basis sets were used for core treatment. The convergence threshold for maximum energy change was set to 10^{-5} Ha/Å and the maximum displacements were set to 0.005 Å. The structures were optimized such that the maximum force on each atom is 0.002 Ha/Å. SCF tolerance was set to 10^{-6} and to get accurate results octupole multipolar expansion scheme was applied throughout our calculations. The adsorption energy (E_{ad}) has been defined as follows:

$$E_{ad} = E(\text{Urea-Tube}) - E(\text{Tube}) - E(\text{Urea}) \quad (1)$$

where $E(\text{Urea-Tube})$ is the total energy of Urea-tube complexes, and $E(\text{Tube})$ and $E(\text{Urea})$ are referred to as the energy of an isolated nanotube and urea, respectively.

3. Results and discussion

In our model, a range of BNNTs armchair forms from (5,5) to (7,7) were built and optimized. The changes in the structural and electronic properties induced by the urea molecule when interacting with the single wall BNNT on the surfaces were determined in this section. The motivation for studying these kind of systems has been pointed out in the literature [38], where it is claimed that the chemical reactivity of the BNNTs can be increased by the chemical modification with the amino group especially molecules have both amino and carboxylic groups.

3.1. Structure optimization and geometry

The optimized structures, geometrical parameters BNNTs studied in the present work, have been shown in Fig. 1. As seen, the optimized diameter for the (5,5), (6,6) and (7,7) armchair BNNTs found to be 7.178, 8.377 and 9.972 Å, respectively. These values are comparable with the values reported by Nirmala and Kolandaivel where calculated diameters found to be 7.95, 9.35 and 10.68 Å, for the (5,5), (6,6) and (7,7) armchair BNNTs, respectively [39]. Essentially, for the single wall BNNTs, two types of B–N bonds can be observed: one type is in parallel with the tube axis, and another that are not in parallel with the tube axis (diagonal bond). The calculated values of parallel bonds of (5,5), (6,6) and (7,7) BNNTs were found to be 1.419, 1.456 and 1.455 Å, respectively. In addition, the diagonal bonds calculated for the mentioned nanotubes are 1.410, 1.453 and 1.453 Å, respectively. These values are in agreement with previously reported data [39–41] which supports the validity of our selected computational model. For each nanotube, the urea molecule was placed outside, inside and at the end of tube and the configurations were denoted by **Uo**, **Ui** and **Ue** symbols, respectively. The results of calculated geometrical parameters of free urea molecule and adsorbed ones have been demonstrated in Table 1. Our findings indicate that the interaction between the urea molecule and the nanotubes introduces local structural deformation in both urea and BNNTs. The results indicate that with aggregation of urea molecule on the outside layer of nanotubes, elongation of bond lengths was observed. For example, adsorption of urea on the outside of BNNT with (5,5) and (7,7) chirality, causes carbonyl bond length increase from 1.231 to 1.232 and 1.234 Å, respectively.

Table 1
Important structural parameters of urea vs. BNNT–urea complexes.

	Free	Uo			Ue		
		(5,5)	(6,6)	(7,7)	(5,5)	(6,6)	(7,7)
C=O	1.231	1.232	1.232	1.234	1.233	1.232	1.229
N–H	1.013	1.015	1.015	1.018	1.016	1.014	1.015
C–N	1.387	1.389	1.387	1.384	1.388	1.388	1.390

Bond lengths are in Angstrom.

Because of lower diameter of BNNT with (5,5) chirality, when urea is located inside of tube the molecule went to outside of the tube after optimization.

3.2. Adsorption of the urea on the BNNT: chirality (n,n)

The results of calculation including total energies, binding energies, HOMO, LUMO and HOMO–LUMO gap energies are collected in Table 1. For the adsorption of urea on the armchair BNNTs structures, three different modes were considered where urea lies inside, outside or in the end of the nanotube. For each mode, various adsorption geometries were considered so that O, N or H atoms of urea molecule were close to boron atom or nitrogen atom of nanotube with the urea molecular axis being vertical or parallel to the surface of the tube and the most stable ones presented in Table 2.

Table 1 reports the binding energies for the adsorption of urea on the outer and inner layers of (5,5) nanotube and it was found to be 4.32 and 6.08 kcal/mol, respectively. The adsorption process for the site adsorption occurs through the N and O atoms of urea and B atom of nanotube. The adsorption behavior of urea on various places of (6,6)BNNT showed similar trend: the adsorption energies found to be 4.63 and 6.46 kcal/mol for the urea adsorption on outside and inside of pristine BNNT (see Fig. 1 for more detail). This finding indicates that urea molecule interacts much stronger with inner layer of single wall boron nitride nanotube. We also found the adsorption behavior of urea upon (7,7) BNNT in the most stable configuration, as shown in Fig. 1. Table 2 also indicates that the adsorption energy of urea at outer and inner layer of BNNT with (7,7) chirality take 5.54 and 7.51 kcal/mol, respectively. This fact indicates that the adsorption in the outer and in the end of nanotube is an energetically unfavorable adsorption process.

3.3. Electronic properties

An important aspect of chemical functionalizations of nanotubes by various groups is to modify their electronic structures, and thus widen their potential applications. In this section, we studied the effects of urea molecule adsorption on the electronic properties of the BN nanotubes. The values of HOMO–LUMO energy gaps for the pristine BNNTs found to be 4.626, 4.638 and 4.586 eV for the (5,5), (6,6), and (7,7) nanotubes, respectively (see Table 2). This parameter is determined from the energy difference between HOMO and LUMO orbitals. Upon the various adsorption process of urea on the (5,5) BNNT, the HOMO–LUMO energy gap of BNNT–urea complex found to be –4.698 and –4.595 eV, calculated for adsorption of urea at outer and inner layer of BNNT with (5,5) chirality, respectively. Besides, adsorption of urea on the various places of BNNT with (6,6) chirality have been examined and the values of HOMO–LUMO energy gap for the adsorption of urea on outer and inner surface of tube found to be –4.627 and –4.568 eV,

Table 2
Calculated total energies, adsorption energies, HOMO, LUMO and ΔE_g energies calculated for pristine and complexes of BNNTs.

	E_{ads}	E_{HOMO}	E_{LUMO}	ΔE_g
Urea				
55		–5.631	–1.005	–4.626
55o	–6.08	–5.517	–0.919	–4.698
55i	–6.02	–5.515	–0.920	–4.595
66		–5.655	–1.017	–4.638
66o	–4.63	–5.608	–0.981	–4.627
66i	–6.46	–5.596	–1.028	–4.568
77		–5.642	–1.056	–4.586
77o	–5.54	–5.589	–1.021	–4.568
77i	–7.51	–5.633	–1.092	–4.541

Adsorption energies in kcal/mol, E_{HOMO} , E_{LUMO} and ΔE_g in eV.

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