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Abstract
We investigate the adsorption of the nucleic acid bases—adenine (A), guanine (G), cytosine (C), thymine (T) and uracil (U)—on the outer wall of a high curvature semiconducting single-walled boron nitride nanotube (BNNT) by first-principles density functional theory calculations. The calculated binding energy shows the order: G > A ≈ C ≈ T ≈ U, implying that the interaction strength of the high curvature BNNT with the nucleobases, G being an exception, is nearly the same. A higher binding energy for the G–BNNT conjugate appears to result from hybridization of the molecular orbitals of G and the BNNT. A smaller energy gap predicted for the G–BNNT conjugate relative to that of the pristine BNNT may be useful in the application of this class of biofunctional materials to the design of next-generation sensing devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Boron nitride nanotubes (BNNTs) have been the focus of several experimental and theoretical studies (e.g. [1–3]) due to their potential applications in high speed electronics. BNNTs are a typical member of the III–V compound semiconductors with a morphology similar to that of carbon nanotubes (CNTs) but with their own distinct properties. A tubular structure of BN can be formed by rolling up a sheet of hexagonal rings, with boron and nitrogen in equal proportions, and will possess peculiar electrical [4], optical [5] and thermal [6] properties, which drastically differ from those of CNTs.

The nucleic acid bases, on the other hand, being the key components of the genetic macromolecules—deoxyribonucleic acid (DNA) and ribonucleic acid (RNA)—play a central role in all biological systems and thus have been a focus of intense research activities over the past five decades. Recently, there has been a keen interest in understanding the interaction between nucleobases and matter, especially nanostructured materials such as carbon nanotubes [7–16] due to the potential application of the unique signature of the latter in probing the structural and conformational changes [17, 18] of the former, and hence leading to new detection mechanisms [19] and medical diagnostic tools.

Very recently, thiol-modified DNA was used to obtain high concentration BNNT aqueous solutions assuming the interaction between DNA and multi-walled BNNTs to be strong [20]. Analysis of the transmission electron microscopy measurements showed that the thiol-modified DNA wraps around the tubular surface of BN. The tubular surface of BN consists of dissimilar atoms and, thus, its interaction with the nucleobases may show different characteristics as compared to that observed in the case of either graphene or CNTs.

Previously, the interaction of nucleobases with graphene [7, 11] and CNTs [12] was predicted to be dominated by van der Waals (vdW) forces as the binding energy is seen to increase with the polarizability of the nucleobases. The

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charge transfer between the nucleobases and CNTs was found to be negligible. In the present study, our motivation is to systematically investigate the self-organization of the nucleobases onto the tubular surface of BN and identify factors playing a role in the differences in the interaction for different base molecules. Wherever possible, we compare the results of our study with the previous studies on CNTs.

2. Methodology

We consider a high curvature (5, 0) single-walled BNNT of 0.416 nm in diameter, which has been predicted to be stable by theoretical calculations [21]. All calculations were performed by employing the plane wave pseudopotential approach within the local density approximation (LDA) [22] of density functional theory (DFT) [23, 24]. The Vienna *ab initio* Simulation Package (VASP) was used [25, 26] with an energy cut off of 850 eV and 0.03 eV Å^{-1} for its gradient. The periodically repeated BNNT units were separated by 15 Å of vacuum to avoid interaction between them. The $(1 \times 1 \times 3)$ Monkhorst Pack grid [27] was used for k-point sampling of the Brillouin zone. The average B–N bond length in the optimized configuration of the pristine BNNT is 1.44 Å, consistent with previously reported DFT calculations ([31] and references therein).

In the calculations of the energy surface describing the interaction of the nucleobases with the BNNT, the nucleobases were allowed to approach the tubular surface in the direction perpendicular to the axis of the tube. In order to simulate an electronic environment resembling more closely the situation in DNA and RNA, the N atom of the base molecules linked to the sugar ring in the nucleic acid was terminated with a methyl group. There is an additional benefit of introducing the small magnitude of steric hindrance due to the attached methyl group. It will help us to imitate a more probable situation in which a nucleobase in a strand would interact with the surface of the BNNT rather than an isolated nucleobase interacting with the BNNT. For simulations based on force fields [9–14], it is certainly possible to include all constituents of DNA, including the sugar–phosphate backbone. In the present first-principles study however, simulation of the nucleobases attached to the backbone (i.e. sugar + phosphate group) is computationally rather expensive.

The optimized configurations of the nucleobases–BNNT conjugate systems were obtained following a similar scheme as employed in the previous study of the BNNT–CNT complex [12]. It consisted of (i) an initial force relaxation calculation step to determine the preferred orientation and optimum height of the planar base molecule relative to the surface of the BNNT. (ii) Calculations of the potential energy surface (figure 1) for nucleobase–BNNT interaction by translating the relaxed base molecules parallel to the BNNT surface covering a surface area 4.26 Å in height, 70° in width, and containing a mesh of 230 scan points. The separation between the base molecule and the surface of the BNNT was held fixed at the optimum height determined in step (i). (iii) A 360° rotation of the base molecules in steps of 5° to probe the energy dependence on the orientation of the base molecules
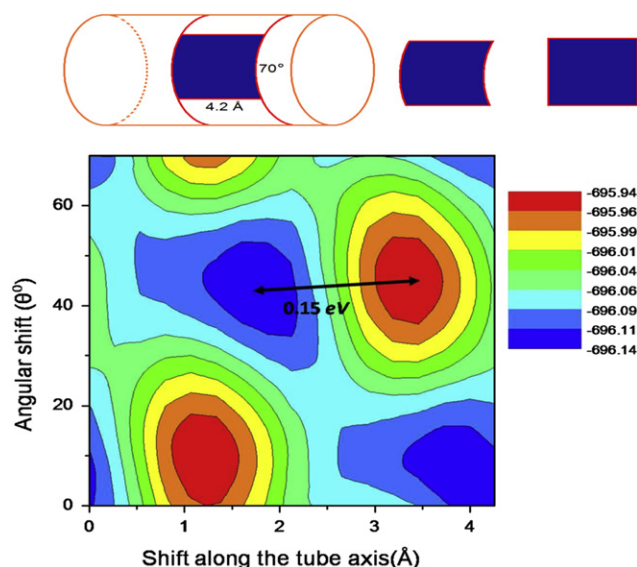

Figure 1. Potential energy surface plot (eV) for guanine scanning the surface of the BNNT. The specifications of the scanned area (rectangle highlighted by dark blue) are shown above. The energy barrier between two adjacent global minima is 0.15 eV. Qualitatively similar features were found in the case of the other four nucleobases.

with respect to the underlying BNNT surface. (iv) A full optimization of the conjugate system in which all atoms were free to relax.

Certainly, in a potential energy surface scan, some lateral restriction against sliding must be applied. However, it is true that, in principle, reorientation through rotations should be considered. This was not done here, for the following two reasons. First, regarding rotations around any axis that lies in the plane of the nucleobase (comparable to 'roll' and 'pitch' for airplanes), the preferred orientation of the nucleobase plane relative to the tube surface is parallel in order to maximize the attractive van der Waals interaction while minimizing the repulsive interaction from overlapping electron clouds. Second, regarding rotations around the axis that goes perpendicular through the plane of the nucleobase (comparable to 'yaw' for airplanes), at least for the larger purine base molecules, the preferred orientation is such that their longer dimension is aligned with the tube axis (as seen in the equilibrium geometries shown in figure 2) again in order to maximize the attractive interaction with the tube surface.

It should be pointed out that LDA due to a lack of the description of dispersive forces is, in principle, not the most optimal choice for calculating interaction energies of systems governed by vdW forces. However, more sophisticated methods, such as many-body perturbation theory, which are more suitable for describing long range forces, become prohibitively expensive for complex systems such as those considered here. Earlier studies [28, 29] have shown that, unlike the generalized gradient approximation (GGA) [30] for which the binding for vdW bound systems does not exist, the LDA approximation does indeed provide a reasonably good description of the dispersive interactions. Also a recent study [7] on the adsorption of adenine on graphite suggests that
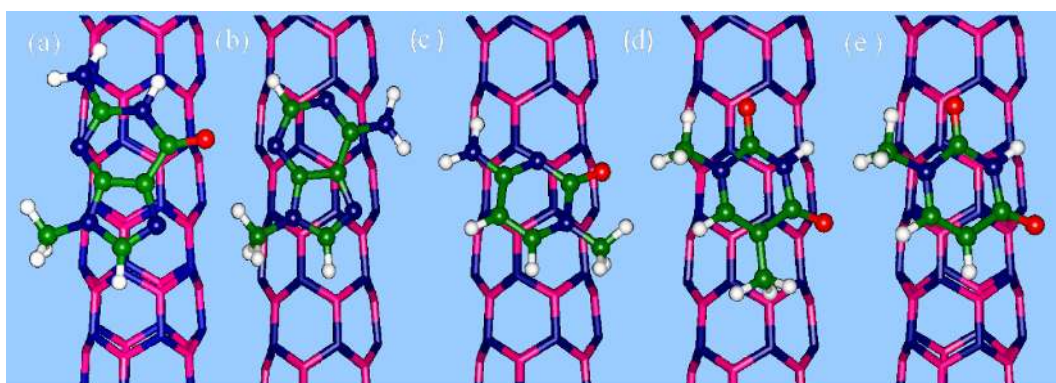
Figure 2. Equilibrium geometry of physisorbed nucleobases on the surface of the BNNT. (a) Guanine, (b) adenine, (c) cytosine, (d) thymine and (e) uracil.

Table 1. Binding energy (E_b), band gap, and nearest-neighbor distance ($R_{base-BNNT}$) of nucleobase conjugated BNNTs. The calculated LDA band gap of the pristine (5, 0) BNNT is 2.2 eV.

System	E_b (eV)	$R_{base-BNNT}$ (Å)	Band gap (eV)
G + BNNT	0.42	2.49	1.0
A + BNNT	0.32	3.06	1.7
C + BNNT	0.31	2.96	1.8
T + BNNT	0.29	2.55	2.0
U + BNNT	0.29	2.86	2.1

the potential energy surface obtained by using LDA and GGA with a modified version of the London dispersion formula for vdW interactions is effectively indistinguishable. Additionally, the LDA equilibrium distance between adenine and graphene obtained by LDA is found to be equal to that obtained using the GGA + vdW level of theory. This gives us confidence that the results obtained in the present study reasonably accurately describe the nucleobase–BNNT interaction.

3. Results and discussion

The calculated base–BNNT binding energy, E_b, the equilibrium base–BNNT distance, and the band gap of the corresponding base–BNNT complex are listed in table 1. The optimized configurations of the nucleobase–BNNT conjugates are shown in figure 2. It should be noted that the base molecule was allowed to approach the tubular surface along the axes perpendicular to that of the tube while obtaining the potential energy surface. In addition to that, as mentioned in the methodology section, we scanned the surface of the tube (step (ii)) shown in figure 1. After that we rotated the base molecule to check if any particular orientation of the base molecule is preferred (optimization step (iii)) and at the end the whole system was optimized, relaxing the BNNT and the nucleobases (optimization step (iv)). The equilibrium configurations shown in figure 2 were the energetically most favorable ones.

None of the nucleobases shows a perfect Bernal's AB stacking. This feature matches with what was found in the interaction of the nucleobases and SWCNTs. There is, however, a slight difference in the stacking of the nucleobases
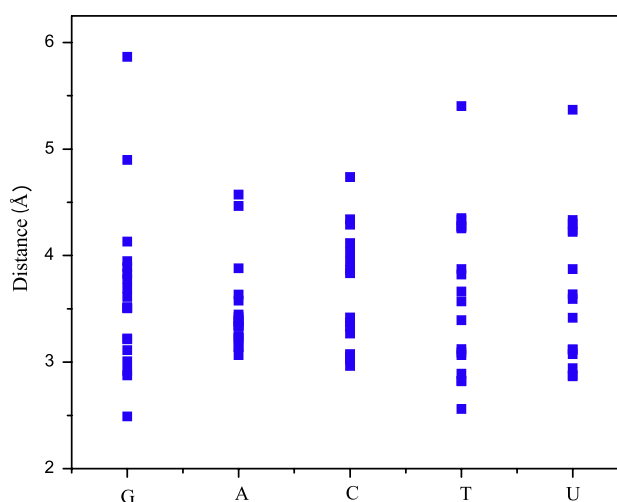

Figure 3. The distance between the nucleobase atoms and the tubular surface atoms in the equilibrium configurations of BNNT conjugates.

between BNNTs and SWCNTs, because BNNTs possess a heteronucleic surface unlike SWCNTs. The partially negatively charged oxygen atom in guanine can interact electrostatically with the polar network of this heteronucleic BNNT surface, specifically in an attractive manner with the partial positive charges on boron, and repulsively with the partial negative charges on nitrogen. This could help to explain our theoretical observation that G + BNNT differs in several ways from A + BNNT, since in the latter combination, adenine lacks the oxygen atom. Thus, the deviation in the stacking arrangement, the higher binding energy (see table 1), and the slight tilting angle could all be consequences of that interaction between the oxygen atom of guanine and the polar network of the BNNT.

The nearest-neighbor distance ($R_{base-BNNT}$) of the individual atoms of the nucleobases from the tubular surface atoms is plotted in figure 3 and is found to depend on the nucleobases. We note that $R_{base-BNNT}$ is comparable to the average distance of organic molecules including amino functional groups and 2,4,6-trinitrotoluene physisorbed on BNNTs [31, 32].
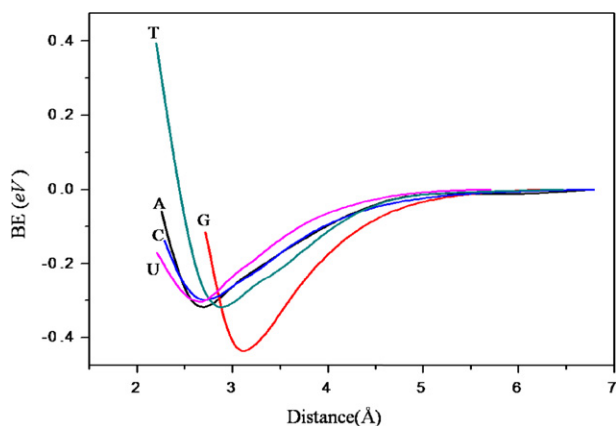
Figure 4. The potential energy variation of the nucleobases interacting with the BNNT as a function of the distance. The distance represents the separation between the center of the mass of the tubular surface and that of the base. A, G, C, T and U are represented by black, red, blue, green and pink lines, respectively. The zero of the energy is aligned to the non-interacting regime of the surface.

Figure 4 shows the energy surface representing the interaction of nucleobases with the BNNT. Here, the distance is taken to be the separation from the center of mass of the tubular configuration to the center of mass of the nucleobases. The asymptotic limit of the energy surface is used to calculate the binding energy (E_b) of the system (table 1) in which the base molecule is moved away from the BNNT along the direction perpendicular to the tubular axis. The binding energy data are presented in table 1.

The magnitude of the calculated binding energy exhibits the following order: $G > A \approx C \approx T \approx U$. It is worth noting that the binding energy of the nucleobases interacting with a high curvature CNT [12] followed the order of $G > A > T > C \approx U$. Since E_b associated with CNTs was found to be correlated with the polarizability of individual bases, it was suggested that the interaction of nucleobases with CNTs was governed by the dispersive force like vdW which varies with the polarizability of the interacting entity. The calculated polarizability values of G, A, C, T and U are 131.2, 123.7, 111.4, 108.5 and $97.6 e^2 a_0^2 E_h^{-1}$, respectively, at the Hartree–Fock level of theory together with the second-order Møller–Plesset corrections [12].

Figure 5 shows the total charge density plot of the representative conjugate system of G physisorbed on the BNNT. The Bader charge analysis does not show a noticeable charge transfer in the conjugate system relative to the pristine BNNT and individual nucleobases; the change in the total charge of the nucleobases is quite small ($<10^{-2}e$). This is in contrast to the cases of covalent functionalized BNNTs [32–34] where a significant charge transfer of the order of $0.36e$ from an organic molecule such as NH_3 and amino functional groups to the BNNT was reported. Our results are consistent with the case of 2,4,6-trinitrotoluene physisorbed on BNNTs reporting a very small charge transfer in the system [31].

In order to further understand the underlying interaction between the nucleobases and BNNTs, we also calculated
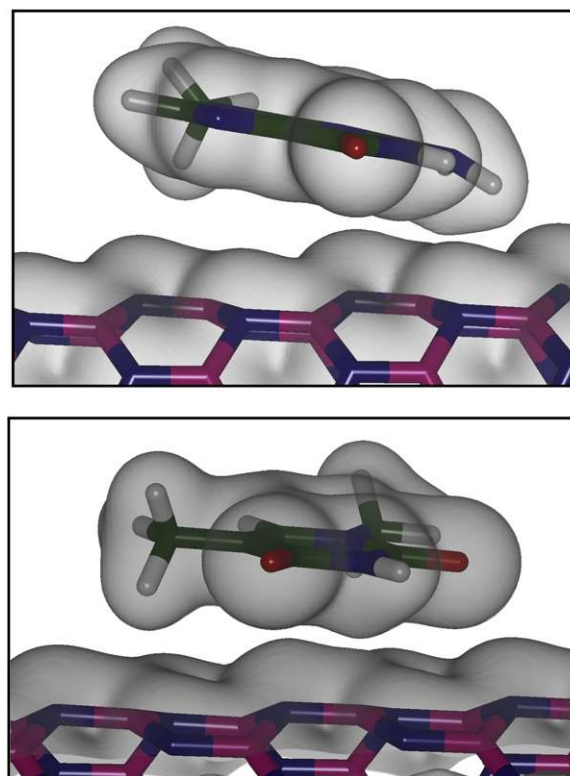

Figure 5. Total charge density of guanine (above) and thymine (below) conjugated BNNTs. The isosurface levels were set at 0.08 bohr^{-3}.

the polarizability of a BN sheet, which comes out to be $265.7 e^2 a_0^2 \ E_h^{-1}$ at the LDA level of theory. The polarizability of a BN sheet is therefore significantly smaller than $402.2 e^2 a_0^2 \ E_h^{-1}$ calculated for graphene at the same level of theory. This suggests that the tubular surface of a BNNT can be expected to be less polarizable than that of a CNT which, in turn, would lead to relatively weaker vdW interactions between BNNTs and nucleobases. This is reflected in the calculated binding energy values of physisorbed nucleobases on BNNTs which are lower in magnitude as compared to those associated with CNTs. For example, the calculated binding energy of the G + BNNT conjugate is 0.4 eV while the corresponding value for the G + CNT conjugate is 0.5 eV.

Through a comparison of the present results with those from a previous study, it is found that the binding energy of nucleobases with (7, 7) BNNTs is significantly higher than that with CNTs [35]. This LDA study using numerical atomic orbitals reported a binding energy of about 1 eV for the G + BNNT conjugate system. This clearly suggests that the lower surface curvature of the (7, 7) BNNT (with a diameter of 9.60 Å) leads to a stronger interaction with the nucleobases than a large surface curvature for the (5, 0) BNNT (with a diameter of 4.16 Å) considered in the present study. A similar trend in the effect of the surface curvature on the binding energy between nucleobases and carbon nanostructures, graphene [11] and CNTs [12] was noted in previous studies.
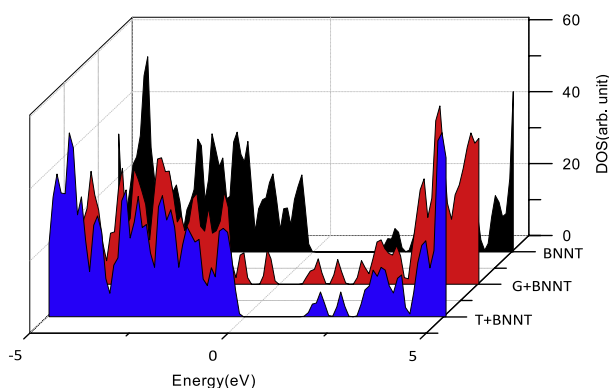
Figure 6. Density of states of a pristine BNNT and guanine and thymine conjugated BNNTs. The zero of the energy is aligned to the top of the valence band.

The semiconducting nature of a BNNT with a band gap of about 2.2 eV can be seen in the calculated density of states shown in figure 6. This is in agreement with the recent LDA calculations on the pristine (4, 0) BNNTs reporting a direct band gap of about 2.0 eV [36]. Both the top of the valence edge and bottom of the conduction edge of BNNTs are associated with the N p-orbitals. The asymmetry in DOS appears to be due to the difference in the coupling strength between the π-orbitals of the BNNT and the base molecule in the valance band compared to the conduction band. In the former case contributions from the nucleobases dominate and contributions from the BNNT dominate in the latter case. The appearance of the mid-gap states (figure 6) in the conjugated BNNT represents a mixing of electronic states of the nucleobases and the BNNT separated at about 2.5 Å. It may be noted that the covalent interaction at the separation of 2.5 Å will be very weak [37]. On the other hand a very small charge transfer from the BNNT to oxygen of guanine may indicate the presence of a relatively weaker electrostatic interaction between the BNNT and guanine. The interaction between BNNTs and nucleobases is however essentially dominated by the vdW forces.

4. Summary and conclusion

In summary, we have investigated the interaction of the nucleobases on a high curvature, zigzag (5, 0) BNNT by a first-principles DFT method. Our calculations show that, except G, the base molecules A, C, T, U of DNA and RNA exhibit similar interaction strengths when physisorbed on BNNTs. It is also observed that the binding energy of the base molecules not only depends upon their individual polarizability but also marginally depends on the degrees of mixing of electronic states with the tubular surface of the BNNT. The strong binding of the BNNT with G compared to the other nucleobases suggests that this interaction can be used in sensing and also for distinguishing this base molecule from other nucleic acid bases.

Acknowledgments

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