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The effect of electric field on the interaction of glycine with (6,0) single-walled boron nitride nanotubes

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Abstract: The interaction between the glycine molecule with the (6,0) zigzag model of single-walled boron nitride nanotubes (BNNTs) with H-terminated at the open end, has been investigated in the presence and absence of an external electric field (EF), using the DFT- B3LYP/6-31G* level of theory. The results demonstrated that glycine is chemisorbed on the (6,0) BNNT and this chemical adsorption can be significantly modified by the intensity of an external EF. It was found that increasing the EF strengthens the interaction between glycine and BNNT; thus, adsorption of glycine on BNNT could be controlled by the intensity of the EF. This result might be useful in the design of novel nano-devices, such as nano-sensors.

Keywords: glycine; density functional theory; boron nitride nanotube (BNNT); electric field.

INTRODUCTION

Boron nitride nanotubes (BNNTs) were first theoretically predicted by calculations and then their synthesis was reported in 1995.¹ Due to their large ionicity,² the properties of BNs are different from their carbon analogues.³ BNNTs possess many unique properties, such as high thermal conductivity, chemical stability,⁴ high oxidation resistivity,⁵ and excellent mechanical properties,⁶ which drastically differ from those of carbon nanotubes (CNTs). Therefore, BNNTs have been proposed as more suitable materials than CNTs for application in the nano-devices and molecular electronic circuits, and they can be used for the development of nanotube-based electronic devices, in material science and biotechnology.⁷

Recently much effort has been devoted to theoretical calculations with the aim of understanding the interaction between various molecules and BNNTs. It is well known, that theoretical studies can be very helpful in the understanding of the nature of interaction of BNNTs with other molecules. Modification of the

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electronic properties of nanotubes by interaction is an important issue for designing nano-devices based on nanotubes. Based on density functional theory (DFT) calculations, the adsorption of various aromatic molecules,⁸ NH₃ and amino functional groups,⁹ organic molecules,¹⁰ nucleic acid bases,¹¹ hydrogen atoms,¹² O₂, N₂ and H₂O,¹³ various metalloporphyrin¹⁴ and transition metal atoms¹⁵ on BNNTs were investigated. These studies indicated that the adsorption of atoms and molecules could effectively modify the electronic structures, and the physical and chemical properties of BNNTs.

Glycine, as the simplest of the α -amino acids,¹⁶ is an important model compound in chemical physics, biophysics and biochemistry.¹⁷ The $-N-O-C(O)-$ structure, which occur in glycine, is a fundamental building block in α -amino acids and proteins.¹⁸ In addition, the adsorption mechanism of amino acids and biological molecules onto nanotubes has attracted a lot of attention during the past years, since it is of great importance from both fundamental and applied points of view. Understanding the interaction between BNNTs and amino acids is important for the investigation the interaction mechanism between BNNTs and biomolecules.^{19–21}

Modification of the structural and electrical properties by application of an external electric field is an important subject for the design of nano-devices. In previous studies,^{22,23} it was found that the geometric and electronic structure of BNNTs can be modified by application of an external electric field; therefore it was considered of interest to investigate the BNNT–glycine system under the influence of an external electric field. In this study, the effect of external EF on the interaction of glycine molecule with SWBNNT (6,0) was investigated.

COMPUTATIONAL DETAILS

The quantum chemical calculations in this work were performed using the Gaussian 03 program package.²⁴ The structures of isolated BNNT, glycine and the BNNT–glycine complex were fully optimized by the DFT/B3LYP method with the 6-31G* basis set. The B and N dangling bonds at the two ends of (6,0) BNNT and the BNNT–glycine complex were saturated by hydrogen to avoid boundary effects. Geometric optimizations were performed until the maximum force and *rms* errors on all atoms were less than 0.00045 and 0.00030 Hartree/Bohr, respectively, which are the “normal” convergence criteria settings in Gaussian 03. The stationary point geometries were fully optimized and characterized as minima (no imaginary frequency) by vibration frequency calculations. The standard direction of the external electric field was along the positive X-axis (Fig. 1d). The numerical values of the applied static EF strengths were 50×10^{-4} and 100×10^{-4} a.u. (1 a.u. = 5.14224×10^{11} V m⁻¹).

Analysis of the electronic properties of the BNNT–glycine complex in the presence and absence of an EF were based on the adsorption energy, HOMO–LUMO gap, dipole moment and charge transfer (natural bond orbital (NBO) charge).

RESULTS AND DISCUSSION

Glycine adsorption on BNNT

The optimized structures for the pristine (6,0) BNNT and glycine are shown in Figs. 1a and 1b, respectively. To model the interaction between BNNT and the

glycine molecule, the glycine molecule was placed perpendicular to the BNNT at a height of 3.676 Å (Fig. 1c) and allowed to relax freely. The optimized structure of the BNNT–glycine complex is shown in Fig. 1d. After optimization, it was found that the glycine molecule preferred to orient parallel with respect to the surface of the BNNT, which is located at the end of the tube with the nearest distance being 1.726 Å.

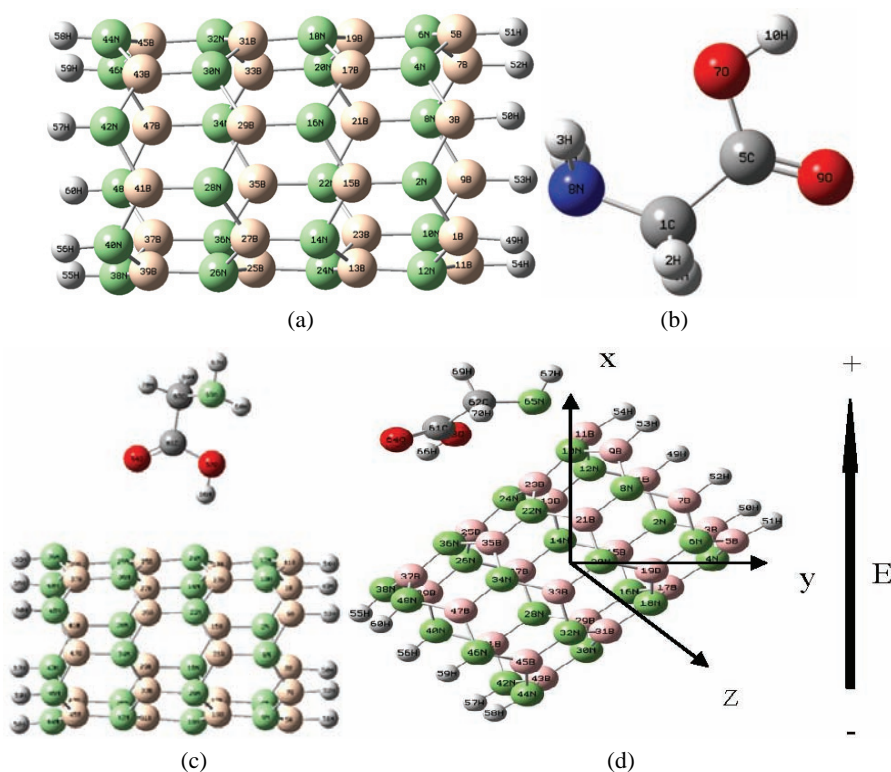


Fig. 1. The full optimized structure of a) BNNT, b) glycine, c) interaction of glycine with (6,0) BNNT and d) optimized structure of the BNNT–glycine complex at zero EF.

The frame of axes used in this study is also shown.

First, the adsorption of glycine on (6,0) BNNT was investigated. The calculated values of the electronic energy of the glycine molecule, (6,0) BNNT and BNNT–glycine complex are reported in Table I, from which it can be seen that the energy of BNNT–glycine complex (-59989.291 eV) was lower in comparison to (6,0) BNNT (-52248.346 eV) and the glycine molecule (-7738.706 eV). These values indicate that the BNNT–glycine complex is energetically stable relative to the separated BNNT and glycine molecule.

TABLE I. E , band gap and dipole moment of BNNT, glycine and the BNNT–glycine complex at zero EF

Compound	E / eV	Band gap, eV	Dipole moment, D
BNNT	-52248.346	4.769	8.572
Glycine	-7738.706	5.376	1.297
BNNT–glycine	-59989.291	5.027	8.179

The adsorption energy of the glycine molecule on the (6,0) BNNT is defined by the following equation:

$$E_{\text{ad}} = E_{\text{BNNT-glycine}} - (E_{\text{BNNT}} + E_{\text{glycine}}) \quad (1)$$

where $E_{\text{BNNT-glycine}}$, E_{BNNT} and E_{glycine} are the total energy of the BNNT–glycine complex, the total energies of the isolated glycine and isolated BNNT, respectively. $E_{\text{ad}} < 0$ denotes an exothermic adsorption, a negative E_{ad} corresponds to a stable adsorption structure and a larger negative adsorption energy means the configuration is more favorable from an energy viewpoint. The adsorption energy was larger than 0.5 eV, which supports the hypothesis that the adsorption mechanism was chemisorptions.^{25–27} The adsorption energy of the BNNT–glycine complex at zero EF is reported in Table II. This result shows that the glycine molecule can be chemically adsorbed on the BNNT sidewall with exothermic adsorption energy of -2.237 eV.

TABLE II. Calculated E_{ad} and band gap of the BNNT–glycine complex, B–N bond length, transferred charge Q and dipole moment, in the presence and absence of an external EF

External EF	$E_{\text{ad}} / \text{eV}$	Band gap, eV	$R_{\text{B11-N65}} / \text{\AA}$	Q / e	Dipole moment, D
0	-2.237	5.027	1.726	0.331	8.179
50	-3.021	4.539	1.672	0.340	14.542
100	-4.126	4.041	1.663	0.343	22.657

Charge transfer is one of the key factors that facilitates the adsorption of an adsorbate onto an adsorbent. The chemical adsorption of glycine onto a BNNT leads to a certain amount of charge transfer. To better understand the chemical adsorption of the glycine molecule onto BNNT, the transferred charge (Q) from glycine to (6,0) BNNT was calculated. A positive value corresponds to charge transfer from glycine to (6,0) BNNT. The Q of glycine molecule to BNNT using the NBO charge,^{28–30} which is less sensitive to the selected basis sets than Mulliken³¹ charge analysis, was obtained. The calculated values of Q at zero EF are reported in Table II, from which, it can be seen that the transferred charge in the absence of EF was significant (0.331 e).

It is essential to calculate the electronic properties of (6,0) BNNT before and after glycine molecule adsorption, to understand better the interaction of the glycine with BNNT. When glycine is adsorbed on the BNNT, the electronic properties of the tube and glycine are changed. The energy levels of the molecular

orbitals, especially the HOMO and LUMO, are excellent indicators of many molecular properties. Thus, the difference between the HOMO and LUMO, known as the band gap ($E_{\text{LUMO}} - E_{\text{HOMO}}$) was studied.

The calculated values of the band gap and dipole moment of the glycine molecule, (6,0) BNNT and the BNNT–glycine complex before application of an EF are given in Table I, according to which, the band gap of the pure (6,0) BNNT is 4.769 eV. The band gap increases to 5.027 eV upon glycine molecule adsorption onto the tube. In addition, the band gap of the BNNT–glycine complex is greater than that of the glycine molecule. The electric dipole moment of the free BNNT (8.572 D), glycine (1.297 D) and the BNNT–glycine complex (8.179 D) are presented in Table I. These results show that the polarization and electro-conductivity of the (6,0) BNNT in the presence of glycine molecule were changed.

The effect of an applied electric field on glycine adsorption

In this work, the adsorption of the glycine on the (6,0) BNNT was explored under the effect of an external EF. The calculated values of the adsorption energy (E_{ad}), B–N bond length ($R_{\text{B11-N65}}$) and charge transfer (Q) in zero, 50×10^{-4} and 100×10^{-4} a.u. EF intensity are reported in Table II. As can be seen, with increasing EF strength, the adsorption energy decreased from -2.237 in the zero external EF intensity to -3.021 and -4.126 eV at 50×10^{-4} and 100×10^{-4} a.u., respectively. These results show that the stability of the BNNT–glycine complex increased with the increasing EF intensity. In addition, an EF can easily modulate the adsorption energy of glycine adsorbed on BNNT.

Under the external electric EF, a single covalent $\text{B}_{\text{BNNT}} - \text{N}_{\text{Glycine}}$ bond is formed ($R_{\text{B11-N65}}$). The $R_{\text{B11-N65}}$ decreased from 1.726 \AA in zero EF intensity to 1.672 and 1.663 for 50×10^{-4} and 100×10^{-4} a.u. EF strengths, respectively.

The optimized structure of BNNT–glycine complex under the applied external EF with 100×10^{-4} a.u. strength is shown in Fig. 2, according to which, the orientation of glycine on (6,0) BNNT changed under the external EF.

As can be seen in Table II, the transferred charge in zero EF intensity, $0.331 e$, increased to $0.343 e$ at 100×10^{-4} a.u. EF strength. These values show that the transferred charge increased with increasing external EF strength. Generally, these results show that interaction of glycine molecule with BNNT was enhanced with increasing external EF strength from zero to 100×10^{-4} a.u. intensity.

One of the important applications of external EF on BNNTs is to modify the electronic structures and thus widen their potential applications. The calculated values of band gap of the BNNT–glycine complex for applied external EF from $F = 0$ to 100×10^{-4} a.u. are given in Table II, from which, it could be understood that with increasing field strength, the band gap decreased from 5.027 at zero external EF to 4.539 and 4.041 at 50×10^{-4} and 100×10^{-4} a.u., respectively. Thus, the electro-conductivity of the BNNT–glycine complex increased under an ex-

ternal EF. The change in the electro-conductivity of the BNNT–glycine system is an important process in the sensor industry.

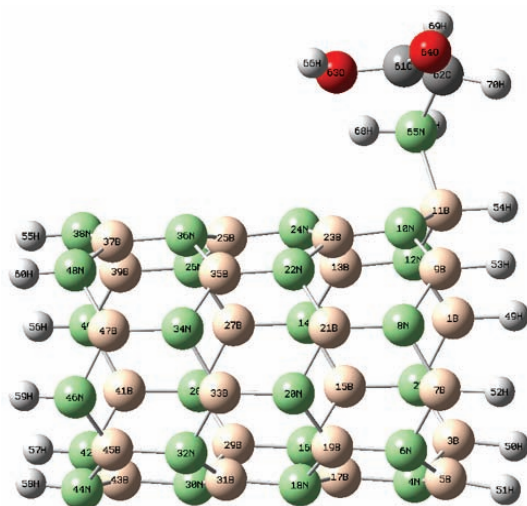


Fig. 2. The BNNT–glycine complex which response to the external EF with 100×10^{-4} a.u. strength is studied in this work at DFT-B3LYP/6-31G* level of theory.

On the other hand, an analysis of the spatial distribution of the frontier orbitals is one way to understand the molecular properties. To explain further the electrical properties of the BNNT–glycine complex under an external EF, the spatial distribution of the molecular orbitals (MOs), especially the frontier MOs including the HOMO and LUMO, were studied. The spatial distribution of the frontier orbitals was performed to obtain a better understanding on the interaction of glycine with (6,0) BNNT. The spatial distribution of the HOMO and LUMO of (6,0) BNNT and the BNNT–glycine complex under various external EF are illustrated in Fig. 3.

As shown in Fig. 3a, large amounts of the charge density of (6,0) BNNT are concentrated at the left and right ends of the tube, implying that the active sites of (6,0) BNNT probably lie in the ends of tube. In addition, this figure shows that the HOMOs and LUMOs of the BNNT–glycine complex are localized around the BNNT at all employed EF intensities. Fig. 3b shows that at zero EF, the major part of LUMO is distributed on the (6,0) BNNT near the glycine molecule and that the HOMO is localized over the whole of the (6,0) BNNT. According to Fig. 3, as the field strength increases to 100×10^{-4} a.u., the HOMO and LUMO are mainly localized at the end of the complex. Some small amount of the LUMO is localized around the B–N bond but there are no HOMO orbitals around the B–N bond.^{32–36}

When an external electric field is applied on the BNNT–glycine system, rearrangements of its atomic charges lead to the separation of the positive and ne-

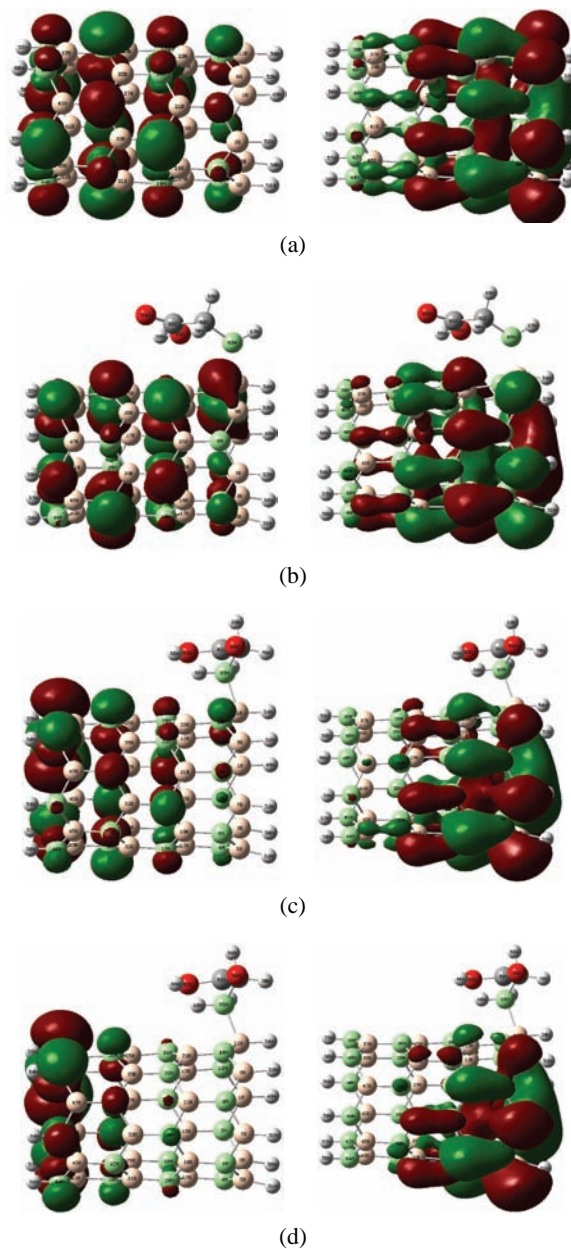


Fig. 3. Orbital spatial distribution of HOMO (right) and LUMO (left): a) optimized structure of (6,0) BNNT, b) the BNNT-glycine complex at zero EF, c) the BNNT-glycine complex at 50×10^{-4} a.u. and d) the BNNT-glycine complex at 100×10^{-4} a.u.

gative charges, which induces an electric dipole moment in the system. Thus, the study of the electric dipole moment under external EFs is important. The calculated values of the electric dipole moment (F in D) for applied external EFs from 0 to 100×10^{-4} a.u. are given in Table II. According to Table II, on application of an EF on the BNNT–glycine complex, the dipole moment increases from 8.179 D at zero EF to 22.657 D at 100×10^{-4} a.u. The significant changes in the electric dipole moment clearly predict that interaction of glycine molecule with (6,0) BNNT increases with increasing external EF intensity.

CONCLUSIONS

In summary, in this work, DFT calculations were performed on the BNNT–glycine complex on application of static electric fields. The glycine molecule is exothermally strongly adsorbed on the sidewall BNNT with high adsorption energy. Therefore, the BNNT–amino acid complex may be useful in the application of this class of biofunctional nanotubes to the design of amino acid delivery vessels. From these calculations, it was concluded that the electronic properties of the BNNT–glycine complex are modified with increasing EF intensity. This result may be useful in the application the BNNT–glycine system under the influence of an EF to the design of biosensor devices. In brief, study of this system under influence of EF intensity is important for the design and proposal of BNNT-based materials.

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ИЗВОД

УТИЦАЈ ЕЛЕКТРИЧНОГ ПОЉА НА ИНТЕРАКЦИЈУ ГЛИЦИНА СА ЈЕДНОСЛОЈНОМ БОР-НИТРИДНОМ НАНОЦЕВИ ТИПА (6,0)

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Испитивана је интеракција између молекула глицина једнослојне бор-нитридне наноцеви, типа (6,0), у одсуству и у присуству спољашњег електричног поља. Примењен је DFT-B3LYP/6-31G* ниво теорије. Резултати показују да се глицин хемисорбира на наноцев и да на хемисорпцију значајно утиче јачина електричног поља. Нађено је да се појачањем електричног поља појачава интеракција између глицина и наноцеви. То значи да се адсорпција глицина може контролисати јачином електричног поља. Овај резултат би могао бити од користи за дизајнирање нових нано-уређаја, као што су нано-сензори.

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